

EPA-600/7-79-217

September 1979

CONF-790449--

Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, IV (April 1979, Hollywood, FL)

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**Contract No. 68-02-3132
Task No. 1
Program Element No. EHE623A**

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Prepared for

**U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460**

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PREFACE

These proceedings for the symposium on "Environmental Aspects of Fuel Conversion Technology" constitute the final report submitted to the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency (IERL-EPA), Research Triangle Park, N.C. The symposium was held at the Diplomat Hotel, Hollywood, Florida, April 17-20, 1979.

This symposium acted as a colloquium for discussion of environmentally related information on coal gasification and liquefaction. The program included sessions on program approach, environmental assessment, and control technology development. Process developers, process users, research scientists, and State and Federal government officials participated in this symposium, the fourth to be conducted by IERL-RTP on the subject since 1974.

Mr. T. Kelly Janes, Chief, Fuel Process Branch, EPA-IERL, Research Triangle Park, N.C., was the Project Officer. Mr. William J. Rhodes, Program Manager, Synthetic Fuels, Fuel Process Branch, EPA-IERL-RTP, was the General Chairman of the symposium. Dr. N. Dean Smith, Project Officer, Fuel Process Branch, EPA-IERL-RTP, was the Technical Chairman.

Mr. Franklin A. Ayer, Manager, Technology and Resource Management Department, and Mr. N. Stuart Jones, Analyst, Technology and Resource Management Department, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, N.C., were symposium coordinators and compilers of the proceedings.

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KEYNOTE ADDRESS

Steven Reznick

Office of Energy, Minerals, and Industry,
U.S. Environmental Protection Agency, Washington, D.C.

Welcome to the fourth edition of our symposia on the environmental aspects of fuel conversion technology. On behalf of the U.S. Environmental Protection Agency (EPA) I wish to thank you for attending and participating in our discussions. The outside observer comparing the agenda for edition 4 to those for editions 1, 2, and 3 might have a sense of *deja vu* because we continue to use many of the same topical headings from session to session. However, those of you who have persisted in the research areas that comprise our program of environmental assessment of synthetic fuels technologies recognize that we are dealing with a network of technical, economic, institutional, and environmental issues analogous to a kaleidoscope. Every time something shakes the system or every time a different vantage point is used, new features surface.

Upon surveying the progress that has been made since the first symposium in St. Louis 5 years ago, I was reminded of the words of a song made popular by Ray McKinley many years ago: "You've come a long way from St. Louie, baby, but you still have a long way to go." In keeping with that theme, I would like to review briefly where we have been, where we are now, and then give you my opinion of what our path must be over the next few years if we are to meet our obligation to guide the development of synthetic fuels technologies in an environmentally sound manner.

The first symposium in May 1974 came shortly after the oil embargo. The intervening 5 years have presented us with a natural gas shortage and a coal strike. The price of our fossil fuels has steadily climbed, pressed by the steady escalation in the price of our imported oil. The most recent OPEC oil price increases continue this dismal trend. Yet we persist in our high per capita consumption of energy because our economy is based on it.

The trend in U.S. energy consumption over the past 30 years is illustrated in Table 1. The growth in the use of oil and natural gas is re-

flected in massive capital investments in distribution systems and equipment utilizing these fuels. During this time the amount of coal used has been comparatively static, undergoing a slight decline and then recovering to the point that 1977 use was slightly above 1950 use. However, as can be seen, coal consumption is expected to more than double by 1990. The historical and anticipated distribution in the use of this coal is illustrated in Table 2.

Included in the industrial/nonenergy category for 1990 is an estimated 75 million tons of coal per year, totaling 5 percent of expected U.S. production for use in synthetic fuels production. It is conceivable that this estimate may be too conservative. In 1977 imports accounted for about 45 percent of the 19.1-million bbl/d used. The projected figures for 1990 indicate that imports will account for 51 percent of some 22 million bbl/d consumed in the United States. In 1978, oil imports dramatically escalated the U.S. trade deficit to over \$28 billion. The economic burden of imports will escalate still further. Compared to 1940, per capita (worldwide) energy consumption will double by 1980, increasing demand—and therefore prices—in the oil market. These economic forces, plus the impacts of geopolitical events (witness the oil embargo of 1973, the recent interruption of oil production in Iran and the present fuel shortage) will certainly accelerate the technological development and commercialization of synthetic fuels from coal.

The U.S. Department of Energy (DOE) has recognized the need to develop a viable synthetic fuels industry and has formulated plans to spur commercialization. As with most Federal agencies, however, budgetary limitations have been imposed, which have pared DOE commercialization support down to a small fraction of the recommended amounts. At the same time, the private sector has been reluctant to risk equity capital investment to attract a sufficient amount of debt capital needed to finance synthetic fuels plant construction. This is par-

TABLE 1. PATTERN OF U.S. ENERGY CONSUMPTION 1950-1990

Source	Consumption in Quads (10^{15} Btu) by Year				
	1950*	1960*	1970*	1977*	1990 [†]
Hydro, nuclear	1.43	1.6	2.9	5.1	14.6
Dry, natural gas	6.15	12.7	22.0	19.6	19.1
Petroleum liquids	13.5	20.1	29.5	37.1	48.2
Coal	<u>12.9</u>	<u>10.2</u>	<u>12.7</u>	<u>14.1</u>	<u>30.3</u>
Total, quads (10^{15} Btu)	34.0	44.6	67.1	75.9	112.2
Average growth rate (%)	2.75	4.17	1.78	3.05	

*Data from U.S. Bureau of Mines cited in: H. R. Linden et al. Perspectives on U.S. and World Energy Problems. Institute of Gas Technology February 1979.

[†]Data from Exxon Company, U.S.A. Energy Outlook 1978-1990. May 1978.

TABLE 2. DISTRIBUTION OF U.S. COAL DEMAND 1960-1990

Sector	Consumption in Quads (10^{15} Btu) by Year*		
	1960	1977	1990
Electric utility	4.45	10.2	22.6
Industrial/nonenergy	4.65	3.7	7.7
Residential/commercial	<u>1.1</u>	<u>0.2</u>	<u>--</u>
Total quads	10.2	14.1	30.3

*Data from Exxon Company, U.S. Energy Outlook 1978-1990. May 1978.

ticularly true for liquefaction and high-Btu gasification plants, which typically require well over billion-dollar investments.

Although this may appear to be a classic confrontation between an irresistible force (of accelerating energy demand) and an immovable object (of investor reluctance), I believe the barrier will quickly crumble when the price of liquid and gaseous fuels from coal becomes competitive with petroleum liquids and natural gas. Then there will be a rush to build synthetic fuels plants.

If EPA is to do its job correctly, the Agency must be prepared with environmental protection guidelines and regulations before or at least coincident with the rush. Otherwise, we face the charge of causing delays and thereby jeopardizing the nation's energy supplies and, consequently, the nation's economic well-being; or we face the charge of underestimating the environmental impacts, thus jeopardizing the nation's environmental well-being. I, for one, don't wish either tag. Let me bring you up to date in our efforts to ensure that we will be prepared. Initially, we reviewed what was already known about the processes for producing synthetic fuels from coal, the types of pollutants emanating from these processes, and the techniques that were available for controlling the release of pollutants. These control methods were evaluated in terms of their adequacy under the air and water standards extant circa 1974. One conclusion drawn was that the amount of existing data available were inadequate and that the reliability of this data were questionable. EPA began to remedy this situation by funding field studies—environmental assessments, we called them—on low- and medium-Btu gasifiers, high-Btu gasifiers, and liquefaction systems. We also researched various methods to control pollutants in product and byproduct streams, waste streams, and fugitive emissions.

As work progressed, it became obvious that environmental assessment involved more than pollutant quantification and control methods evaluation. Removal efficiency for Pollutant X might be, say, 98 percent; but was that good enough? The only way to know was to quantify, or at least estimate the acceptable concentration level of Pollutant X in the environment for which the risk of hazard was very small. The necessity to establish goals against which to measure the effectiveness of control methods

led to the development of what we call multimedia environmental goals (MEGs). These were initially developed for a limited number of chemical species, but as the scope of EPA's mandated responsibilities has grown through the Toxic Control Substances Act, the Priority Pollutant List, and similar addenda, the list of MEG species has expanded to keep pace.

A companion development to MEGs were the source analysis models, or SAMs. SAMs were based on the use of simplified assumptions about pollutant transport and transformation in the environment in order to provide a rapid, standardized method of estimating pollutant loadings, which are then compared to MEG values.

As this framework for effects estimation has been developed, we have also refined our measurement data base through more comprehensive and more precise measurements. Additional chemical species have been identified and assayed, sampling and analysis techniques have been refined, data quality control procedures have been employed, and biological methods have been added to our evaluation arsenal.

Over the next 4 days you will share with each other the details of your individual contributions since our last meeting. As you listen, I believe that you will agree with me that, indeed, we have come a long way from St. Louis. The next question is: Where do we go from here?

We believe we have laid a solid foundation of research to scope the environmental problems associated with developing a synthetic fuels industry. Now, our thrust is to integrate this information into a format that will make it directly useable to guide plant designers, plant operators, EPA regulatory offices, EPA enforcement offices, and the State counterparts to these EPA offices.

Presently, we are planning two major vehicles for presenting this information. These are two report series that we term environmental guidance documents (EGDs) and environmental assessment reports (EARs). A given EGD will summarize for a given technology—for example, low-Btu gasification—what is known about the environmental effects from pollutants that have been identified for the various systems encompassed within the energy technology. It will survey the techniques available to control these pollutants and give suggested pollutant discharge limits. In addition, it will project the

future development of effluent, emission, and solid waste disposal standards.

In projecting future standards, it is obvious that we will need the active involvement of the EPA program and enforcement offices. Even though these offices are heavily committed to a multitude of other currently more pressing problems, they have responded quite well to our overtures for a coordinated approach on synfuels.

The second report series, EARs, will focus on specific systems, such as the Lurgi system for low- and medium-Btu gasification. Technical, economic, and environmental effects information will be assembled to present process descriptions; characterization of input materials, products, and waste streams, performance, and costs for various control alternatives; analysis of environmental regulatory requirements; and,

finally, a projection of environmental impacts.

Lest I appear overly optimistic as I contemplate the prospect of producing a series of "best sellers," I remind myself and you that we still have a long way to go. Budgetary limitations and shifting priorities, both internal to and external to EPA, will provide the usual hurdles to program continuity and intensity. But even if we manage to avoid these bureaucratic problems, we still face substantive problems in collecting, refining, validating, and analyzing data to provide a solid quantitative basis for our conclusions and recommendations. I hope these recommendations will achieve a balance of technology and economy to provide environmental protection as the synfuels industry expands.

We look forward to working with you to meet this challenge. Thank you for your support.

Session I: GENERAL APPROACH

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MULTIMEDIA ENVIRONMENTAL GOALS

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Abstract

A key element in the Industrial Environmental Research Laboratory's (IERL) environmental assessment methodology is the development of multimedia environmental goals (MEGs). MEGs addressed here are desirable control levels of chemical substances in discharges to the environment. The purpose of MEGs development, the strategy used in deriving MEG values, and the format established for their presentation are discussed briefly. Several aspects of MEGs for polycyclic organic compounds are discussed.

INTRODUCTION

It is widely recognized that coal conversion is accompanied by the formation of a myriad of chemical substances and that, in large-scale operations, these chemicals may be released to the environment. It is the responsibility of the U.S. Environmental Protection Agency (EPA) to ensure that when commercial conversion processes become operational in the United States, they will reflect optimum strategies for environmental control.

Conservative estimates suggest that by the year 2000, more than 3.3 M bbl/d oil equivalent will be supplied by synthetic fuels from coal. In addition, as much as 38 million tons of coal may be gasified for ammonia synthesis.¹ The dimension, complexity, and severity of potential environmental impacts of the conversion industry require that a holistic environmental approach be adopted if problems are to be prevented. Potential effects on workers and on the surrounding human populations and ecosystems will be influenced by the quantity and composition of environmental discharges. Releases to air and water, as well as solid wastes disposed to land, must be considered. In addition to the acute effects, chronic effects from low-level exposures must be evaluated. Problems resulting

from process upsets must be anticipated. Clearly, compliance with present environmental standards will not be sufficient to safeguard public health and welfare because many conversion-related pollutants are not currently addressed by Federal guidelines. Consideration must be given to impacts from all chemical species that might be discharged.

To provide for comprehensive environmental assessments, the Industrial Environmental Research Laboratory at Research Triangle Park (IERL-RTP) is developing a procedure to facilitate quantitative evaluation and comparison of streams and processes with respect to their potential environmental impacts. The methodology prescribes a systematic approach to interpreting data obtained in environmental assessment projects. The need for multimedia environmental goals (MEGs) arises in this context. To fully characterize waste streams for environmental assessment, pollutant levels must be related to their environmental effects. The development of MEGs is a first attempt at a procedural approach to evaluate and rank a large number of pollutants for the purpose of environmental assessment.

DEVELOPMENT OF MEGs

Multimedia environmental goals are defined as levels of contaminants or degradents (in ambient air, water, or land or in emissions or effluents conveyed to ambient media) that will not produce negative effects in the surrounding populations or ecosystems, or that represent control limits demonstrated to be achievable through technology. Emphasis thus far in the MEGs development has centered around specifying three types of goals—levels desirable in ambient media, levels existing in ambient media (natural background), and levels believed safe for exposure of limited duration.

There are several practical considerations in the development of environmental goals:

- A method is needed to classify pollutants for comprehensive coverage without having to

*Speaker.

**TABLE 1. TYPES OF INFORMATION SUPPLIED IN BACKGROUND
INFORMATION SUMMARIES**

Information Type	Specific Data Supplied
Identifying Information	Category; subcategory; identification number; preferred chemical name; subspecies; formula; synonyms; description; WLN
Properties	Atomic number; periodic group; atomic weight; molecular weight; melting point; freezing point; boiling point; density; vapor density; vapor pressure; solubility in water; solubility in liquid; octanol partition coefficient; pK_a ; pK_b
Characteristics, Associated Compounds	Chemical characteristics; compound associations; mineral associations; formation; characteristic chemical reactions; biodegradability; persistence in atmosphere; metabolites; precursors
Occurrence in Air	Rural; urban; industrial air conc ($\mu\text{g}/\text{m}^3$); odor threshold
Occurrence in Water	Level identified in drinking water, surface water, ground water, seawater, or estuarine ($\mu\text{g}/\text{L}$)
Occurrence in Land	Typical level in soil ($\mu\text{g}/\text{g}$); occurrence in marine sediments, or earth's crust; association with coal or petroleum
Other Occurrences	Occurrence in food, body, aquatic organisms, and vegetation; dietary intake/nutrient value; total intake; uses, production, etc.; sources
Human Toxicity Data	Compounds likely to be toxicologically similar; acute human effects; chronic human effects; relative toxicity of assoc. CPDS; bioaccumulation; biological half-life, reported no-effect dosages; synergisms/antagonisms; absorption routes
Animal Toxicity Data	Acute effects; chronic effects; no-effect levels; LD_{50} or lowest lethal dose (mg/kg , oral rat data preferred); lowest lethal concentration or LC_{50} (mg/m^3); lowest toxic concentration reported (mg/m^3)
Information Relative to Genotoxic Potential (Oncogenicity, Teratogenicity, Mutagenicity)	Evidence of carcinogenicity or teratogenicity (assoc. cpds. considered); evidence of noncarcinogenicity; EPA/NIOSH ordering number (based on oncogenicity or teratogenicity); lowest dosage producing oncogenic or teratogenic response (mg/kg); adjusted ordering number (based on oncogenicity or teratogenicity); evidence of mutagenicity; results of Ames' Test
Aquatic Toxicity	TLM-96 (ppm); sublethal effects; bioaccumulation potential; fish tainting level (PPM); fish tainting, qualitative information
Phytotoxicity	Effects of vegetation (air [$\mu\text{g}/\text{m}^3$], irrigation, nutrient solutions, soil)
Standards, Criteria, Recommendations, Recognition	Primary and Secondary Ambient Air Quality Standards; National Emission Standards for Hazardous Air Pollutants; TLV (established by ACGIH); ACGIH designation as simple asphyxiant or carcinogen; subject of NIOSH criteria document or hazard review document; OSHA designation as cancer suspect agent; NIOSH recommendation; drinking water standards or criteria; water quality criteria for protection of aquatic life, protection of livestock, or irrigation; Toxic Pollutant Effluent Limitations; Recommendations of U.S. Dept. of Agriculture and Land-grant Institutions; FDA declarations; included in National Cancer Institute list of carcinogens to man; included in EPA Consent Decree List; Chemical Industry Institute of Toxicology recognition

consider individually millions of compounds.

- A procedure is needed to quantify relative toxicity of classes of compounds as well as individual compounds. This procedure would allow a "most-toxic-first" ordering approach logically derived from a step-by-step evaluation and linkage between chemical and bioassay characterization.
- Existing standards and guidelines should be incorporated.
- Overall format for presentation of goals should allow direct comparison of existing and projected "best technology" controlled emission levels with emission goals having environmental significance.
- A uniform approach in applying existing health and ecological effects data is needed as well as a means for directly delineating health/ecological effects data gaps.

The primary objective in compiling MEGs is to provide an index that will allow quantitative comparison and evaluation of the hazard associated with a large number of chemical substances. The MEGs project began with the compilation of a list of chemical contaminants associated with fossil fuel processes. The more than 600 chemicals on the list were organized into categories that effectively grouped chemically and toxicologically similar substances. (Identification numbers for specific compounds were subsequently assigned on the basis of the category organization.) In the next step of the MEGs development, existing Federal regulations and guidelines applicable to chemical substances were assembled. Other types and sources of available information relevant to environmental goals were also identified. Finally, a suitable presentation format, the MEG chart, was adopted, and a 1-page information summary was prepared to accompany and support the numerical goals for each chemical. Types of information provided in the summaries are listed in Table 1.

Quantitative Comparison of Pollutants

In order to establish goals, it is necessary to define equivalent or normalized concentrations of individual chemical species in multimedia; i.e., air, water, or soil (or solid waste). These equivalent levels are needed to serve as reference values and thus provide a basis for comparing

diverse pollutants. One common denominator selected for this purpose in the MEGs methodology is a *conservative* threshold (no effect) level.

The concept of threshold is based on the premise that there exists for every chemical substance some definable concentration below which that substance will not produce a toxic response. Threshold level is illustrated in Figure 1. It is defined on a dose vs. response plot as the intersection of a dose-response curve with the ordinate. Unfortunately, the human threshold has been determined (with confidence) for very few pollutants (e.g., lead).

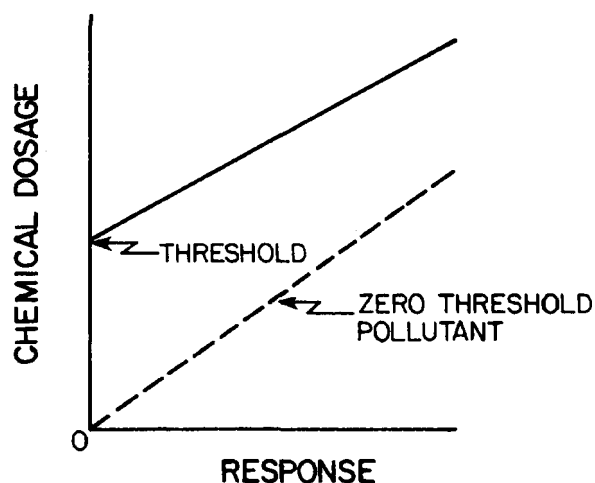


Figure 1. Illustration of chemical pollutant threshold level.

In the absence of data necessary to obtain precise threshold levels from dose-response curves, alternative methods for projecting "safe" levels for chemical pollutants have been proposed. Conservative no-effect levels (below threshold concentrations) may be predicted from mathematical models. Continuous exposure to these predicted levels may be considered "safe" by some factor more than or equal to 1.

Estimated Permissible Concentrations—

Predicted, continuous-exposure, no-effect levels constitute one set of MEGs called estimated permissible concentrations (EPCs). EPCs for air, water, and soil are derived through sim-

ple mathematical models that relate available information (such as threshold limit values [TLVs[®]] for workroom air² or animal toxicity data) to a conservative continuous-exposure, no-effects level. Separate EPCs are specified on the basis of human health effects or ecological effects.

The objective in formulating a method for deriving EPCs was to establish a hierarchy of models that would permit the calculation of EPCs for a large number of compounds on the basis of information available. In the absence of the preferred types of data (i.e., levels associated with observed effects on man), models allowing estimation of EPCs on the basis of minimal data were needed. Models adopted to derive EPCs for air and water were selected from models previously suggested in the literature. The 1976 report, *Estimated Permissible Concentrations of Pollutants for Continuous Exposure* by Handy and Schindler,³ was used extensively as a source for these models. In addition, a simple method was developed to relate water and soil EPCs. The systems of models used in specifying EPC values for human health and for ecology are outlined in Table 2.

Calculated EPCs together with the existing Federal guidelines applicable to specific chemicals comprise the class of MEG values called ambient level goals. Another class of MEG values, emission level goals, is discussed below.

Emission Level Goals—

Emission level goals describe maximum concentrations of chemicals in waste streams discharged to the environment. Emission goals for chemicals may be derived from EPCs through application of a dilution factor. Dilution factors applied to EPCs represent the ratio of emission concentration to consequential ambient concentrations and must be source-specific. The resulting emission goals reflect acceptable chemical loadings in ambient media.

Alternatively, a second set of MEG values called minimum acute toxicity effluents (MATEs) may be used as emission level goals. These values describe concentrations believed safe for short-term exposure (acute exposure). EPCs and MATEs differ in exposure duration. MATEs are derived through a procedure similar to the method for calculating EPCs. EPC values for a given chemical are always lower than corresponding MATE values. However, di-

lution factors are not used with MATEs, so these values represent very conservative emission goals.

Natural background levels constitute a third set of MEGs applicable to discharge streams. Used with a dilution factor, these levels may be applied as ultraconservative emission level goals. For some chemicals, levels detected in ambient media are reported, but toxicity data are unavailable. This set of goals may serve as guidelines in the absence of environmentally significant MEG values.

Zero Threshold Pollutants

The number of compounds classified as suspected carcinogens grows larger every year. The 1977 *Registry of Toxic Effects of Chemical Substances*⁴ lists 2,091 substances as "Suspected Carcinogens"; i.e., reported to cause tumors in some animal species.

Many researchers in the field of oncology believe that the concept of threshold levels, as previously discussed in this paper, does not apply to carcinogenic, teratogenic, or mutagenic pollutants. Historically, these compounds have been referred to as "zero threshold" chemicals to indicate that a nonzero threshold level could not be specified. The theoretical dose-response curves for such compounds intersect the origin as indicated by the dotted line in Figure 1. The "zero threshold" approach implies that exposure to a carcinogen at any concentration, even for a brief interval, can be expected to increase the risk of a tumorigenic effect. This philosophy precludes specifying EPCs for any chemical reported to be carcinogenic or teratogenic. It also precludes setting priorities among zero threshold pollutants except in terms of associated risk.

Although EPA has recently adopted an approach to assess health risks from environmental carcinogens,⁵ relatively few such assessments are expected to be completed in the near future. (Studies on cadmium and POM were drafted in 1978 in response to the Clean Air Act Amendments of 1977,^{6,7} and analyses for suspected carcinogens listed in the Consent Decree have recently been published in the *Federal Register*.⁸) However, limited resources require that risk assessment analyses be conducted on a priority basis.

Clearly, an alternative to risk assessment is

**TABLE 2. MODELS USED IN THE DERIVATION OF
ESTIMATED PERMISSIBLE CONCENTRATIONS (EPCs)
BASED ON HEALTH AND/OR ECOLOGICAL EFFECTS**

Medium	Model Number	EPC Model	Comments
Air ($\mu\text{g}/\text{m}^3$)	AHS	Lowest ambient standard or criterion for air based effects ($\mu\text{g}/\text{m}^3$)	Federal guidelines for ambient air based on human health effects include primary Ambient Air Quality Standards (40 CFR, Part 50); National Emissions Standards for Hazardous Air Pollutants (40 CFR, Part 51).
	AH1*	$\frac{10^3}{420} \times \text{TLV or NIOSH recommendation (mg/m}^3\text{)}$	Lower value is used when both TLV and NIOSH recommendations are available. A value of 5,000 ppm is used in place of TLV for simple asphyxiants.
	AH2*	$0.107 \times \text{LD}_{50} \text{ (mg/kg)}$	Used only in the absence of AH1 LD_{50} (oral, rat) is used when available. Other lethal dose values are substituted when LD_{50} (oral, rat) is not available.
	AH3*	$0.081 \times \text{LD}_{50} \text{ (mg/kg)}$	Used only in the absence of AH1 LD_{50} (oral, rat) is used when available. Other lethal dose values are substituted when LD_{50} (oral, rat) is not available. Lowest reported human or mammalian lethal or toxic concentration data are used.
	AC1	$\frac{10^3}{420} \times \text{TLV or NIOSH recommendation (mg/m}^3\text{)}$	MEG_{AC1} values reflect carcinogenic potential as well as other types of health effects.
	AC2	$\frac{10^3}{6} + \text{Adjusted ordering number based on carcinogenic potential.}$	Adjusted ordering numbers increase with carcinogenic potential. Health effects other than oncogenic effects are not reflected.
	AT	$\frac{10^3}{6} + \text{Adjusted ordering number based on teratogenic potential.}$	Adjusted ordering numbers increase with teratogenic potential. Health effects other than teratogenic effects are not reflected.
Water ($\mu\text{g}/\text{l}$)	WHS	Most stringent drinking water standard or criterion ($\mu\text{g}/\text{l}$)	Federal guidelines for contaminant levels in drinking water are specified in the following: National Primary Drinking Water Regulations; EPA 1976 Water Quality Criteria; NAS/NAE 1972 Water Quality Criteria.
	WH1*	$15 \times \text{EPC}_{\text{AH1, 2, or 3}} \text{ (}\mu\text{g}/\text{m}^3\text{)}$	Most stringent MEG value for air is used.
	WH2*	$13.8 \times \text{TLV or NIOSH recommendation (mg/m}^3\text{)}$ or $0.4 \times \text{LD}_{50} \text{ (mg/kg)}$	Model involving LD_{50} is used only if TLV or NIOSH recommendation is not available. LD_{50} (oral, rat) is used where available. Other lethal dose values are substituted when LD_{50} (oral, rat) is not available.
	WC	$15 \times \text{EPC}_{\text{AC1 or 2}} \text{ (}\mu\text{g}/\text{m}^3\text{)}$	More stringent EPC_{AC} is used.
	WT	$15 \times \text{EPC}_{\text{AT}} \text{ (}\mu\text{g}/\text{m}^3\text{)}$	Values reflect genotoxic effects.
Land ($\mu\text{g}/\text{g}$)	LH1	$0.2 \times \text{Most stringent EPC}_{\text{WH}} \text{ (}\mu\text{g}/\text{l})$	ORIGINAL LAND MODEL HAS BEEN MODIFIED. EQUATIONS GIVEN HERE REPRESENT ORIGINAL LAND MODEL MULTIPLIED BY 100.
	LT	$0.2 \times \text{EPC}_{\text{WT}} \text{ (}\mu\text{g}/\text{l})$	
Air ($\mu\text{g}/\text{m}^3$)	AES	Lowest ambient standard or criterion for air based on effects ($\mu\text{g}/\text{m}^3$)	National Secondary Ambient Air Quality Standards (40 CFR, Part 50) are the only Federal guidelines for air based on ecological effects.
	AE	$0.1 \times \text{Lowest 24-hr concentration having an effect on vegetation (}\mu\text{g}/\text{m}^3\text{)}$	Effective levels reported for exposures other than 24 hours are adjusted. Only common plant species are considered.
Water ($\mu\text{g}/\text{l}$)	WES	Most stringent criterion for water based on ecological effects ($\mu\text{g}/\text{l}$)	Federal guidelines for contaminant levels in water based on ecological effects are specified in 1972 NAS/NAE Water Quality Criteria; 1976 EPA Quality Criteria for Water; and 1968 NTAC Water Quality Criteria. When MEG_{WES} is available, other MEG_{WE} values do not appear on MEG charts.
	WE1	$0.05 \times \text{Lowest reported TLM (}\mu\text{g}/\text{l})$	TLM-96 is used most often. Level for most sensitive species (may be either marine or freshwater) is used in calculations. MEG_{WE1} is not presented on MEG chart if MEG_{WE3} is available.
	WE2	Lowest concentration reported to cause tainting of fish flesh ($\mu\text{g}/\text{l}$)	
	WE3	$\text{Recommended application factor} \times \text{Lowest reported TLM (}\mu\text{g}/\text{l})$ or $0.2 \times \text{Reported hazard level (}\mu\text{g}/\text{l})$	Specific application factors and hazard levels are taken from 1972 NAS/NAE Water Quality Criteria and 1976 EPA Quality Criteria for Water. EPC_{WE3} , if available, supersedes EPC_{WE1} .
	WE4	$\text{Maximum allowable concentration in fish (}\mu\text{g}/\text{kg}) + \text{Highest reported concentration factor}$	Maximum contaminant concentrations in fish are specified by the FDA.
Land ($\mu\text{g}/\text{g}$)	LE	$0.2 \times \text{Most stringent WE (}\mu\text{g}/\text{l})$	ORIGINAL LAND MODEL HAS BEEN MODIFIED. THESE EQUATIONS REPRESENT ORIGINAL LAND MODEL MULTIPLIED BY 100.

* Carcinogenic, teratogenic, and mutagenic effects are not considered.

Subscript Key: A (air); W (water); L (land); S (standard or criteria); H (health effects); C (carcinogenicity); T (teratogenicity); E (ecological effects); numbers refer to specific models

needed if priorities are to be established among suspected carcinogens in the near term. Also a straightforward method for comparing suspected carcinogens with noncarcinogens must be adopted to evaluate environmental control strategies. The dictum that "every effort should be made to reduce environmental contamination by carcinogens to the lowest possible level" is not specific enough to be useful in interpreting data for comprehensive environmental assessments. Specifying MEGs for suspected carcinogens is one alternative to risk assessment that can supply the suspected carcinogen rankings needed now for decisionmaking by IERL.

In fact, not all researchers in oncology agree with the zero threshold concept. Cornfield⁹ concluded, on the basis of statistical analysis of the dose-response relationship, that "the existence of a no-effect or threshold level for the carcinogenic compound administered is not precluded." Dinman has presented evidence to suggest that a finite number of molecules are required within a cell before a carcinogenic response can be triggered.¹⁰

In reality, there may or may not be a nonzero "safe" level for carcinogens. At any rate, there are MEG values for some carcinogens called (with some misgiving) EPCs and MATEs. To preface the discussion of EPCs for zero threshold pollutants, some general remarks on carcinogens and the nature of the data available from carcinogen testing are presented.

Information on Carcinogens Relevant to MEGs—

Epidemiological data provide the most reliable indication of carcinogenic risk to human health, but these data are sparse and difficult to evaluate. Precise human exposure levels resulting in cancer are almost never known. Most of the available human effects data refer to chemical mixtures rather than to specific chemical compounds. For example, occupational cancer associated with coal and petroleum products has long been recognized, but the specific chemicals responsible are not positively identified. Mixtures rather than specifics remain indicted. A February 1978 National Cancer Institute listing names the following among the compounds observed to cause cancer in man: soots, tars, pitches, asphalts, cutting oils, shale oils, creosote oils, high-boiling petroleum oils, coke

oven effluents, and various combustion products. No specific polycyclic compounds are included in the list.¹¹

As early as 1947, the latent period associated with occupational exposure to oils, pitch, and tar products was documented. Figure 2, adapted from a paper by S. A. Henry appearing in the *British Medical Bulletin*, indicates the time elapsing from onset of employment to manifestation of neoplasia in two groups of workers.¹² The activity associated with all these mixtures is probably attributable to certain polycyclics, but without better information on the chemical composition of the substances, the information remains unusable for assessment.

Presently, the best qualitative evaluations of carcinogenic risk for chemicals are supplied in the monographs prepared by the International Agency for Research on Cancer (IARC). This agency is part of the World Health Organization

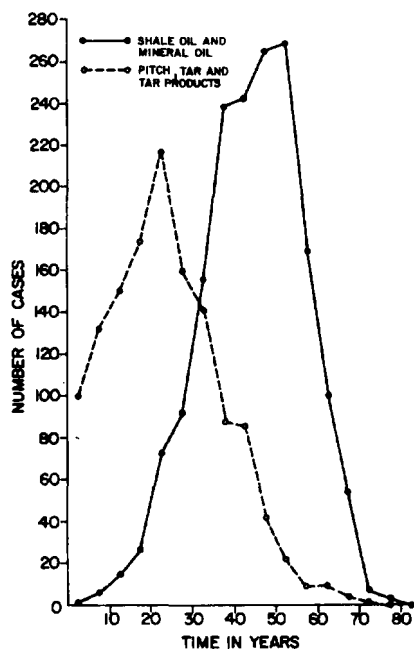


Figure 2. Latent period associated with exposure to oil and tar substances. (The graph indicates time elapsing from onset of employment to manifestation of a cutaneous papilloma or epithelioma in 1,335 persons in contact with pitch, tar, or tar products compared with 1,719 persons in contact with shale oil or mineral oil.)

and has prepared monographs on the evaluation of carcinogenic risks of chemicals to man for some 65 substances. The stated objective of the IARC program is "to achieve and publish a balanced evaluation of data through the deliberations of an international group of experts in chemical carcinogenesis and to put into perspective the present state of knowledge with the final aim of evaluating the data in terms of possible human risks..."¹³ The evaluations by IARC reflect biological data, epidemiological studies and other observations in man, and environmental data.

Almost all carcinogenic compounds in man have been demonstrated carcinogenic in one or more animal species. It is generally accepted that animal studies provide important information to evaluate carcinogenic risk to man. It must be emphasized that all compounds reported to be carcinogenic are not equally potent. Effective dosages vary widely. For example, pyrene produced tumors in mice only after 10 g/kg were administered. At the other extreme, benzo(a)pyrene with n-dodecane is reported to cause skin cancer in mice at a level of 2 µg/kg.¹⁴ Carcinogen studies in animals also indicate that latent periods associated with specific dosages may vary widely between compounds. Latent period is the length of time between the initial application of carcinogen and the appearance of the first tumor. In general, potent carcinogens have shorter latent periods than weak carcinogens.¹⁵ Response to carcinogens in experimental animals may be reported as the occurrence or frequency of neoplasms compared to control animals.

Results of carcinogenic studies in experimental animals (without evaluation) are available in two compendiums. The *Registry of Toxic Effects of Chemical Substances*⁴ reports species tested and lowest effect dosages for suspected carcinogens, although no details of the studies are given. Another reference, *Survey of Compounds Which Have Been Tested for Carcinogenic Activity* (commonly referred to as the Public Health Series List No. 149),¹⁶ gives more complete information. Unfortunately, the list is not current, the most recent volume covering compounds tested in 1972 to 1973.

MEGs for Suspect Carcinogens —

MEGs for individual compounds that are suspected carcinogens are based on "adjusted

ordering numbers." These numbers, derived from the available experimental animal data for each compound, serve as an index to indicate the potency or hazard associated with a given chemical. Adjusted ordering numbers are influenced primarily by the lowest effective dosage reported and animal species affected. The numbers have no physical meaning because they are obtained using an arbitrary weighting system. They are used in MEGs because they allow ranking of carcinogens on the basis of available information. Adjusted ordering numbers used in the MEGs methodology are derived from the ordering numbers developed in the 1976 EPA report, *An Ordering of the NIOSH Suspected Carcinogens List Based Only on Data Contained in the List*.¹⁷

Adjusted ordering numbers for organic suspected carcinogens currently addressed by MEGs range from 1 to 3×10^6 . EPCs for air for suspected carcinogens are calculated using the model outlined below. MATEs for suspected carcinogens are calculated using a similar equation.

The following assumptions are made in formulating the model.

Adjusted ordering numbers increase with carcinogenic potency, indicating genotoxic potential. Goals for a given substance should be inversely proportional to the adjusted ordering number.

An ambient air concentration of 1 ng/m³ may be considered the lowest concentration of concern. Therefore, the model for zero threshold pollutants should predict a goal of ≤ 1 ng/m³ for highly potent carcinogens or teratogens.

$$EPC_{Air} = \frac{K}{\text{adjusted ordering number}}$$

where K = 1/6 to satisfy the <1 ng/m³ assumption for B(a)P.

APPLICATION OF MEGS METHODOLOGY TO POLYCYCLIC ORGANIC COMPOUNDS

Polycyclic organic compounds are chemicals containing two or more fused aromatic rings. Hetero atoms of oxygen, nitrogen, or sulfur may be present as well as alkyl, hydroxy, or other ring substituents. Polycyclic organics constitute a class of compounds of particular interest in

EPA's synfuels program. They are known to be present in conversion processes and have received special attention because certain polycyclics are recognized carcinogens. Application of the current MEGs methodology to polycyclics as a group has effectively organized and ranked many of these compounds.

Organization

A total of 124 polycyclic compounds are included in the MEGs master list. Six major MEGs categories contain subcategories devoted to polycyclic compounds. These groupings were adopted in order to relate compounds according to structural similarities that affect chemical separation and analysis. Subcategories are distinguished by numbers of rings and by the presence of heterocyclic O, N, or S. Nonalternant structures are separated from other polycyclic hydrocarbons because of their unique resonance characteristics. Descriptions of MEGs subcategories containing polycyclic compounds and representative structures are presented in Table 3.

Background Information

Background information summaries addressing all polycyclics appearing on the MEGs master list have been prepared, and MEG values are specified for 85 of these compounds. (MEG values presently cannot be provided for the remaining polycyclics because sufficient information is not available.) Interesting highlights and statistics from the information summaries for polycyclics follow:

- Conflicting rules of nomenclature for polycyclics have led to confusion. Nomenclature endorsed by the International Union of Pure and Applied Chemistry is used in the MEGs.
- Molecular weights for polycyclics addressed range from 128 (naphthalene) to 342 (tribenzylene benzene, a nonalternant structure). Water solubilities are reported to be quite low for polycyclics, although the presence of impurities may alter solubilities substantially.
- Almost all the polycyclics addressed are associated with coal tar. Many have been identified in atmospheric particulate sam-

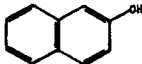
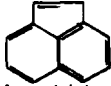
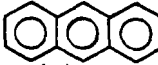
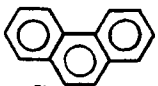
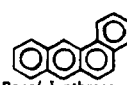
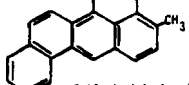
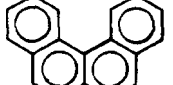
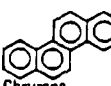
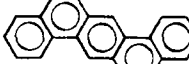
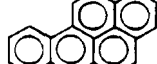
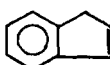
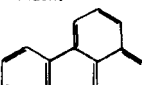
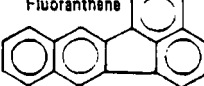
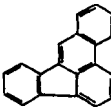
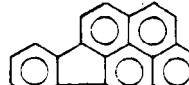
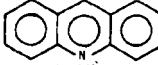
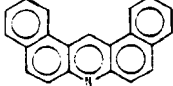
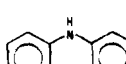
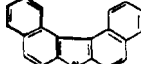
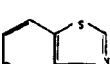
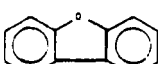
ples. Concentrations of specific compounds in ambient media are reported in 45 summaries.

- Substantial concentrations in foods are reported for certain polycyclics (e.g., chrysene in vegetables: 395 $\mu\text{g/kg}$). Many polycyclics including heterocycles occur naturally in plants.
- Lipid solubilities, although seldom reported explicitly, may be deduced from animal test data when the material is administered in a lipid-type vehicle. Indications of lipid solubilities for 10 polycyclics are reported in the summaries.
- Degradation of polycyclics in the atmosphere is affected by solar radiation.
- Most polycyclics are planar structures. An exception is benzo(c) phenanthrene, a four-ring compound.
- Very limited acute toxicity data are available for polycyclics. Virtually no toxicological data are available for the oxygen heterocycles or for the sulfur heterocycles. No evidence suggests that these heterocyclic compounds are carcinogenic.
- Of the 37 polycyclic hydrocarbon groups addressed by MEGs, 24 are reported to be tumorigenic in animals. Alkylation of parent structures may strongly influence their carcinogenicity. (Example: alkyl derivatives of benzo(c)phenanthrene.)
- Nine nitrogen heterocycles have demonstrated carcinogenic activity. Many others in this group have no data available.
- The TLV[®] recommended by the American Conference of Governmental Industrial Hygienists for particulate polycyclic aromatic hydrocarbons (PAH) is 0.2 mg/m^3 . This TLV[®] recognizes the carcinogenic potential of PAH collectively. A TLV[®] of 0.2 mg/m^3 is also recommended for coal tar pitch volatiles. This specification includes naphthalene, anthracene, acridine, phenanthrene, and fluorene, collectively. The purpose of the TLV[®] is to minimize concentrations of higher weight polycyclic hydrocarbons that are carcinogenic.

EPC Values and Ambient Concentrations for Air

EPC values and ambient concentrations for

TABLE 3. MEGs SUBCATEGORIES FOR POLYCYCLICS WITH REPRESENTATIVE STRUCTURE

SUBCATEGORY	REPRESENTATIVE STRUCTURES		
18C. Fused Ring Hydroxy Compounds	 Hydroxy naphthalene		
21A. Two-and Three-Ring Fused Polycyclic Hydrocarbons	 Acenaphthalene	 Anthracene	 Phenanthrene
21B. Four Ring Fused Polycyclic Hydrocarbons	 Benz(a)anthracene	 3-Methylcholanthrene	 Benzo(c)phenanthrene
21C. Five Ring Fused Polycyclic Hydrocarbons	 Chrysene	 Pyrene	
21D. Compounds with More Than Five Fused Rings	 Dibenz(a,h)anthracene	 Benzo(a)pyrene	 Perylene
22A. Two-and Three-Ring Fused Nonalternant Polycyclic Hydrocarbons	 Indene		
22B. Four Ring Fused Nonalternant Polycyclic Hydrocarbons	 Fluoranthene		
22C. Five Ring Fused Nonalternant Polycyclic Hydrocarbons	 Benzo(k)fluoranthene		 Benzo(b)fluoranthene
22D. Nonalternant Compounds with More Than Five Fused Rings	 Indeno(1,2,3-cd)pyrene		
23B. Nitrogen Heterocycles with Fused Six-Membered Rings	 Quinolines	 Acridine	 Dibenz(a,j)acridine
23C. Pyrrole and Fused Ring Derivatives of Pyrrole	 Indole	 Carbazole	 Dibenzo(c,g)carbazole
23D. Nitrogen Heterocycles Containing Additional Heteroatoms	 Benzothiazole		
24B. Oxygen Heterocycles with Three or More Fused Rings	 Dibenzofuran		
25B. Sulfur Heterocycles with Two or More Fused Rings	 Methylthiophene		 Dimethylthiophene

air for selected polycyclic compounds are presented in Table 4. The bases for the MEG values for each compound are indicated.

Rankings for polycyclics derived by the MEGs methodology are basically consistent with the broad rankings supplied by the National Academy of Science (NAS) and the evaluations by IARC. In Table 5, carcinogen rankings furnished by MEGs are compared with suggested ratings used by NAS and comments by IARC. The table includes all polycyclics addressed by MEGs with adjusted ordering numbers greater than 4. All polycyclics with positive carcinogen codes (as assigned in Reference 21) are also listed in the table. It should be noted that the only major inconsistencies in the rankings of highly potent carcinogens occur for benzo(a)anthracene and dibenz(a,h)pyrene. The IARC evaluations for these compounds are of particular interest.

On the basis of lung cancer mortality in the United States and in other countries, some investigators have concluded "that the lung cancer death rate in men increases by approximately 5 percent for each increment of pollution as indicated by 1 ng/m³ of B(a)P." Participants of the symposium on *General Air Pollution and Human Health with Special Reference to Long-term Effects* (held in Stockholm, March 1977) have agreed that this estimate; i.e., 5 percent, should be "regarded as an upper limit of the possible effect of atmospheric pollution."¹⁸

No United States standards for polycyclics exist, although 13 polycyclic compounds are listed in the EPA Consent Decree List. Standards for polycyclics established by other countries, however, are of interest. In 1972, the U.S.S.R. adopted a level of 150 ng/m³ as a maximum acceptable concentration of benzo(a)pyrene in workplace air. In 1973, the U.S.S.R. adopted a standard of 1 ng/m³ for benzo(a)pyrene in ambient air.¹⁹ The Republic of Germany has adopted a standard of 250 ng/L for carcinogenic polycyclic aromatic hydrocarbons in drinking water. The German standard became effective January 31, 1975.²⁰

The Russian standards for benzo(a)pyrene are based primarily on work by Janyшева¹⁹ involving intratracheal instillations of benzo(a)pyrene into the lungs of laboratory rats. The maximum noncarcinogenic dose to the rat was determined to be 0.02 mg of benzo(a)pyrene. This noncar-

cinogenic dose in the rat was extrapolated to a maximum noncarcinogenic dose for humans on the basis of organ mass (1,000 g for human lung, 1.5 g for rat).

STATUS OF MEG PROGRAM

To date, background information summaries and MEG charts addressing a total of 640 chemicals have been prepared. In November 1977, 216 summaries and charts were published, and publication of charts and summaries addressing 586 additional compounds is pending. The new MEG volumes will contain updated summaries and charts for 195 organics previously addressed so all organics data are contained in one reference.

The methodology for generating MEGs has been applied successfully to yield numerical goals of at least one type for 572 chemical substances. (This total does not include all compounds addressed by preliminary MATE values. Background information summaries have not yet been compiled for all of the inorganic substances listed in the preliminary MATE tabulations). Preparation of MEGs for inorganics is currently in progress.

A candidate list of compounds to be addressed by MEGs in the future has been compiled. Criteria for inclusion of compounds in the candidate list are association with fossil fuels processes or interest to EPA regulatory offices. A large number of alkylated polycyclics and nitrogen heterocycles appear on the candidate list.

Early this year, a peer review of EPA's environmental assessment²² methodology raised several issues that will influence future MEGs work. One source of concern was that persistence in the environment is not specifically considered in the current MEGs. An indication of uncertainty of the range associated with specific MEG values is also needed. The safety factors incorporated in the models for deriving EPCs and MATEs deserve careful review because compounding safety factors may result in overly stringent MEG values. A footnote system to indicate the basis for each MEG value should be used in final tabulations in future reports. The need for a systematic review of the overall methodology and of specific MEG values was also pointed out. Finally, the appropriateness of the nomenclature used in the MEGs, par-

ticularly regarding the term minimum acute toxicity effluents (MATE), was questioned.

It should be emphasized that the multimedia environmental goals are not to be used as regulations. They are designed to specify levels that may be compared for various pollutants in order to assess various control technologies. A conservative approach has been applied consistently to specify MEG values. Models used for MEG calculations incorporate safety factors to ensure that the values generated err on the safe rather than on the high side. Also, where conflicting information required for MEGs is reported, the more conservative value is used in the MEGs calculations.

Projecting optimum control strategies for an industry slated for future operation is an ambitious undertaking. It involves identifying environmental problems that might arise and assessing their magnitude. Even while environmental effects posed are speculative, priorities must be established so research efforts may focus on the problems believed to be most serious. Clearly, priorities must be established in a systematic manner. MEGs provide the vital link between environmental effects and desirable control levels needed for comprehensive environmental assessment. It is imperative that the methodology for generating MEGs remain flexible so that the most reliable and most up-to-date information can be reflected in the values. The ultimate goal in environmental assessment is to assure that regulations necessary to protect the environment can be formulated and that control technology to meet such requirements is available when needed.

ACKNOWLEDGMENTS

Work on the MEGs is funded by the U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, Contract 68-02-3132. The project officer is T. Kelly Janes.

REFERENCES

1. Mann, Charles E., and James N. Heller. Coal Profitability: An Investor's Guide. *Coal Week*. McGraw-Hill Publications Co. 1979. p. 47-53.
2. TLV's: Threshold Limit Values for Chemical Substances and Physical Agents in the

Workroom Environment with Intended changes for 1976 and 1977. American Conference of Industrial Hygienists. 1976, 1977.

3. Handy, Robert, and Anton Schindler. *Estimation of Permissible Concentrations of Pollutants for Continuous Exposure*. U.S. Environmental Protection Agency. Research Triangle Park, N.C. EPA/600/2-76/155. p. 43.
4. Fairchild, Edward J., ed. *Registry of Toxic Effects of Chemical Substances, Volumes I and II*. National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare. Cincinnati, Ohio. DHEW Publication Number (NIOSH) 78-104-B. September 1977.
5. Interim Procedures and Guidelines for Health Risk and Economic Impact Assessments of Suspected Carcinogens. *Federal Register*. 41:2402. May 25, 1976.
6. *Carcinogen Assessment Group's Assessment of Carcinogenic Risk from Population Exposure to Cadmium in the Ambient Air* (draft). Office of Research and Development, U.S. Environmental Protection Agency. Washington, D.C. May 1978. 44 p.
7. *Carcinogen Assessment Group's Preliminary Report on POM Exposures* (draft). Office of Research and Development, U.S. Environmental Protection Agency. Washington, D.C. July 1978. 15 p.
8. Environmental Protection Agency Water Quality Criteria. *Federal Register*. 44(52): 15926-15981. March 15, 1979.
9. Cornfield, Jerome. Carcinogenic Risk Assessment. *Science*. 198:693-699. November 18, 1977.
10. Dinman, Bertram D. "Nonconcept" of "No-Threshold": Chemicals in the Environment. *Science*. 175:495-497. February 4, 1972.
11. *National Cancer Institute List of Carcinogenic Chemicals and Mixtures*. National Institutes of Health, U.S. Department of Health, Education, and Welfare. Bethesda, Md. February 3, 1978.
12. Henry, S. A. Occupational Cutaneous Cancer Attributable to Certain Chemicals in Industry. *British Medical Bulletin* (London). 4:389-401. 1947.
13. *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Volumes I-XVIII*. International Agency for Research on Cancer, World

**TABLE 4. SUMMARY OF AIR EPCs AND AMBIENT AIR CONCENTRATIONS FOR
SELECTED POLYCYCLICS**

ID Number	Compound	Ambient Level Reported ($\mu\text{g}/\text{m}^3$)	Most Stringent Air EPC ($\mu\text{g}/\text{m}^3$)	Basis for EPCs
21A140	Anthracene	0.00035-0.002	133	Lowest effective dose for tumor- igenic response in mice is 3300 mg/kg.
21A180	Phenanthrene	0.0004-0.006	3.8	Lowest dose for tumorigenic response in mice is 71 mg/kg
21B040	Benz(a)anthracene	0.029	0.11	Lowest effective dose for tumor- igenic response in mice is 2 mg/kg.
21B060	7,12-Dimethylbenz(a)anthracene	-	0.0006	Tumors in 7 species reported. Lowest effective dose is 21 $\mu\text{g}/\text{kg}$.
21B080	3-Methylcholanthrene	-	0.009	Tumors in 8 species reported. Lowest effective dose is 0.312 mg/kg.
21B100	Benzo(c)phenanthrene and alkyl derivatives	0.006	0.5	Lowest effective dose for tumor- igenic response in mice is 10 mg/kg.
21B120	Chrysene	2.3×10^{-4}	5.29	Lowest effective dose for tumor- igenic response in mice is 99 mg/kg.
21B160	Triphenylene	0.0024	-	...
21B180	Pyrene	450	556	Lowest effective dose reported for tumorigenic response in mice is 10 g/kg.
21C040	Benzo(g)chrysene	-	38	Lowest effective dose reported for tumorigenic response in mice is 720 mg/kg.
21C060	Dibenz(a,c)anthracene	0.009	23.5	Lowest effective dose reported for tumorigenic response in mice is 440 mg/kg.
21C080	Dibenz(a,h)anthracene	0.0032-0.032	0.0002	Tumors in 5 species are reported. Lowest effective dose is 0.006 mg/kg.
21C100	Benzo(a)pyrene	4×10^{-5} to 4×10^{-4}	5×10^{-5}	Tumors in 6 species are reported. Lowest effective dose is 2 $\mu\text{g}/\text{kg}$.
21C120	Benzo(e)pyrene	9.0×10^{-4}	7	Tumors in 2 species are reported. Lowest effective dose is 140 mg/kg.
21C140	Perylene	0.0001	-	...
21C160	Picene	6.5×10^{-5}	6	Lowest effective dose for tumor- igenic response in mice is 111 mg/kg.
21D020	Dibenzo(a,h)pyrene	-	9	Lowest effective dose for tumor- igenic response in mice is 165 mg/kg.
21D040	Dibenzo(a,i)pyrene	-	0.1	Tumors in 2 species reported. Lowest effective dose is 2 mg/kg.
21D060	Dibenzo(a,l)pyrene	-	3	Lowest effective dose for tumor- igenic response in mice is 48 mg/kg.
21D080	Benzo(ghi)perylene	0.003	-	...
21D100	Coronene	8.0×10^{-7} to 2.13×10^{-6}	-	...
22B020	2,3-Benzofluorene	3.05×10^{-3}	-	...
22B040	Fluoranthene	-	162	LD ₅₀ (oral,rat): 2000 mg/kg.

TABLE 4 (continued)

ID Number	Compound	Ambient Level Reported ($\mu\text{g}/\text{m}^3$)	Most Stringent Air EPC ($\mu\text{g}/\text{m}^3$)	Basis for EPCs
22C020	Benzo(k)fluoranthene	-	3.9	Lowest effective dose for tumor- igenic response in mice is 72 mg/kg.
22C040	Benzo(j)fluoranthene	0.001	15	Lowest effective dose for tumor- igenic response in mice is 288 mg/kg.
22C060	1,2:5,6-Dibenzofluorene	-	31.5	Lowest effective dose for tumor- igenic response in mice is 590 mg/kg.
22C080	Benzo(b)fluoranthene	0.0005-0.02	2.1	Lowest effective dose for tumor- igenic response in mice is 40 mg/kg.
22D020	Indeno(1,2,3-cd)pyrene	-	3.9	Lowest effective dose for tumor- igenic response in mice is 72 mg/kg.
23B120	Phenanthridine	-	162	Based on acridine. LD ₅₀ (oral, rat): 2000 mg/kg.
23B140	Benzo(f)quinoline	0.2×10^{-3}	162	Based on acridine. LD ₅₀ (oral, rat): 2000 mg/kg.
23B160	Benzo(h)quinoline	3×10^{-4}	162	Based on acridine: LD ₅₀ (oral, rat): 2000 mg/kg.
23B180	Benz(a)acridine	2×10^{-4}	-	...
23B200	Benz(c)acridine	0.0006	25	Lowest effective dose for tumor- igenic response in mice is 468 mg/kg.
23B220	Dibenz(a,j)acridine	4×10^{-5}	0.59	Lowest effective dose for tumor- igenic response in mice is 11 mg/kg.
23B240	Dibenz(a,h)acridine	8×10^{-5}	0.5	Lowest effective dose for tumor- igenic response in mice is 10 mg/kg.
23B260	Dibenz(c,h)acridine	-	54.5	Lowest effective dose for tumor- igenic response in mice is 1,020 mg/kg.
23C080	Carbazole	-	41	Lowest lethal dose (oral, rat): 500 mg/kg.
23C120	Benzo(c)carbazole	-	45	Lowest effective dose for tumor- igenic response in mice is 840 mg/kg.
23C140	Dibenzo(a,i)carbazole	-	28	Lowest effective dose for tumor- igenic response in mice is 510 mg/kg.
23C160	Dibenzo(c,g)carbazole	-	0.2	Tumors in 4 species reported. Lowest effective dose is 8 mg/kg.
23C180	Dibenzo(a,g)carbazole	-	14	Lowest effective dose for tumor- igenic response in mice is 270 mg/kg.
25B040	Benzo(b)thiophene	-	41	Lowest lethal dose (intraperi- toneal, mouse): 512 mg/kg.

TABLE 5. COMPARISON OF CARCINOGENICITY RATINGS FOR POLYCYCLICS

Compound	Adjusted Ordering Numbers (Basis for EPC's)	Ratings suggested by National Academy of Science(21)*	Indications of Carcinogenicity	
			IARC Comments(12)	
Benzo(a)pyrene	3,314,500	+++	Produced tumors in all 9 animal species reported tested. Latent periods shorter than for other polycyclics with possible exception of dibenz(a,h)anthracene.	
Dibenz(a,h)anthracene	754,833	+++	Tumors produced in 8 animal species. Both local and systemic carcinogenic effects observed. Effective at low doses. Single dose effective in newborn mice.	
7,12-Dimethylbenz(a)anthracene	272,808	++++	Not addressed	
3-Methylcholanthrene	18,683	+++	Not addressed	
Dibenz(a,i)pyrene	1,612	+++	Rapid appearance of local sarcoma observed from subcutaneous injection in mice and hamsters. Skin painting on mice was also effective but less active than benzo(a)pyrene.	
Benzo(a)anthracene	1,562	+	Carcinogenic in mice by several routes. Effective oral dose similar to methyl cholanthrene but without gastrointestinal tract tumors.	
Dibenzo(c,g)carbazole	679	+++	Carcinogenic in rat, mouse, hamster, and possibly dog. Both local and systemic effects observed. Appears to be stronger respiratory tract carcinogen than benzo(a)pyrene in hamster.	
Benzo(c)phenanthrene (and -CH ₃ derivatives)	312	+++	Not addressed	
Dibenzo(a,h)acridine	312	++	Skin tumors and lung tumors in mice observed following skin painting or subcutaneous administration. Not tested adequately by other routes or in other species.	
Dibenzo(a,i)acridine	284	++	Skin tumors in mice followed topical application. Subcutaneous administrations at highest dosage produced local sarcomas and lung tumors. Not tested in other species.	
Benzo(b)fluoranthene	78	++	Produced skin tumors in mice following repeated skin painting, but only at levels 10 times higher than effective benzo(a)pyrene levels. Not tested by other routes.	
Dibenzo(a,i)pyrene	64	+	Subcutaneous administration in mice resulted in sarcomas in all animals. Not treated by other routes or in other species.	
Phenanthrene	44	-	Not addressed	
Benzo(k)fluoranthene	43	-	Not addressed	
Indeno(1,2,3-cd)pyrene	43	+	A complete carcinogen and initiation of skin carcinogenesis in mice, but of lower potency than benzo(a)pyrene. Local sarcomas followed subcutaneous injection in mice. Not treated by other routes as in other species.	
Methyl chrysenes	39	Not listed	Not addressed	
Chrysene	32	±	Skin tumors in mice followed repeated painting at high concentrations only. High dose, subcutaneous injections produced low incidence of tumors often long induction time.	
Picene	28	Not listed	Not addressed	
Benzo(e)pyrene	23	-	Data from a skin painting experiments in mice evoked weaker response than benzo(a)pyrene or dibenz(a,h)anthracene. Not tested by other routes.	
Dibenzo(a,h)pyrene	19	+++	Carcinogenic effects demonstrated following repeated skin painting in mice and injections in mice and rats. Not tested by other routes or in other species.	
Dibenzo(a,g)carbazole	12	±	Not addressed	
Benzo(j)fluoranthene	11	++	A high incidence of skin carcinomas results from repeated skin painting in mice. Not tested in other species or by other routes.	
Cholanthrene	Not listed	++	Not addressed	
Dibenz(a,c)anthracene	7	+	Not addressed	
Benzo(c)acridine	7	Not listed	Skin tumors in mice followed topical application. Bladder tumors in rats followed paraffin wax pellet implantation. Not tested by other routes or in other species.	
Benzo(a)carbazole	6	±	Not addressed	
Dibenz(a,i)carbazole	6	±	Not addressed	
Dibenz(c,h)acridine	6	±	Not addressed	
Dibenz(a,g)fluorene	5	+	Not addressed	
Dibenz(a,j)anthracene	No values given	+	Not addressed	
Dibenz(a,c)fluorene	Not listed	±	Not addressed	

*Carcinogenicity code given by NAS:

- not carcinogenic
- ± uncertain or weakly carcinogenic
- + carcinogenic

++, +++, ++++ strongly carcinogenic

Indications of carcinogenicity, refer to the Public Health Service Survey listed in reference 16 of this paper.

- Health Organization. Geneva, Switzerland. October 1978.
14. Cleland, J. G., and G. L. Kingsbury. *Multi-media Environmental Goals for Environmental Assessment, Volumes I and II*. Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency. Research Triangle Park, N.C. EPA-600/7-77-136a. November 1977.
 15. Grice, D. H., T. DaSilva, et al. *The Testing of Chemicals for Carcinogenicity, Mutagenicity, and Teratogenicity*. Department of Health and Welfare Canada. September 1973. 183 p.
 16. *Survey of Compounds Which Have Been Tested for Carcinogenic Activity, 1972-73 Volume*. National Cancer Institute, U.S. Department of Health, Education, and Welfare. Bethesda, Md. PHS Publication Number 149. 1973. p. 1.
 17. *An Ordering of the NIOSH Suspected Carcinogens List Based Only on Data Contained in the List*. Office of Toxic Substances, U.S. Environmental Protection Agency. Washington, D.C. EPA-560/1-76-003. March 1976. 132 p.
 18. Lucier, George W., and Gary E. R. Hood, ed. *Environmental Health Perspectives*. 22:185 p. February 1978.
 19. Shabad, L. M. On the So-Called MAC (Maximal Allowable Concentrations) for Carcinogenic Hydrocarbons. *Neoplasma*. 22(5): 459-468. 1975.
 20. Eisenbeiss, F., H. Hein, R. Joester, and G. Naundorf. The Separation by LC and Determination of Polycyclic Aromatic Hydrocarbons in Water Using an Integrated Enrichment Step. *Chromatography Newsletter*. 6(1):8. February 1978.
 21. *Biologic Effects of Atmospheric Pollutants. Particulate Polycyclic Organic Matter*. Division of Medical Sciences, National Research Council, National Academy of Sciences. Washington, D.C. 1972.
 22. *Environmental Assessment Methodology Workshop*. Sponsored by the Environmental Protection Agency, Office of Energy Minerals & Industry, Industrial Environmental Research Laboratory, Research Triangle Park; and Industrial Environmental Research Laboratory, Cincinnati. Airlie House, Va. January 16-18, 1979.

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SOURCE ANALYSIS MODELS FOR ENVIRONMENTAL ASSESSMENT

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Abstract

A series of source analysis models (SAMs) have been developed to treat the results of emissions assessments of stationary pollutant sources to evaluate potential environmental impact. These models provide a framework for making structured comparisons between measured effluent stream pollutant concentrations and threshold, allowable ambient concentrations (termed multimedia environmental goals or MEGs). Model outputs can thus be used to rank sources or effluent streams from a source with respect to potential environmental impact, evaluate alternate emission control strategies, or set priorities for control technology development. Three models have been or are being developed:

- *A rapid-screening model based on direct effluent stream concentration comparisons,*
- *A screening model incorporating a dilution factor approximation to pollutant dispersion, and*
- *A regional site evaluation model based on detailed treatment of pollutant dispersion.*

This paper describes features of each of these, contrasts elements of their development, and notes example applications in environmental assessment programs.

INTRODUCTION

Since 1975, the Energy Assessment and Control Division of the U.S. Environmental Protection Agency's Industrial Environmental Research Laboratory (EPA-IERL/EACD) has conducted environmental assessment (EA) programs that focus on identifying and resolving multimedia environmental risks from energy systems and fuel processes. The primary purposes of these EAs are to provide the research data base to support standards development by EPA program offices and to guide IERL control technology development programs to ensure

that appropriate controls are available when needed. Thus, these programs centralize data, quantify emissions and risks, evaluate control options, and recommend R&D priorities.

To coordinate the approach and output of each of the EAs, IERL/EACD is conducting several methodology development tasks that define standardized procedures to be followed in obtaining and evaluating process and environmental data. Standardized sampling, chemical analysis, and bioassay procedures are being specified; environmental objectives are being defined; and formats for comparing emission data and environmental objectives are being developed. This paper describes results of efforts to date to develop a series of source analysis models (SAMs) that address the need to define methods of comparing emission data with environmental objectives or multimedia environmental goals (MEGs).

Figure 1 illustrates the environmental assessment approach. This figure shows the two parallel activities involved in an EA: control technology evaluation and environmental data acquisition, and environmental objectives development. These two activities are brought together in the task labeled environmental alternatives analysis. In this analysis, results from process or effluent stream emissions assessments are compared to MEGs to form the basis for defining the outputs of an environmental assessment, as shown in the figure. The tool used to perform these comparisons is the source analysis model (SAM). The SAM, therefore, is the format used to compare pollutant loadings to the environment from a pollutant source to defined MEGs, thereby quantifying the potential environmental impact of a discharge stream or pollutant source. Results from these comparisons can subsequently be used to define such EA outputs as:

- Establishing more detailed sampling and analysis needs,
- Identifying problem pollutants,
- Quantifying discharge stream or source hazard potential,

*Speaker.

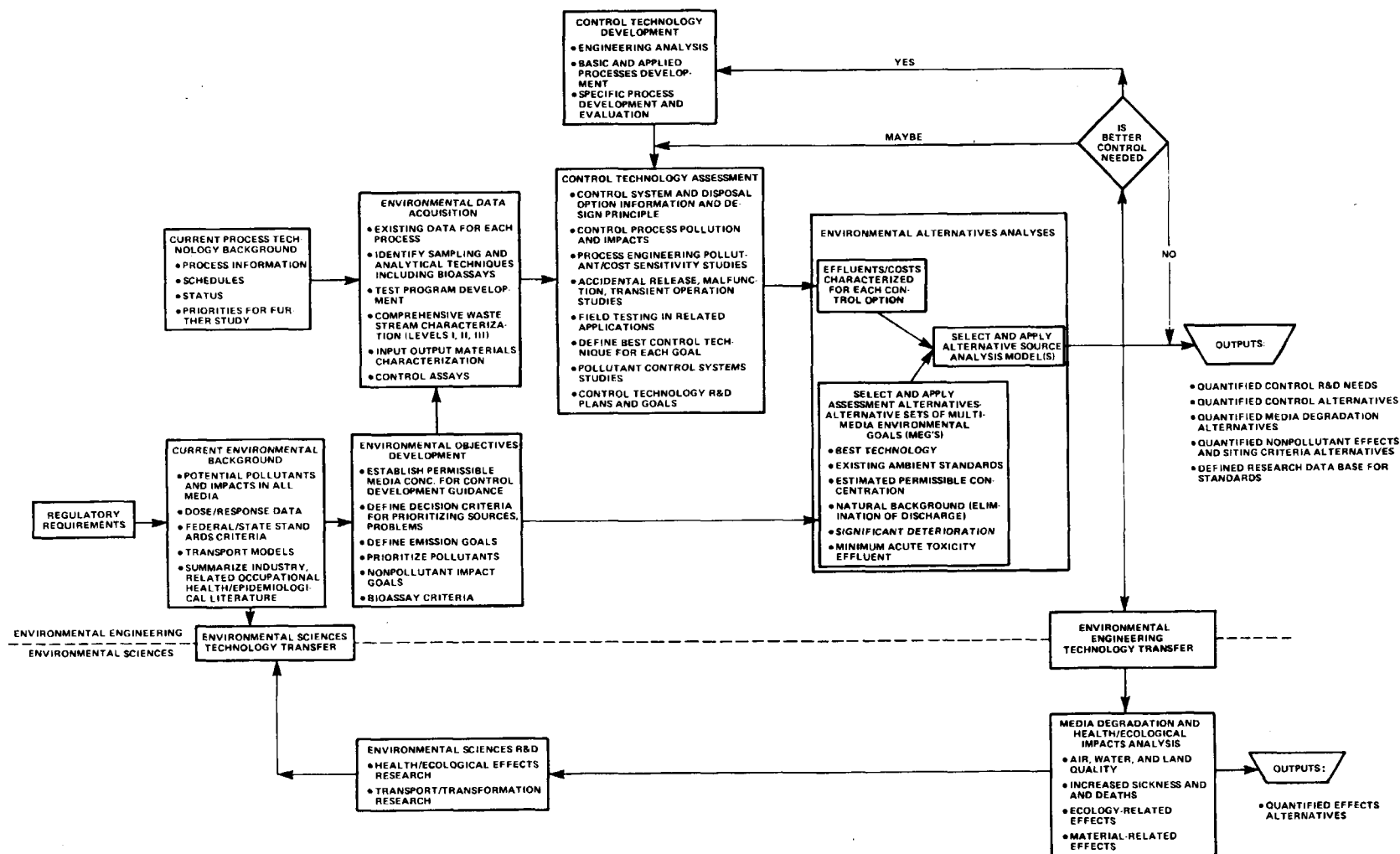


Figure 1. Environmental assessment program approach.

- Ranking discharge streams and sources with respect to potential for adverse environmental impact,
- Evaluating alternative control/disposal options for a given discharge stream, and
- Establishing control technology R&D needs.

In line with EA needs, SAMs are being developed in three levels of detail in the treatment of dispersion. The simplest model, SAM/IA, has been designed for rapid-screening purposes and, as such, includes no effluent transport or transformation analysis.¹ Goal comparisons employ the minimum acute toxicity effluent (MATE) MEG. The second model, SAM/I, has been designed for intermediate screening.² It includes some simple approximations to effluent stream/pollutant transport and employs ambient-based multimedia environmental goals. SAM/II will be designed for regional site evaluation and will include more sophisticated consideration of pollutant transport and transformation, cross media effects, and population exposure. All levels of the SAM, however, assume that:

- Only the MEG master list of about 650 specific chemical compounds^{3,4} need be considered in potential toxicity evaluations,
- The set of MEG values defined are appropriate indicators of threshold levels for adverse health or ecological effects, and
- Pollutant synergisms and antagonisms can be neglected.

Figure 2 illustrates the projected application of each level of SAM in the tiered EA approach. As the figure shows, the rapid-screening SAM/IA model finds primary use in evaluating Level 1 and Level 2 sampling and chemical analysis results. SAM/IA evaluations of Level 1 data serve to identify potential problem discharges and to point out pollutant species requiring Level 2 analysis. SAM/IA evaluations of subsequent Level 2 data close the loop and give screened pollutants and screened problem discharges.

The intermediate-screening SAM/I model finds optional use in treating Level 1 results but is primarily used to evaluate Level 2 data. Results from SAM/I-Level 2 evaluations confirm problem discharges and identify Level 3 monitoring needs. In turn, the regional site evaluation SAM/II model is designed to treat Level 3 data and quantify the potential impact of the problem discharges and pollutants.

The following section discusses features of

each level of analysis model being developed, contrasts specific elements of each model, and presents examples of each application. The discussion, in turn, treats the rapid-screening model, the intermediate-screening model, and the projected form of the regional site evaluation model.

RAPID-SCREENING SAM/IA

As noted in the introduction, the SAM/IA model has been designed as a rapid-screening tool for evaluating environmental assessment sampling and chemical analysis data. Thus, the model approach does not include treatment of effluent stream dispersion or pollutant chemical transformation. Instead, potential hazard estimates employ the minimum acute toxicity effluent (MATE) MEG.³

Two hazard indices are defined in the model: the potential degree of hazard (PDOH) and the potential toxic unit discharge rate (PTUDR). The PDOH is the ratio of the effluent stream concentration of a pollutant species to that species' MATE value:

$$PDOH_i = \frac{\text{Discharge concentration of compound } i}{\text{MATE of compound } i}$$

Thus, the PDOH is a measure of the existence of a potential hazard. Both health and ecological PDOHs can be defined for gaseous, liquid, and solid effluent streams consistent with appropriately defined MATE values.

The PTUDR is defined as the product of the PDOH with the effluent stream discharge rate:

$$PTUDR_i = PDOH_i \cdot \text{stream flow rate.}$$

Thus, the PTUDR is a measure of the magnitude of a potential hazard.

The PDOH and PTUDR are calculated for each pollutant species analyzed in the discharge stream, or in the case of Level 1 evaluations, for the most toxic species in an analyzed Level 1 sample fraction. Thus, to obtain a measure of the toxic potential presented by the total effluent, individual pollutant PDOH and PTUDR are summed to give total stream PDOH and PTUDR. In turn, to estimate the magnitude of a multieffluent pollutant source, stream total PTUDRs may be summed to give a source total PTUDR.

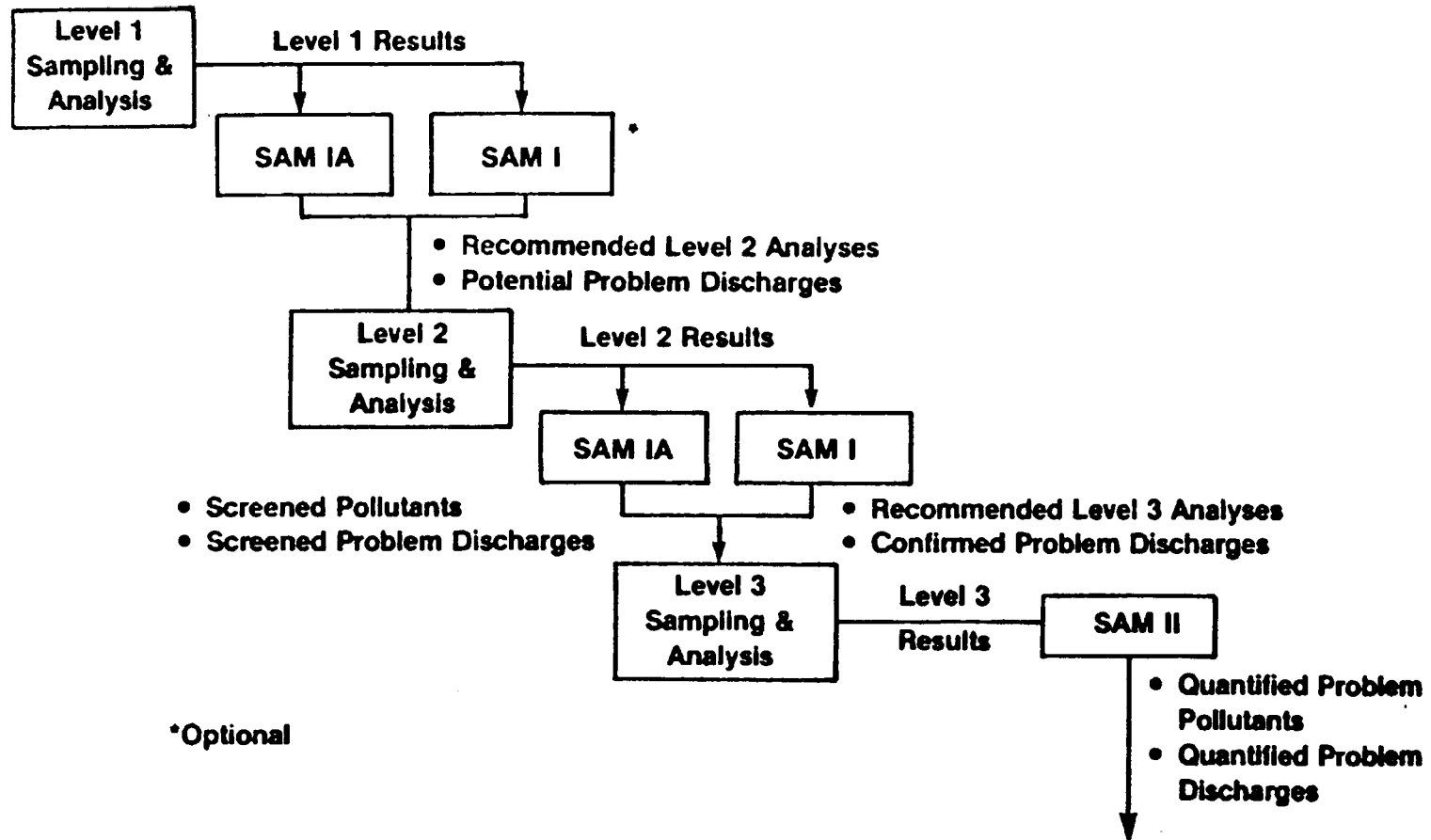


Figure 2. SAM application in the tiered assessment approach.

Tables 1 and 2 illustrate the use of these SAM/IA concepts to evaluate inorganic analysis data from a coal-fired utility boiler. Table 1 shows the results of a SAM/IA assessment of the inorganic component of the boiler's flue gas stream, including particulate composition. The table lists PDOH and PTUDR values for the 30

components assayed. Table 2 shows total stream PDOH and PTUDR values for the four effluent streams coming from the boiler, for two sets of operating conditions: baseline or uncontrolled for NO_x, and controlled for NO_x. The table indicates that the flue gas stream dominates the unit's potential hazard. Further, when

TABLE 1. PDOH AND PTUDR FOR UTILITY BOILER FLUE GAS (INORGANIC): SAM/IA

MEG Category	Component	Flue Gas Concentration ($\mu\text{g}/\text{dscm}$)	MATE: Health ($\mu\text{g}/\text{m}^3$)	PDOH: Health	PTUDR: ^a Health (Mg/s)
32	Be	9.0	2	4.5	0.312
36	Ba	2250	500	4.5	0.312
41	Tl	2.6	100	0.026	0.002
42	CO	3.07×10^4	4.0×10^4	0.768	0.053
	CO ₂	2.72×10^8	9.0×10^6	30.2	2.09
45	Sn	6.4	1.0×10^4	6.4×10^{-4}	4.4×10^{-5}
46	Pb	74	150	0.49	0.034
47	NO _x	1.16×10^6	9000	129	8.93
	NH ₄	10.5	150	0.07	0.005
49	As	95	2	47.5	3.29
50	Sb	3.9	50	0.078	0.005
51	Bi	44	410	0.107	0.007
53	SO ₂	4.18×10^6	1.3×10^4	322	22.3
	SO ₃	1.45×10^4	1000	14.5	1.00
	SO ₄	6500	1000	6.5	0.450
54	Se	9.9	200	0.050	0.003
55	Te	4.1	100	0.041	0.003
56	F	84	2000	0.042	0.003
57	Cl	270	400	0.675	0.047
62	Ti	6100	6000	1.02	0.070
63	Zr	270	5000	0.054	0.004
65	V	260	500	0.52	0.036
69	Mo	150	5000	0.03	0.002
71	Mn	240	5000	0.048	0.003
72	Fe	4.5×10^4	700	64.3	4.45
74	Co	66	50	1.32	0.092
78	Cu	280	200	1.4	0.097
81	Zn	420	4000	0.105	0.007
82	Cd	1.8	10	0.18	0.012
83	Hg	3.1	50	0.062	0.004
TOTAL				630	43

^aFlue gas flow rate of 69.3 kg/s.

TABLE 2. PDOH AND PTUDR FOR UTILITY BOILER DISCHARGES UNDER BASELINE AND NO_x CONTROLLED OPERATION: SAM/IA

Stream	Baseline		Controlled for NO _x	
	PDOH	PTUDR (kg/s)	PDOH	PTUDR (kg/s)
Flue gas	630	43,300	502	34,900
Cyclone ash	18.1	18.8	15.6	15.8
ESP ash	23.3	6.1	22.7	6.1
Bottom ash slurry	18.0	56.9	17.1	52.8
TOTAL	43,400			35,000

NO_x emissions are controlled (31 percent reduction), potential flue gas hazard is reduced, reducing overall total source potential hazard.

A second example serves to illustrate how the SAM/IA model can be used to identify Level 2 sampling needs based on Level 1 results. This example also introduces the concept of "looping," in which results from successive Level 1 analytical steps are used to rule out the existence of certain compound categories in a sample and thereby decrease the calculated PDOH.

The concentration of total vapor phase organic compounds (as collected by the organic module of the source assessment sampling system [SASS] train) in the coal feeder vent discharge stream was 780 mg/m³ as shown by recent data from a Level 1 source test of a low-Btu gasifier.⁵ With liquid chromatography separation, the LC6 fraction accounted for 79 mg/m³. Based only on this information, the calculated PDOH for the LC6 fraction would be 460 as shown in Table 3, based on the conservative assumption that the entire LC6 fraction consisted of the most toxic species potentially present in the fraction: 2-aminonaphthalene. This LC6 PDOH would thus be added to those for the other organic and inorganic categories to obtain the stream total PDOH. Further Level 2 analyses would be required for at least the 38 compounds in MEG

categories 5, 8, 10, 13, 19, and 23 listed in Table 3. These compounds have MATE values less than 79 mg/m³, so based only on the information that compounds eluting in the LC6 fraction are emitted at 79 mg/m³, these compounds would be flagged for Level 2 elucidation.

However, when results from the LC fraction infrared analysis are included with the TCO and gravimetric data, calculated PDOH decreases. In the example the IR report noted that the sample consisted of phenols and cresols (MEG category 18), carboxylic acids (category 8), and heterocyclic nitrogen compounds (category 23). Thus, assuming that amines (category 10), thiols (category 13), alcohols (category 5), and halophenols (category 19), are present only in negligible quantities, the calculated PDOH for the LC6 fraction decreases to 360, based on dibenz(a,h) acridine, as shown in Table 4. The table also indicates that Level 2 elucidation of 28 species in MEG categories 8, 18, and 23 would now be suggested.

Finally, incorporating results from the low-resolution mass "spectrometry analysis further reduces the calculated PDOH and the scope of needed Level 2. In the example, the LRMS report noted the strong presence of phenols (intensity = 100) and a weaker presence of heterocyclic nitrogen compounds (intensity = 10). Based on this, we can assume that the maximum

TABLE 3. LOW-Btu GASIFIER, COAL FEEDER VENT ORGANIC EXTRACT:
LC6 EVALUATION: TCO/GRAV DATA

MEG Number	Compound	MATE (mg/m ³)	PDOH ^a (Entire Assayed Level is the Compound)
10C220	2-Aminonaphthlene	0.17	470
23B240	Dibenz (a,h) acridine	0.22	360
23B220	Dibenz (a,j) acridine	0.25	320
10C080	Ansindines	0.50	160
13A140	Perchloromethanethiol	0.80	99
23C160	Dibenzo (c,g) carbazole	1.0	79
10A020	Methylamine	1.2	66
18B060	1,4-Dihydroxybenzene	2.0	40
13A100	Benzenethiol	2.1	38
23C020	Pyrrole	2.7	29
23D020	Benzothiazole	4.3	18
10C100	1,4-Diaminobenzene	4.5	18
23D040	Methylbenzothiazoles	4.7	17
08D280	Phthalate esters	5.0	16
23C180	Dibenzo (c,g) carbazole	6.0	13
18A120	2,2'-Dihydroxydiphenyl	6.8	12
23B200	Benz (c) acridine	11	7.2
23C040	Indole	11	7.2
23C140	Dibenzo (a,i) carbazole	12	6.6
18A140	Xylenols	13	6.1
18A180	Polyalkyl phenols	15	5.3
23B020	Quinoline	16	4.9
05B100	1-Phenylethanol	18	4.4
23C120	Benzo (a) carbazole	19	4.2
18B020	Catechol	20	4.0
18A040	Cresols	22	3.6
23C080	Carbazole	23	3.4
19B020	Chlorinated cresols	23	3.4
23B260	Dibenz (c,h) acridine	23	3.4
18A100	Phenylphenols	23	3.4
18A160	Alkyl cresols	24	3.3
10D020	N,N-Dimethylaniline	25	3.2
18A080	Ethylphenols	25	3.2
18A060	2-Methoxyphenol	33	2.4
18B080	1,2,3-Trihydroxybenzene	36	2.2
23C060	Methylindoles	45	1.8
23B040	2-Methylquinoline	55	1.4
10B100	Morpholine	70	1.1

^aEmission level = 79 mg/m³.

TABLE 4. LOW-Btu GASIFIER, COAL FEEDER VENT ORGANIC EXTRACT:
LC6 EVALUATION; IR + TCO/GRAV DATA

MEG Number	Compound	MATE (mg/m ³)	PDOHa (Entire assayed level is the compound)
23B240	Dibenz (a,h) acridine	0.22	360
23B220	Dibenz (a,g) acridine	0.25	320
23C160	Dibenzo (c,g) carbazole	1.0	79
18B060	1,4-Dihydroxybenzene	2.0	40
23C020	Pyrrole	2.7	29
23D020	Benzothiazole	4.3	18
23D040	Methylbenzothiazoles	4.7	17
08D280	Phthalate esters	5.0	16
23C180	Dibenzo (a,g) carbazole	6.0	13
18A120	2,2'-Dihydroxydiphenyl	6.8	12
23B200	Benz (c) acridine	11	7.2
23C040	Indole	11	7.2
23C140	Dibenzo (a,i) carbazole	12	6.6
18A140	Xylenols	13	6.1
18A180	Polyalkyl phenols	15	5.3
23B020	Quinoline	16	4.9
23C120	Benzo (a) carbazole	19	4.2
18B020	Catechol	20	4.0
18A040	Cresols	22	3.6
23C080	Carbazole	23	3.4
23B260	Dibenz (c,h) acridine	23	3.4
18A100	Phenylphenols	23	3.4
18A160	Alkyl cresols	24	3.3
18A080	Ethylphenols	25	3.2
18A060	2-Methoxyphenol	33	2.4
18B080	1,2,3-Trihydroxybenzene	36	2.2
23C060	Methylindoles	45	1.8
23B040	2-Methylquinoline	55	1.4

^aEmission level = 79 mg/m³.

concentration of LC6 category 18 compounds would be 72 mg/m³ and that the maximum concentration of category 23 species would be 7.2 mg/m³, with negligible category 8 compounds present. This information reduces the calculated PDOH for the LC6 fraction to 36, based on 1,4-dihydroxybenzene, as shown in Table 5. The table also shows that Level 2 would now be indicated for only 18 compounds in MEG categories 18 and 23.

INTERMEDIATE-SCREENING SAM/I

The SAM/I model has been designed for intermediate screening purposes to evaluate Level 1 (optionally) and Level 2 data. To address these objectives, the model includes elementary treatment of pollutant dispersion or dilution to ambient levels but does not incorporate ambient chemical reaction or transformation. Because pollutant dispersion is treated, potential

**TABLE 5. LOW-BTU GASIFIER, COAL FEEDER VENT ORGANIC EXTRACT:
LC6 EVALUATION; LRMS + IR + TCO/GRAV DATA**

MEG Number	Compound	MATE (mg/m ³)	PDOH ^a (Entire assayed level is the compound)
18B060	1,4-Dihydroxybenzene	40	36
23B240	Dibenz (a,h) acridine	0.22	33
23B220	Dibenz (a,j) acridine	0.25	29
18A120	2,2-Dihydroxydiphenyl	6.8	11
23C160	Dibenzo (c,g) carbozole	1.0	7.2
18A140	Xylenols	13	5.5
18A180	Polyalkyl phenols	15	4.8
18B020	Catechol	20	3.6
18A040	Cresols	22	3.3
18A100	Phenylphenols	23	3.1
18A160	Alkylcresols	24	3.0
18A080	Ethylphenols	25	2.9
23C020	Pyrrole	2.7	2.7
18A060	2-Methoxyphenol	33	2.2
18B080	1,2,3-Trihydroxybenzene	36	2.0
23D020	Benzothiazole	4.3	1.7
23D040	Methylbenzothiazoles	4.7	1.5
23C180	Dibenzo(a,g) carbazole	6.0	1.2

^aEmission level = 72 mg/m³ for category 18 species.
7.2 mg/m³ for category 23 species.

hazard estimates employ the minimum ambient level goal (ALG_m) MEG.

As in SAM/IA, two hazard indices are defined in SAM/I: the PDOH and the PTUDR. Here, though the PDOH is defined as the ratio of the estimated maximum ambient concentration of a pollutant species resulting from the effluent stream to the ALG_m for that species:

$$PDOH_i = \frac{\text{Estimated maximum ambient concentration of compound } i}{\text{Minimum ambient level goal for compound } i}$$

Again, the PDOH is a measure of the existence of a potential hazard. Correspondingly, the PTUDR is defined as the product of the PDOH with the effluent stream mass discharge rate and represents a measure of the magnitude of the potential hazard:

$$PTUDR_i = PDOH_i \cdot \text{stream mass flow rate.}$$

The PDOH is calculated for each pollutant species analyzed in the discharge stream, or in the case of Level 1 evaluations, for all species in an analyzed Level 1 sample fraction whose potential ambient level concentration exceeds its corresponding ALG_m. The PTUDR is calculated for each species whose PDOH is greater than unity. Stream total PDOH and PTUDR and source total PTUDR are obtained as they were in SAM/IA, with specific provision for incorporating the concept of "looping" described above.

To obtain the estimated maximum ambient concentration of a pollutant because of the discharge stream, SAM/I employs approximate dispersion models to account for the dilution of a discharge concentration to an ambient concen-

tration. Models have been developed for gaseous, liquid, and solid discharges into appropriate receiving bodies within air, water, and land media. Figure 3 illustrates the discharge stream/receiving body combinations treated. The figure shows that any given gaseous, liquid, or solid waste stream from a source can be discharged in a number of ways to air-, water-, or land-receiving media. For example, a liquid or solid stream can be discharged to a river-, lake-, or ocean-receiving body. In these cases the final receptor medium is surface water; thus, the use of water MEGs is appropriate for potential hazard evaluations. Adverse effects both to human health and to ecosystems are possible for river- and lake-receiving bodies, so health and ecological evaluations are appropriate. For ocean dumping, only ecological evaluations are meaningful because direct human health impacts from ocean dumping are assumed negligible.

Similarly, liquid and solid streams can be discharged to deep well, sump (or waste pond), irrigated field, wastepile, plowed field, cavity, or fill site-receiving bodies in the land medium. For liquid discharges and solid leachates, the final receptor medium is groundwater, so water MEG, health-based evaluations are appropriate. For leached soil residue the final receptor medium is the land, so land MEG, ecologically based evaluations are appropriate.

The underlying physical picture for all the SAM/I dispersion models is that of a discharge stream entering an entraining ambient flow. After mixing takes place, the pollutant stream dispersion, or dilution factor can be approximated by the ratio of the entraining stream volumetric flow rate to the discharge stream flow rate. SAM/I defines a discharge stream dilution factor, K , in just such a manner:

$$K = \frac{\text{Entraining stream volumetric flow rate}}{\text{Discharge stream volumetric flow rate}}$$

Therefore, the estimated maximum ambient concentration for a pollutant species is the ratio of the discharge concentration to the dilution factor.

Dilution factors have been defined for all the receiving boilers shown in Figure 3. In the dispersion models used to calculate these dilution factors, entraining flow characteristics and certain discharge stream characteristics have been

internally parameterized based on estimates of nationwide averages of these characteristics. Thus, only discharge stream flow rate remains a model variable. Further, several model discharge stream flow rates have been defined, spanning discharge flow rate range of interest. Typical dilution factors have been assigned to each of these model streams. Therefore, the SAM/I user need only know the discharge rate of the stream under evaluation, and receiving body discharged into, to perform SAM/I calculations.

As an example, for gaseous effluent streams discharged into the atmosphere, a Gaussian plume dispersion model⁶ was used to predict maximum ground level pollutant concentrations. Here, the entraining flow is the atmosphere. The entraining flow characteristics, atmospheric stability, and wind speed are given values within the model typical of nationwide average conditions. Further, discharge stream stack height is internally parameterized by relating average stack height to average source flow rate (e.g., large utility power plants, sources with flue gas discharge rates in the Mg/s range have stack heights around 200 m, whereas small commercial or industrial boilers, with flue gas flow rates in the kg/s range have about 10 m stacks). Thus, for SAM/I evaluations a user need only know discharge flow rate to be able to assign an approximate dilution factor.

The defined SAM/I dilution factor, as a function of effluent stream discharge rate, for the various effluent stream/receiving bodies is summarized in Table 6. Details of the models used to assign these dilution factors are reported elsewhere.²

An example of the use of the SAM/I model is presented in Table 7, where the Level 1 inorganic analysis data for the coal-fired utility boiler, treated by SAM/IA in Table 1, is evaluated through SAM/I. In this example, one notes that the flue gas flow rate is 69.3 kg/s. Reference to Table 6 requires a dilution factor of 1,000. Calculated PDOH and PTUDR values for the 26 components assayed that have ALG values as well as stream totals are shown in Table 7. Further use of SAM/I calculations in evaluating control technology application and in identifying Level 2 analysis needs is analogous to the use of SAM/IA as presented in Tables 2 through 5.

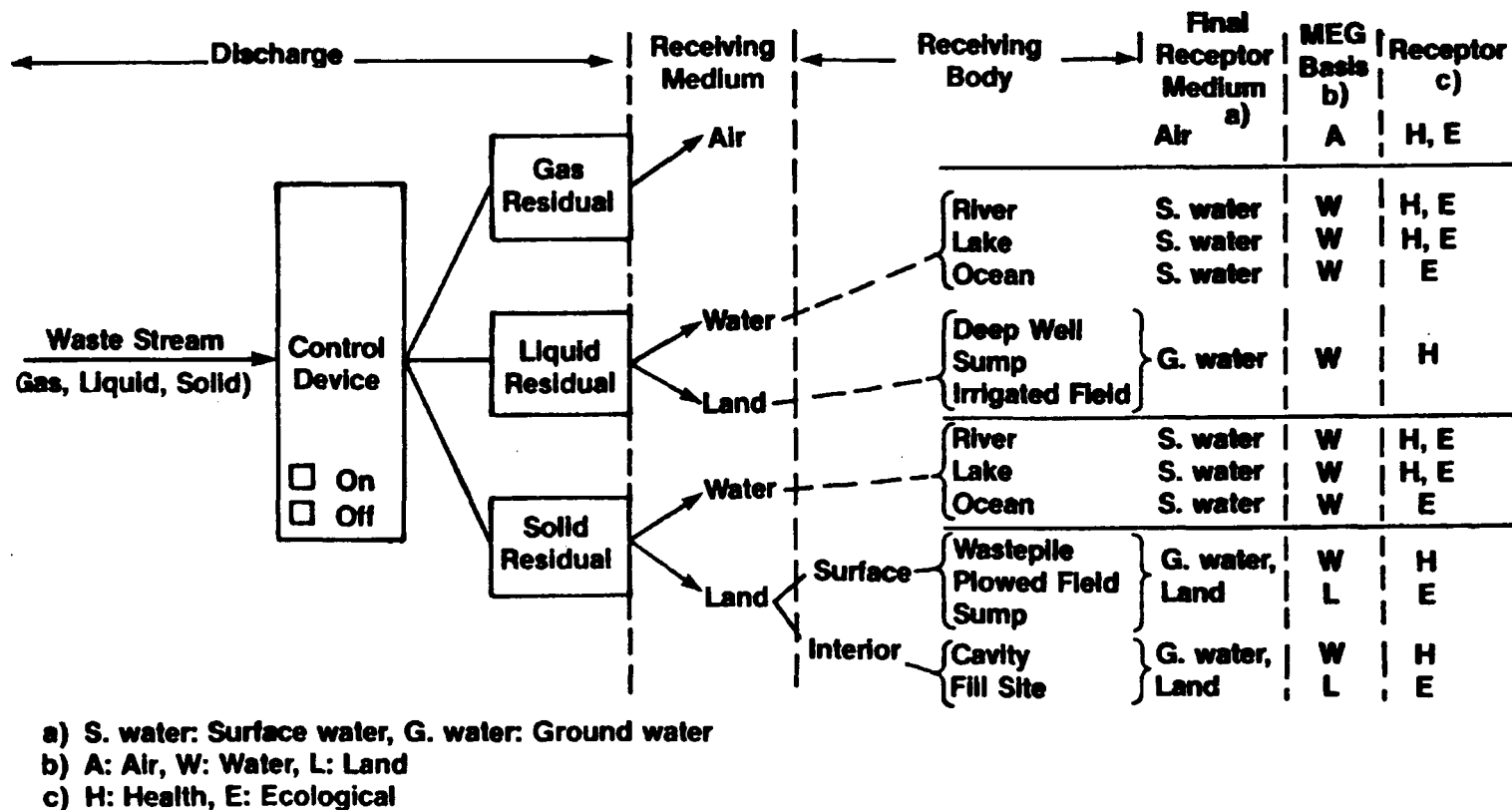


Figure 3. SAM/I pollutant discharge overview.

TABLE 6. SUMMARY OF MODEL STREAM DISCHARGE RATES AND DILUTION FACTORS

Discharge Stream Type	Gas		Liquid/Soluble Solid			
Receiving Body	Air		River/Lake		Ocean	
Discharge Rate Q (g/s) and Dilution Factor K	Q	K	Q	K	Q	K
	2.5 x 10 ⁶ 6.5 x 10 ⁵ 1.3 x 10 ⁵ 6.8 x 10 ³ 5.4 x 10 ²	1 x 10 ² 3 x 10 ² 1 x 10 ³ 5 x 10 ³ 2 x 10 ⁴	1 x 10 ⁵ 1 x 10 ⁴ 1 x 10 ³ 1 x 10 ² 1 x 10 ¹	1.6 x 10 ² 1.6 x 10 ³ 1.6 x 10 ⁴ 1.6 x 10 ⁵ 1.6 x 10 ⁶	3 x 10 ⁴ (Barge)	1 x 10 ³

Discharge Stream Type	Liquid		Liquid/Soluble Solid				Leached Solid	
Receiving Body	Deep Well		Irrigated Field		Sump, Waste Pile, Plowed Field, Cavity, Fill Site		Any Land Body	
Discharge Rate Q (g/s) and Dilution Factor K	Q	K	Q	K	Q	K	Q	K
	Any	1	Any	100	Any	10 ^a 100 ^b	Any	1

^aLarge receiving body with base diameter d ≥ 10m.

^bLarge receiving body with base diameter d < 10m.

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REGIONAL SITE EVALUATION, SAM/II

The SAM/II model will be designed for regional site evaluation purposes for specific evaluation of Level 3 data. It will be the most mathematically detailed model in the SAM series in its treatment of pollutant dispersion and will include treatment of population exposed to ambient levels to measure the impact of a potential environmental hazard. Where possible, the model will factor in pollutant species chemical transformations.

Individual components of the SAM/II model are presently being developed. To date, only the formulation for gaseous stream emissions to the atmosphere is sufficiently developed to be reported. In this model the hazard index used is termed the potential impact factor, I. This is defined to be the sum of the number of people exposed to ambient pollutant levels, weighted by the ambient PDOH exposure, wherever the

ambient PDOH exceeds 0.1. Mathematically, the potential impact factor can be expressed as:

$$I = \sum_i P \cdot PDOH_i \cdot dA; PDOH_i \geq 0.1$$

Here, i denotes a pollutant species, P is the exposed population (function of A), PDOH_i is the ambient potential degree of hazard as defined in the SAM/I model (also function of A), and A denotes the area of integration, defined as being that area where PDOH_i exceeds 0.1.

The same Gaussian dispersion model used in SAM/I is employed to estimate PDOH_i as a function of distance for the discharge. However, in SAM/II source characteristics (stack height, effluent flow rate) are not parameterized and model sources are not defined. Instead, these characteristics are treated as user-supplied inputs.

Table 8 is an example of the use of this impact

TABLE 7. PDOH AND PTUDR FOR UTILITY BOILER FLUE GAS (INORGANIC): SAM/I

MEG Category	Component	Flue Gas Concentration ($\mu\text{g}/\text{dscm}$)	ALG _m : Health ($\mu\text{g}/\text{m}^3$)	PDOH: a Health	PTUDR: b Health (Mg/s)
32	Be	9.0	0.01	0.09	
36	Ba	2250	1.0	2.3	0.16
41	Tl	2.6	0.24	0.011	
42	CO	3.07×10^4	1.0×10^4	0.003	
45	Sn	6.4	0.24	0.03	
46	Pb	74	0.36	0.20	
47	NO _x	1.16×10^6	100	12	0.83
	NH ₄	10.5	43	2.4×10^{-4}	
49	As	95	0.005	19	1.3
50	Sb	3.9	1.2	0.003	
51	Bi	44	0.7	0.063	
53	SO ₂	4.18×10^6	80	52	3.6
	SO ₃	1.45×10^4	2.4	6.0	0.42
	SO ₄	6500	2.4	2.7	0.19
54	Se	9.9	0.03	3.3	0.23
55	Te	4.1	0.24	0.017	
62	Ti	6100	14	0.44	
65	V	260	1.2	0.22	
69	Mo	150	12	0.012	
71	Mn	240	12	0.020	
72	Fe	4.5×10^4	107	0.42	
74	Co	66	0.10	0.66	
78	Cu	280	0.50	0.56	
81	Zn	420	9.5	0.044	
82	Cd	1.8	0.02	0.090	
83	Hg	3.1	0.01	0.31	
TOTAL				100	6.7

^aDilution factor of 1000; $\text{PDOH} = \frac{\text{Concentration}}{1000 \times \text{ALG}_m}$.

^bFlue gas flow rate of 69.3 kg/s.

factor formulation in ranking the potential environmental hazard of stationary combustion sources.⁷ The table shows calculated potential impact factor for flue gas emissions of the calculated 10 potentially most hazardous sources. Total emissions estimates for the criteria pollutants—NO_x, SO_x, CO, and hydrocarbon—with

the addition of particulate phase sulfates, trace elements, and polynuclear aromatic compounds were used in the calculation, along with estimates of nationwide urban and rural population densities. The table shows, not surprisingly, that coal-fired utility and industrial sources dominate the potential hazard ranking.

TABLE 8. POTENTIAL IMPACT FACTOR RANKING FOR STATIONARY CONVENTIONAL COMBUSTION SOURCES: FLUE GAS EMISSIONS

Equipment Type/Fuel	Potential Impact Factor
1. Small Watertube Stoker -- Coal	6.7×10^{11}
2. Small Firetube Stoker -- Coal	5.6×10^{11}
3. Tangential Utility -- Coal	1.9×10^{11}
4. Wall Fired Utility -- Coal	1.1×10^{11}
5. Wall Fired Industrial -- Coal	7.8×10^{11}
6. Large Watertube Stoker -- Coal	7.6×10^{10}
7. Vertical & Stoker -- Coal	5.7×10^{10}
8. Cyclone Utility -- Coal	4.1×10^{10}
9. Opposed Utility -- Coal	2.1×10^{10}
10. Tangential Utility -- Oil	2.7×10^9

SUMMARY

A series of source analysis models for evaluating tiered environmental assessment sampling and chemical analysis results in terms of quantifying the potential environmental impact of a discharge stream or pollutant source is under development. Elements of the form of each of these have been presented and illustrated through several example applications demonstrating potential uses in an environmental assessment.

REFERENCES

- Schalit, L. M., and K. J. Wolfe. *SAM/IA: A Rapid Screening Method for Environmental Assessment of Fossil Energy Process Effluents*. EPA-600/7-78-015. February 1978.
- Anderson, L. B., et al. *SAM I: An Intermediate Screening Method for Environmental Assessment of Fossil Energy Process Effluents*. Acurex Corp., Mountain View, Calif. Acurex Report TR-79-154. December 1978.
- Cleland, J. G., and G. L. Kingsbury. *Multimedia Environmental Goals for Environmental Assessment, Volume I*. EPA-600/7-77-136a. November 1977.
- Kingsbury, G. L. *Master List of Organic Substances to be Addressed by Multimedia Environmental Goals*. Research Triangle Institute. Research Triangle Park, N.C. October 1978.
- Page, G. C. *Environmental Assessment: Source Test and Evaluation Report—Chapman Low-Btu Gasification*. EPA-600/7-78-202. October 1978.
- Turner, D. B. *Workbook of Atmospheric Dispersion Estimates*. U.S. Public Health Service AP-26. 1970.
- Salvesen, K. G., et al. *Emission Characterization of Stationary NO_x Sources: Volume I Results*. EPA-600/7-78-120a. June 1978.

INTERAGENCY RESEARCH ON THE ENVIRONMENTAL TRANSPORT AND EFFECTS OF SYNFUELS-RELATED SUBSTANCES

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Abstract

The Interagency Energy/Environment R&D Program, initiated in late 1974, comprises over 300 major research and development projects being conducted by 17 Federal agencies and departments. The program is planned and coordinated by the U.S. Environmental Protection Agency's (EPA) Office of Research and Development. The projects in this program cover a wide spectrum of investigation—from basic and applied research on the movement of energy-related substances through the environment and their health and ecological effects, to development of systems for control of these substances, to socioeconomic studies of the future impacts of the U.S. energy development.

This presentation gave an overview of the objectives and the general status of selected projects under the interagency program. The projects described were selected to present a cross-section of the work being done on the health and ecological effects, and transport through the environment, of substances potentially released by synthetic fuel production and use.

The presentation on this subject was made by Dr. Tucker. He began by briefly reviewing the history of the Interagency Energy/Environmental R&D Program, the Federal agencies involved, the energy processes of concern, and the historical breakdown of funding for various research areas. Documentation of this information is available in References 1 through 14.

Of the 200-plus projects sponsored under this program that relate to the movement and fate of substances in the environment and their effect on human and ecological health, approximately

50 deal with synthetic fuels processes or substances that could be released from synfuels production or use. For purposes of this presentation, 20 of those projects were briefly described. These projects were selected to illustrate the breadth of ongoing research in the biological and physical sciences and how it complements the Environmental Assessment and Environmental Control Technology programs that were the primary topics of this symposium.

The projects were organized into four general areas:

- Human health effects
- Ecological effects
- Transport and fate
- Measurement and instrumentation

The projects that were discussed are listed in Tables 1 through 4. Project personnel and reference documents are listed for those who are interested in obtaining detailed information on the individual projects.

There is potential for mutual benefit from greater contact between some of these projects and the various synfuels environmental assessments being sponsored by the U.S. Environmental Protection Agency (EPA) and other Federal and private groups. A recommendation was made that presentations on several transport and effects projects be included on the program for the next EPA synfuels symposium.

REFERENCES

1. *Interagency Energy/Environmental R&D Program.* U.S. Environmental Protection Agency. EPA-600/7-77-007. March 1977.
2. *Who's Who in the Interagency Energy/Environmental R&D Programs IV.* U.S. Environmental Protection Agency.

*Speaker.

**TABLE 1. SELECTED HUMAN HEALTH EFFECTS PROJECTS FROM THE
INTERAGENCY ENERGY/ENVIRONMENTAL R&D PROGRAM**

<u>PROJECT</u>	<u>CONTACT</u>	<u>REFERENCE</u>
Repository of Samples	D. L. Coffin EPA/HERL Research Triangle Park North Carolina 27711 (919) 541-2586 FTS 629-2586	7
Genetic and Carcinogenic Hazards	Numerous contacts; see ref. 3, pp. 9-10	3, 5, 6, 7, 8
Extrapolation and Risk Assessment	D. G. Hoel NIEHS Research Triangle Park North Carolina 27711 (919) 541-3441 FTS 629-3441	2, 3
Industrial Hygiene	A. Thomas NIOSH 5600 Fishers Lane Room 8-48 Rockville, MD 20857 (301) 443-3843	3, 7

**TABLE 2. SELECTED ECOLOGICAL EFFECTS PROJECTS FROM THE
INTERAGENCY ENERGY/ENVIRONMENTAL R&D PROGRAM**

<u>PROJECT</u>	<u>CONTACT</u>	<u>REFERENCE</u>
Aquatic Effects of Synfuel Discharges	K. E. Biesinger EPA/ERL 6201 Congdon Blvd. Duluth, MN 55804 (218) 727-6692 FTS 683-9512 H. L. Bergman University of Wyoming Laramie, WY 82071 (307) 766-4330	3, 8
Coastal Ecosystems	H. Tait USFWS NSTL Station, MS 39529 (601) 688-2091 FTS 494-2091 E. D. Schneider EPA/ERL South Ferry Road Narragansett, RI 02882 (401) 789-1071 FTS 838-4843	3, 4, 5
Vegetative Stabilization of Spent Shale	E. F. Harris EPA/IERL 5555 Ridge Avenue Cincinnati, OH 45268 (513) 684-4417	7, 8
Subsidence from In-Situ Coal Gasification	E. R. Bates EPA/IERL 5555 Ridge Avenue Cincinnati, OH 45268 (513) 684-4417	

**TABLE 3. SELECTED TRANSPORT AND FATE PROJECTS FROM THE
INTERAGENCY ENERGY/ENVIRONMENTAL R&D PROGRAM**

<u>PROJECT</u>	<u>CONTACT</u>	<u>REFERENCE</u>
Dynamics of Refinery/ Petrochemical Wastes in Marine Waters	H. M. McCammon DOE/OHER Washington, D.C. 20545 (301) 353-5547 FTS 233-5547	3, 5
Dynamics of Refinery Wastes in Lake Michigan	Same as above.	3, 5

**TABLE 4. SELECTED MEASUREMENT AND INSTRUMENTATION PROJECTS
FROM THE INTERAGENCY ENERGY/ENVIRONMENTAL R&D PROGRAM**

<u>PROJECT</u>	<u>CONTACT</u>	<u>REFERENCE</u>
Secondary Organic Air Pollutants from Gasifi- cation Plants	R. K. Patterson EPA/ESRL Research Triangle Park North Carolina 27711 (919) 541-2254 FTS 629-2254	
Composition of Synfuel Wastes	A. Alford EPA/ERL Athens, GA 30605 (404) 546-3525 FTS 250-3525	14
Portable GC for Organics	L. Doemeny NIOSH 4676 Columbia Parkway Cincinnati, OH 45226 FTS 684-4266	
Standard Reference Materials	C. Gravatt NBS Washington, D.C. 20234 (301) 921-3775	3, 4

- EPA-600/9-78-002 (NTIS Number PB 284 375). June 1978.
3. *Who's Who V: The Interagency Energy/Environmental R&D Program Directory and Index*. U.S. Environmental Protection Agency. EPA-600/9-79-017. June 1979.
 4. *Interagency Energy/Environmental R&D Program—Status Report III*. U.S. Environmental Protection Agency. EPA-600/7-77-032 (NTIS Number PB 265 443). April 1977.
 5. *Fiscal Year 1976/Health and Environmental Effects Research Program Abstracts*. U.S. Environmental Protection Agency. EPA-600/7-77-004 (NTIS Number PB 265 381). January 1977.
 6. *Interagency Program in Energy-Related Health and Environmental Effects Research: Project Status Report*. U.S. Environmental Protection Agency. EPA-600/7-79-009 (NTIS Number PB 290 578). January 1979.
 7. *EPA Program Status Report: Oil Shale*. U.S. Environmental Protection Agency. EPA-600/7-78-020. February 1978.
 8. *EPA Program Status Report: Oil Shale 1979 Update*. U.S. Environmental Protection Agency. EPA-600/7-79-089. March 1979.
 9. *Energy/Environment II*. U.S. Environmental Protection Agency. EPA-600/9-77-025. November 1977.
 10. *Energy/Environment III*. U.S. Environmental Protection Agency. EPA-600/9-78-022 (NTIS Number PB 290 558). October 1978.
 11. Gage, Stephen J., et al. *Final Report of the Interagency Working Group on Environmental Control Technology for Energy Systems*. The Council on Environmental Quality. November 1974.
 12. King, Donald, and Warren R. Muir, et al. *Report of the Interagency Working Group on Health and Environmental Effects of Energy Use*. The Council on Environmental Quality. November 1974.
 13. Ray, Dixy Lee. *The Nation's Energy Future*. U.S. Atomic Energy Commission. WASH-1281, U.S. GPO Stock Number 5210-00363. December 1973.
 14. *Identification of Components of Energy-Related Wastes and Effluents*. U.S. Environmental Protection Agency. EPA-600/7-78-004 (NTIS Number PB 280 203). January 1978.

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DEPARTMENT OF ENERGY ENVIRONMENTAL ASSESSMENT PROGRAM FOR COAL CONVERSION

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Abstract

Implicit in the U.S. Department of Energy's (DOE) charge to foster the development of commercially viable coal gasification and liquefaction processes is the requirement that this technology be environmentally acceptable. While wide-scale use of this technology over the next several decades is not predicted, synfuel alternatives such as coal conversion will significantly contribute to domestic energy supply over the long term.

DOE's environmental assessment activity, oriented toward evaluating the environmental impact ultimately associated with a sizable synthetic fuels industry, is conducted to guide here-and-now RD&D and policy decisions. A series of time-phased environmental assessments parallel the development and scaleup of the technology. Major areas of environmental concern and uncertainty are singled out in NEPA documentation that accompanies scaleup activity. Environmental concerns that go beyond current regulatory and siting requirements for energy technologies are addressed in DOE documents including environmental development plans that are prepared for each emerging technology. Individual, detailed project milestones require formalized environmental status reports to ensure that environmental concerns and issues are satisfied.

It is the objective of DOE environmental assessment to look beyond the single demonstration plant facility and to project the potential impact of a mature coal conversion industry. Such an assessment is complex and ambitious. It involves integrating and synthesizing a number of environmental factors—emission, effluent, and solid waste source characterizations; control capabilities; health effect determinations; anticipation of regulatory requirements; resource demands; social-economic considerations; and cost-benefit analyses.

Because complex technical, economic, and

public issues are at stake, conclusions tend to be judgmental and, of course, are sensitive to the scenario under consideration. DOE has a complement of interdepartmental and intradepartmental activities to expand the data base, both in the field and in terms of studies, to improve the analysis process and the credibility of the assessments. This presentation will overview these evolving assessment processes.

INTRODUCTION

Webster defines assessment as the act of determining the importance, size, or value of a given thing. The U.S. Department of Energy's (DOE) environmental assessment activity is concerned with:

- Evaluating human and ecological effects of the environmental intrusions that are associated with energy conversion processes, especially those involving coal conversion;
- Fully characterizing the nature of these pollutant releases; and
- Determining the efficacy and practicability of control technology that is deployed to mitigate and limit such releases.

Obviously, assessment is highly dependent on the qualities singled out in accounting. In the area of synfuels conversion, considerable effort is needed to help define and quantify the controlling environmental qualities. Ideally, the assessment will key to those areas where significant environmental impacts are experienced.

In this presentation I hope to:

- Briefly outline some of the obvious difficulties confronting an environmental assessment activity, the primary one being the lack of hard operating data for synfuels facilities;
- Describe the manner and means by which DOE is forming a set of interdisciplinary teams to address a series of process/site-specific environmental characterizations to

DOE ENVIRONMENTAL ASSESSMENT PROGRAM FOR COAL CONVERSION

BACKGROUND

- MOVING TARGETS AND COMPLEXITY OF PERFORMING OVERALL INDUSTRY ORIENTED ASSESSMENT
- EVOLVING DOE ORGANIZATION
- DEVELOPING ENVIRONMENTAL ASSESSMENT PROGRAM

PROCEDURES TO ENSURE "ENVIRONMENTAL ACCEPTABILITY"

- PLANNING AND DOCUMENTATION
- COMPLIANCE REGULATIONS - OFFICE OF FOSSIL ENERGY PROGRAMS (FEP)
- FUTURE STANDARDS AND COMMERCIALIZATION IMPACTS - ASSISTANT SECRETARY FOR ENVIRONMENT (ASEV)
- PROCESS/SITE SPECIFIC CHARACTERIZATION AND ASSESSMENTS

ON-GOING ACTIVITIES

- BASE PROGRAM HIGHLIGHTS
- CONTROL TECHNOLOGY ASSESSMENTS

SUMMARY

Figure 1. DOE environmental assessment program for coal conversion.

fulfill the aforementioned data need; and

- Indicate the important and significant role generic environmental (core program) R&D has had and will continue to have on such an endeavor (Figure 1).

The intent is to recognize the diverse environmental assessment and acquisition activity ongoing within the department.

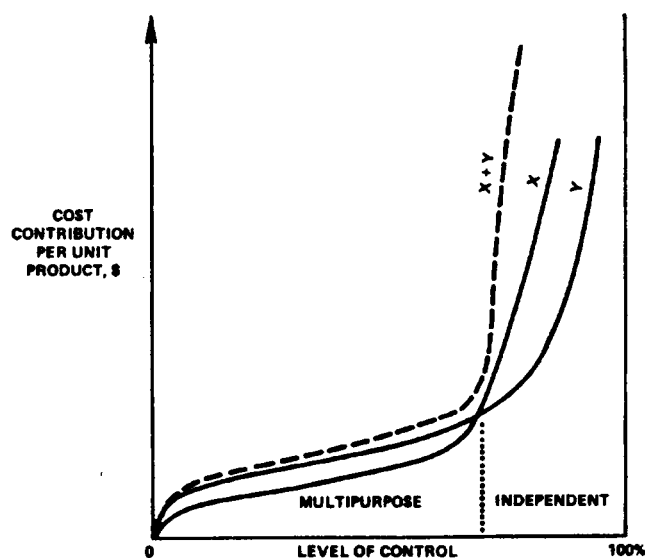
BACKGROUND

Public Law 95-91, which on August 5, 1977 created the U.S. Department of Energy (DOE), charges the Agency with promoting and developing "environmentally acceptable" energy technologies. Recent legislation to further guide EPA regulatory efforts in the area of emissions, the Clean Air Act Amendments of 1977, speaks of encouraging the use of best control technology that is "economically achievable." DOE's main thrust is to provide and support economic energy options, while EPA is dedicated to preserving and improving the quality of the environment, cost and resource considerations having been of critical although secondary import. Administration officials indicate that increased attention is to be given to economic and resource considerations in the setting of emissions standards. This is as it should be, for *ideally* DOE and EPA form a true complement in sustaining and improving life quality. Enhanced

energy and environmental goals are inseparable.

One should take a systems approach in arriving at "preferred energy choices." "Environmentally acceptable," "economically achievable," and "preferred choices" are "soft," qualitative terms that are in the process of acquiring quantitative meaning as legislation is implemented and new energy options and concomitant environmental regulations develop. But this takes time. With synfuels there are presently a number of moving targets: changing resource availability, improvements to and new processes for the technology, promulgation, and tightening of environmental standards, and changing economic climate. In addition to "uncertainty" because of the evolving nature of the technology and boundary conditions in which the technology must operate is the uncertainty associated with incomplete knowledge. This is especially critical to the life sciences, to allow prediction of long-term human health and ecological impacts. The situation is complicated by an overlap of largely subjective social-economic value judgments and of speculative future energy resource demands.

In an ideal decisionmaking process, comprehensive environmental assessment of "benefits" vs. "costs" might be made to establish priorities for energy options. One could envision the selection of individual "benefit" criteria (energy



EXAMPLES OF CONTROL SYNERGISMS

MULTIPURPOSE CONTROL	POLLUTANT	INDEPENDENT CONTROL
1. PHYSICAL COAL CLEANING	X SULFIDES Y ASH	CHEMICAL EXTRACTION PULVERIZATION/FLOATATION CELLS
2. ACTIVATED SLUDGE	X REFRACTORY ORGANICS Y DEGRADABLE ORGANICS	ACTIVATED CARBON/ CHEMICAL OXIDATION HOLDING POND
3. SCRUBBER	X PARTICULATES Y SULFUR DIOXIDE	ESP/BAG HOUSE INCREASED CONTACT AND REAGENT

Figure 2. Examples of control synergisms.

availability, jobs, affluence) and corresponding "cost" criteria (environmental control costs, health and safety risks, loss in aesthetics, etc.). The weak link in such a comparison is the assignment of weighing factors and, ultimately, values to "equate" the individual criterion. At present one is left with "apples and oranges." Thus, the assessment by necessity becomes subjective and judgmental.

Environmental Controls

In the area of environmental controls, as technology becomes more efficient, one might compare process control cost and emission level for a single pollutant. Real-world emissions, ef-

fluents, and solid waste boundary conditions, which control plant design and operation, are multivalued. In many instances, the function and performance of the environmental control processes are multipollutant-oriented (Figure 2). Thus, even with characterization of control hardware, analysis of cost-effectiveness relative to complying with a set or series of environmental standards is exceedingly complex and not wholly practical.

In scrutinizing environmental process control costs in such a manner one must consider total energy costs. When processes are compared, it is erroneous to compare only environmental control costs. Quite conceivably, an overall process systems tradeoff may exist with low costs

associated with the coal conversion train balanced by high environmental control costs and vice versa. Because pollution regulations are boundary conditions, (i.e., specifications similar, say, to product purity) that must be met by the coal conversion process as integral parts to the overall process, scientists are cautioned against segregating pollution controls from the rest of the process.

Occupational and Public Health Effects

As one can appreciate, the health inputs to a cost-benefit analysis are several orders more difficult. All of the coal conversion processes involve bioactive materials (both organics and trace elements) that have not been previously produced on the scale envisaged for commercial synfuels operations. Many of the potentially adverse human effects are low-level and take years to diagnose and quantify. Human (i.e., worker) exposure in pilot-plant operations represents an exceedingly small "window" in time and exposure and, because of the developmental nature of such pilot operations, they cannot be considered truly representative of commercial synfuels activity. Existing sister industries; e.g., coking and petroleum industries, are being drawn on to provide guidance. For the present, one must resort to progressively more sophisticated biological screening tests and make the tenuous extrapolation to man. This should not be construed to say that synfuels is in a unique position because with increasing vigilance toward toxic and bioactive materials (RCRA and TSCA), a number of established industries are and will be subject to similar mammal-to-man extrapolations. Emphasis is placed on the considerable progress being made in facilitating this animal-man linkage as part of DOE's base/core research program. In the human health area, the present state of knowledge and statistical base are too uncertain to quantitatively translate worker and ambient-exposure levels into sickness, disease, and loss of life, except in isolated cases.

Ecological Effects

A similar situation exists in extrapolating ecological effects observed in pilot operations to full-scale facilities. In many instances, the pilot

plant is located in an industrial area that is already highly contaminated, the contribution of pilot plant being insignificant relative to the existing baseline. Again, the question arises of how representative the operations of a pilot facility are relative to a full-scale plant. Ecological effects tend to be regional, site and process, specific. This erects an additional barrier against meaningful ecological input to overall technology assessment.

Assessment Methodologies

Regional and national environmental impact assessments suffer from similar uncertainties; e.g., the accuracy of the dispersion models used in analysis and assumed pollutant source releases. Perhaps the weakest link, for want of better input data, is the energy development scenario and concomitant source terms. Normally, the synfuels technologies are expected to comply with assumed standards, with nonregulated pollutants considered in a cursory manner. The resultant predicted ambient emission levels are no better than these assumptions. They will, however, give some index of potential ambient "hot-spots" and regional problem areas. The real uncertainty in the evaluation is how this data translates to human health effects and life quality. This uncertainty has been the same problem EPA has had to wrestle with and has dealt with primarily through the pragmatic approach of going to standards oriented at "best available control technology" at the point of release (e.g., as in the case of the utility industry). One can probably expect a similar approach with synfuels.

Thus, the various inputs to comprehensive environmental assessment of future coal conversion industry (e.g., control technology, health, ecological, social, economic, and resource considerations) are at various stages of development, making it difficult to grant creditability to any overall future environmental assessment.

The approach DOE is taking with this difficult problem is to integrate the environmental assessment activity with specific technology and projects activities, with generic-related environmental research providing complementary support. The organization, the methodology, and ongoing environmental assessment activities, including general support activities, will be

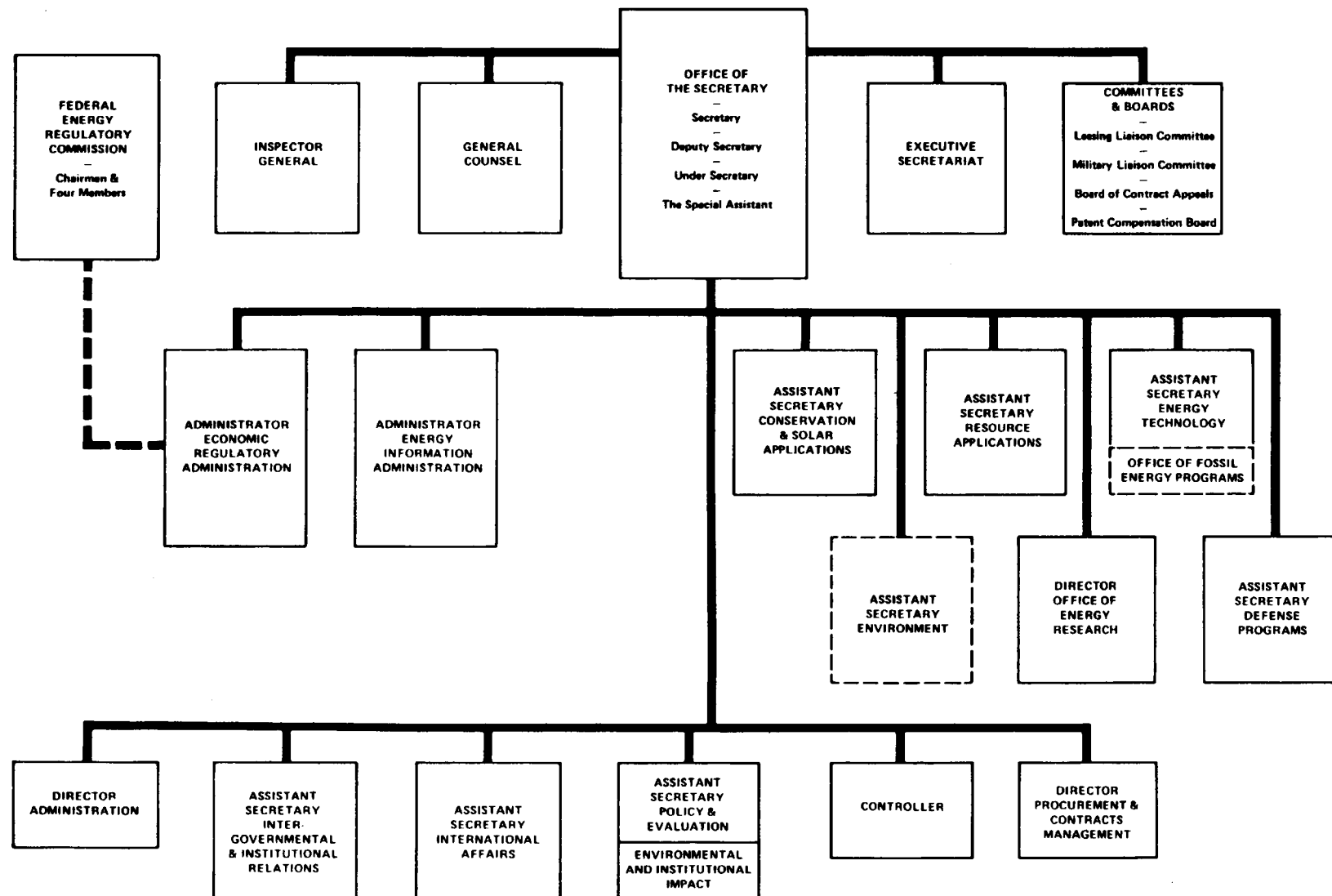


Figure 3. Department of Energy.

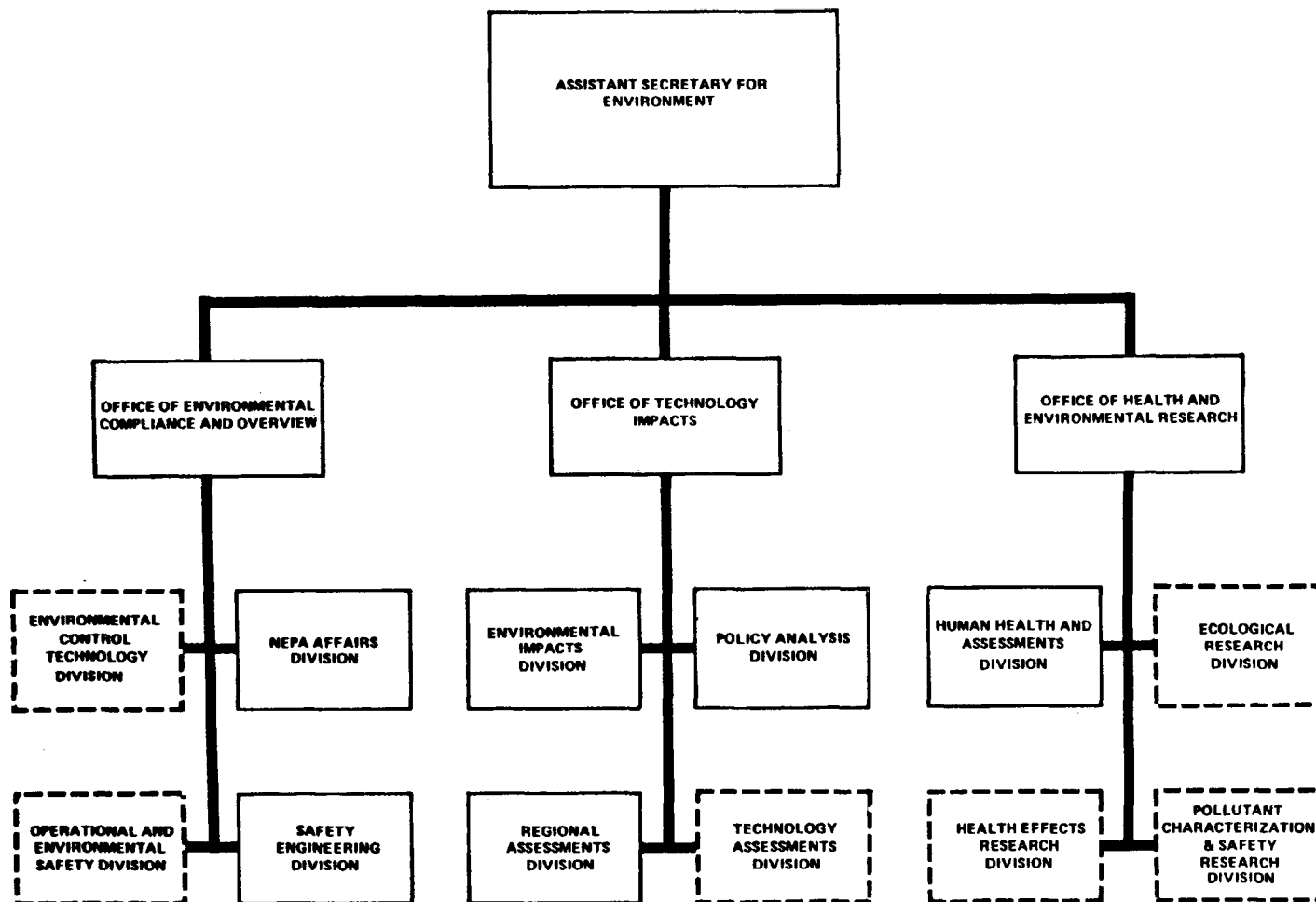


Figure 4. Assistant Secretary for Environment (ASEV).

discussed. These activities provide target environmental assessments that will ultimately rule on the "environmental acceptability" of a candidate technology.

DOE ORGANIZATION AND ENVIRONMENTAL GOALS

The Department has been in existence for about 18 mo. It was created primarily to integrate and consolidate the Federal energy programs then distributed among several agencies with differing energy mandates and objectives. While the basic structure has been formalized, responsibilities are still being refined by assistant secretaryships (Figure 3). Responsibility for past synfuels environmental activities has mainly resided with the Assistant Secretary for Environment (ASEV) and Fossil Energy Programs (FEP) organizations (Figures 4 and 5). The fact that environmental concern naturally spreads from top management to the line-divisions that are developing the technology has rightly led to considerable environmental activity outside of ASEV. What has developed is a logical interface based on line-divisions having primary responsibility for meeting NEPA and compliance re-

quirements, with ASEV exercising overview responsibility and implementing a comprehensive research program oriented to environmental effects. ASEV has in large part assumed an anticipatory role in assessing the environmental impact of commercialization activities and future standards, with ASET providing consultation. The end product of such assessment activity provides complete input and support to DOE policy decisions. It is useful to single out major organizational components within DOE's *synfuels* environmental assessment along with key personnel (Figure 6). The responsibility for site and process activities (e.g., NEPA requirements [EIS], securing permits, meeting compliance standards both for discharges and plant operation) resides with the FEP project officer, with assistance from an environmental support group within FEP. For environmental information-gathering and assessment activities beyond those legally required for plant operation, FEP looks for support from ASEV.

METHODOLOGY OF ENSURING ENVIRONMENTAL ACCEPTABILITY

Major DOE programmatic efforts are re-

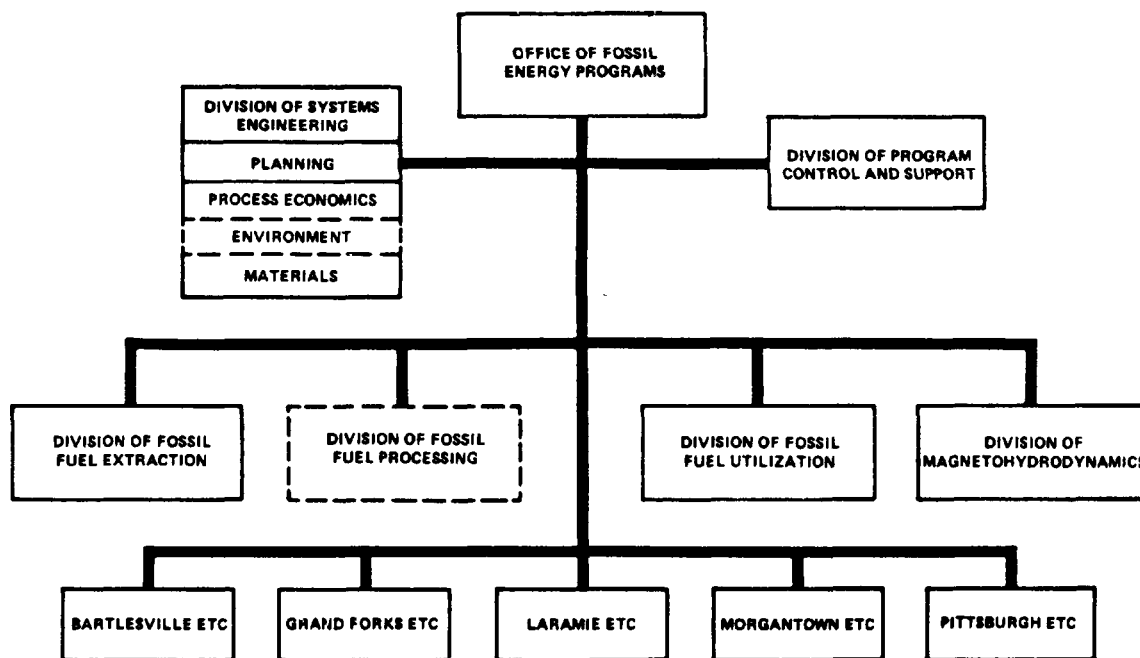


Figure 5. Office of Fossil Energy Programs (FEP).

		<u>ORGANIZATION</u>	<u>KEY PERSON</u>	<u>FUNCTION</u>
DOE	ASEV	NATIONAL LABORATORIES	VARIABLE	IMPLEMENTER
		POLLUTANT CHARACTERIZATION & SAFETY RESEARCH DIVISION	P. DUHAMEL	
		HEALTH EFFECTS RESEARCH DIVISION	G. STAPLETON	
		ECOLOGICAL RESEARCH DIVISION	R. LEWIS	
		ENVIRONMENTAL CONTROL TECHNOLOGY DIVISION	F. WITMER	
	FEP	OPERATIONAL AND ENVIRONMENTAL SAFETY DIVISION	D. LILLIAN	OVERVIEW & GUIDANCE
		TECHNOLOGY ASSESSMENTS DIVISION	B. ALMUALA	
		SYSTEMS ENGINEERING DIVISION	B. BARATZ	
		GASIFICATION	J. NARDELLA	
		LIQUEFACTION	VARIABLE	
EPA NIOSH		FOSSIL FUEL PROCESSING DIVISION	VARIABLE	ADVISORY
		FOSSIL ENERGY TECHNOLOGY CENTERS	VARIABLE	
		INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY	W. RHODES	
		DIVISION OF ENVIRONMENTAL INVESTIGATIONS	B. PALLAY	
		DIVISION OF PHYSICAL SCIENCES AND ENGINEERING	J. TALTY	

Figure 6. Project/site-oriented environmental synfuel assessments—major participants.

quired to have a technology program task definition for budgeting and scheduling, consistent with the developmental sequence necessary to advance and evaluate the technology. An environmental development plan (EDP) is prepared to accompany and supplement the technology program plan to assure that anticipated environmental uncertainties are addressed and become part of the DOE program at each stage of development, as appropriate (Figure 7). The synfuel EDPs have been prepared jointly by ASEV and FEP. Early versions of EDPs (FY 1977 and 1978), because of the difficulty of achieving a meaningful technology-environmental couple, listed environmental concerns and requirements and tentative milestones for

addressing the concerns but did not assign priorities or funding requirements to the specific tasks. Subsequent update is anticipated to outline environmental priorities along with budgetary requirements.

The technology program (e.g., liquefaction, high-Btu gasification, and low/intermediate-Btu gasification) is comprised of a series of process-specific projects with individual milestones and timelines. As a project evolves from early R&D, a series of developmental stages are oriented toward scaleup and ultimate commercialization. At each major phase of such a system acquisition train, ASEV, in an overview function, prepares an environmental readiness document (ERD), which critically reviews the environmen-

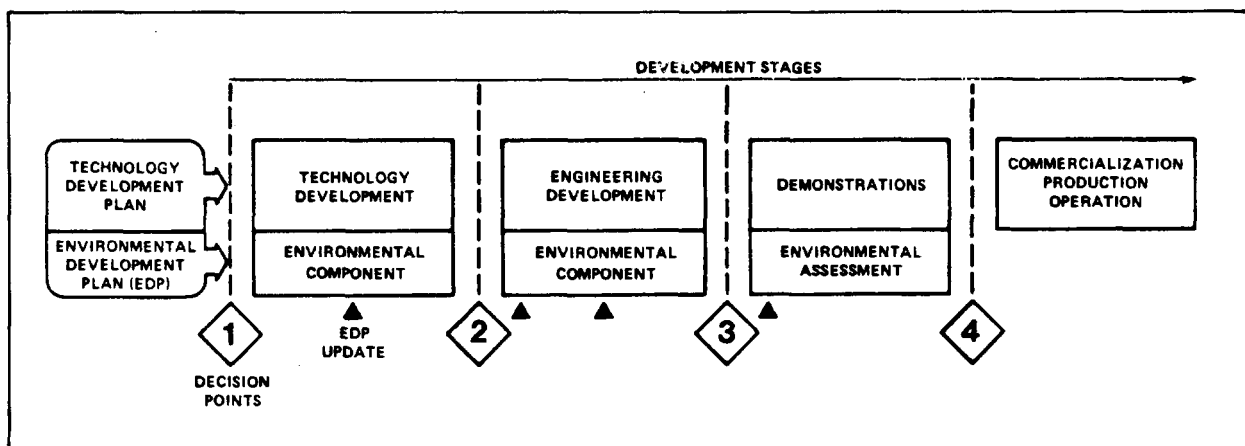


Figure 7. Energy systems acquisition program—EDPs.

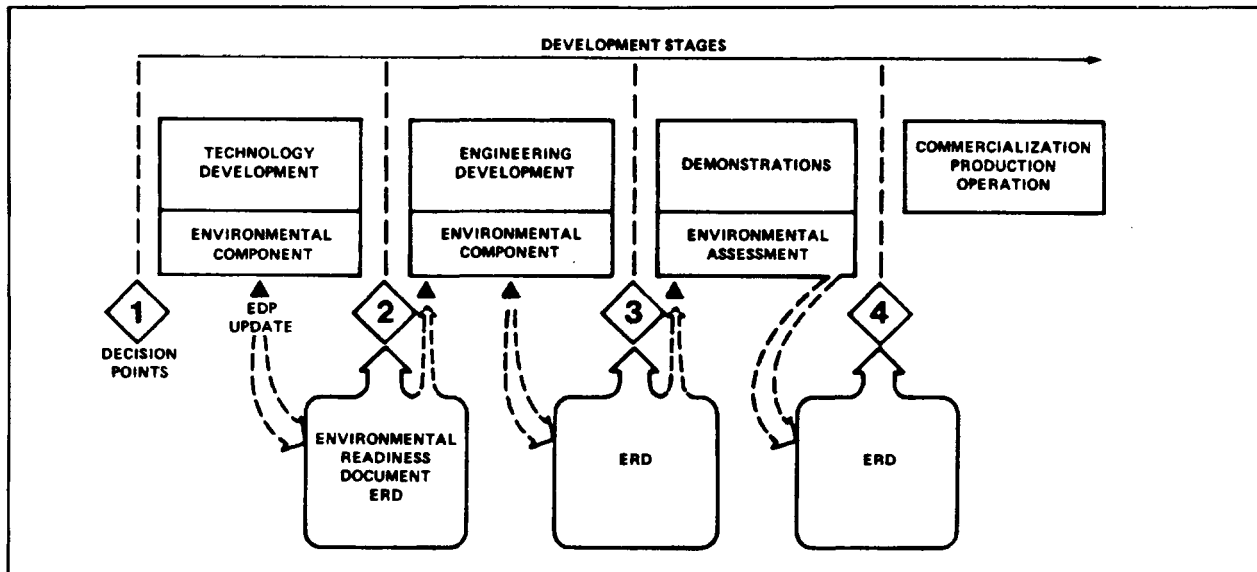


Figure 8. Energy systems acquisition program—ERDs.

tal status of the developmental project and emphasizes environmental gaps that may exist and that require resolution (Figure 8).

The resolution of environmental uncertainties that still may exist when a process is brought to pilot and/or demoscale is addressed in a site- and process-specific environmental characterization and assessment. An example of such an activity is the Gasifiers-in-Industry Environmental Assessment program currently conducted by Oak Ridge National Laboratory (ORNL) for ASEV, which will be reported on later. A series of field-oriented environmental plans are currently in preparation for major FEP projects; e.g., H-Coal, SRC, and high-Btu gasification. It should be noted that these process-specific environmental evaluations are developed jointly with FEP in concert with advice and counsel from EPA and NIOSH. Suffice it to say that DOE does not consider "environmental acceptability" and "meeting current compliance standards" synonymous. Thus, DOE has initiated a hierarchy of program control documentation and planning to assure that environmental requirements are systematically addressed in the synfuels process development sequence. What, of course, is needed now is implementation of these planning exercises in concert with pilot, demo, and commercial plant activities. Hard data above and beyond that re-

quired for compliance purposes are critically needed. It is emphasized that normal emission releases, effluent discharges, solid waste disposal practice, and ecological characterizations for facility operations can be adequately handled under existing regulatory licensing and permit procedures. The direction the detailed incremental field environmental characterizations take must respond to the technical direction and priorities assigned to the individual processes by FEP technologists and DOE energy planners.

ONGOING ENVIRONMENTAL ACTIVITIES

While comprehensive, process-specific environmental assessment studies constitute a relatively new undertaking, DOE has had a broad-based environmental characterization and assessment program for the emerging synfuels processes. Varied generic RD&D activity within ASEV and FEP has laid a foundation for much of the process-specific joint activity currently underway. In recognition of ongoing environmental support activity, select recent accomplishments of various groups are highlighted (Figures 9 and 10), the organizational and functional relation between groups having been previously identified. Detailed information relating to ongoing inter- and intra-DOE en-

AREA

HEALTH EFFECTS RESEARCH

- DEVELOPED WIDELY USED AMES-TEST BIOLOGICAL (MUTAGENIC) SCREENING PROTOCOLS
- DETERMINED THAT SYNFUEL BIOACTIVITY DISPROPORTIONATELY RESIDES IN BASIC FRACTION (E.G. 90% OF BIOACTIVITY IN 10% OF MATERIAL)
- VERIFIED THAT HUMAN CELL *IN VITRO* (OUT OF BODY) BIO SCREENING REPRESENTATIVE OF *IN VIVO* (IN BODY) RESULTS
- DEVELOPED SCREENING TESTS (SKIN GRAFT TECHNIQUES) WHICH PERMIT ANIMAL-HUMAN RESPONSES TO BE COMPARED

POLLUTANT CHARACTERIZATION & SAFETY

- DEVELOPED PORTABLE SPILL MONITOR FOR AROMATIC COMPOUNDS

Figure 9. Select accomplishments DOE base/generic environmental program.

ECOLOGICAL RESEARCH

- DEVELOPED PREDICTIVE AND MODELING CAPABILITY FOR NUCLEAR FALLOUT PHENOMENA
- MODELED MULTI-POLLUTANT REGIONAL IMPACT (INCLUDING ACID RAIN)

ENVIRONMENTAL CONTROL TECHNOLOGY

- CORROBORATED DESIGN ADEQUACY OF SYNFUEL PROCESSES (COALCON, DRY BOTTOM ASH LURGI ETC.)
- SINGLED OUT AREAS OF SECONDARY CONCERN (WASTEWATER, SOLIDS DISPOSAL)

SYSTEMS ENGINEERING

- DEVELOPED PROCEDURAL GUIDELINES FOR FIELD BASELINE MONITORING
- QUANTIFIED WATER RESOURCE IMPACTS (INCLUDING USE OF SALINE WATERS) FOR SYNFUEL FACILITIES

Figure 10. Select accomplishments DOE base/generic environmental program (continued).

vironmental efforts are well documented in publications, annual reports, and symposia proceedings. While highlights are shown of several activities, I am not familiar enough with them to discuss in detail these activities and their EH&S ramifications.

In recognition of the *depth* of the individual program within DOE and the types of generic activity in which a single organizational entity

is involved, I have taken the liberty of selecting representative synfuel-related activities within the Environmental Control Technology Division (ECT). This seems fitting considering the engineering orientation of this symposium.

ECT assessment studies have attempted to parallel major scaleup activities within industry and within FEP. Proposed gasification and liquefaction facility designs have been analyzed

	CURRENT STANDARDS	FUTURE STANDARDS
GENERIC, PROCESS ORIENTED ISSUES	● COMPLIANCE STANDARDS WILL BE MET. ● UNCERTAINTY WITH REGARD TO SOLIDS DISPOSAL TECHNIQUES RESULTING FROM RCRA.	● TIGHTER CONTROL OF REFRACTORY ORGANICS CONTAINED IN AQUEOUS EFFLUENTS MAY BE EXERCISED (TSCA). ● USE OF CONTAMINATED WATERS IN COOLING TOWERS MAY BE PRE-CLUDED. ● PROCESS SLUDGES, BLOW-DOWNS AND EVAPORATION POND SLUDGES MAY REQUIRE TREATMENT (RCRA).
SITE SPECIFIC ISSUES	● TO BE ADDRESSED IN EIS. ● REVIEW OF DETAILED DESIGN AND OPERATING PROCEDURES TO ENSURE COMPLIANCE. ● ON-SITE CHARACTERIZATION TO VERIFY.	● UNKNOWN AT PRESENT

Figure 11. Perceived adequacy of environmental control technology for gasification.

	CURRENT STANDARDS	FUTURE STANDARDS
GENERIC, PROCESS ORIENTED ISSUES	SAME AS GASIFICATION	SAME AS GASIFICATION PLUS ● TRANSPORTATION AND HANDLING OF HIGH BOILING AROMATIC FUELS MAY POSE SPECIAL PROBLEMS, I.E. SPILL CONTROL AND CLEAN-UP ETC.
SITE SPECIFIC ISSUES	SAME AS GASIFICATION	UNKNOWN AT PRESENT

Figure 12. Perceived adequacy of environmental control technology for liquefaction.

from the standpoint of meeting compliance standards and evolving NSPS for the reference technology. Most of these studies come to the same conclusion; namely, that the proposed environmental control processes appear adequate, except for some minor uncertainties that can

only be resolved through in-plant monitoring and surveillance (Figures 11 and 12). Of course, the cost of implementing the control options is the subject of debate.

Uncertainty exists regarding future standards relating to evolving TSCA and RCRA im-

	QUENCH WATER FROM GETC SLAGGING-BED UNIT, PPM	QUENCH/CONDENSATE WATER FROM ORNL HYDROLYSIS UNIT, PPM	TYPICAL OUTPUT FROM LABORATORY WASTEWATER TREATABILITY PROCESS TRAINS ^{1/} , PPM	ANTICIPATED REGULATIONS PPM
PHENOL	4,000 - 6,000	3,000	0.010	0.3
NH ₃	8,000 - 10,000	30,000	5 - 10	5.0
H ₂ S	N. D.	800	0.1	0.2
CN ⁻	N. D.	70	0.05	0.1
SCN ⁻	N. D.	1,000		
PNA	N. D.	5 - 10	0.005	?
TOC	9,000 - 10,000	20,000	5 - 50	
BOD			NIL	30
COD			NIL	350

^{1/} FIELD DEMONSTRATION PLANNED - TREATMENT TRAINS INCLUDED VARIOUS COMBINATIONS OF STEAM STRIPPING, SOLVENT STRIPPING, BIOLOGICAL DIGESTION, CARBON ABSORPTION, AND CHEMICAL OXIDATION (OZONATION).

N. D. - NOT DETERMINED.

Figure 13. Composition of select coal gasification wastewaters.

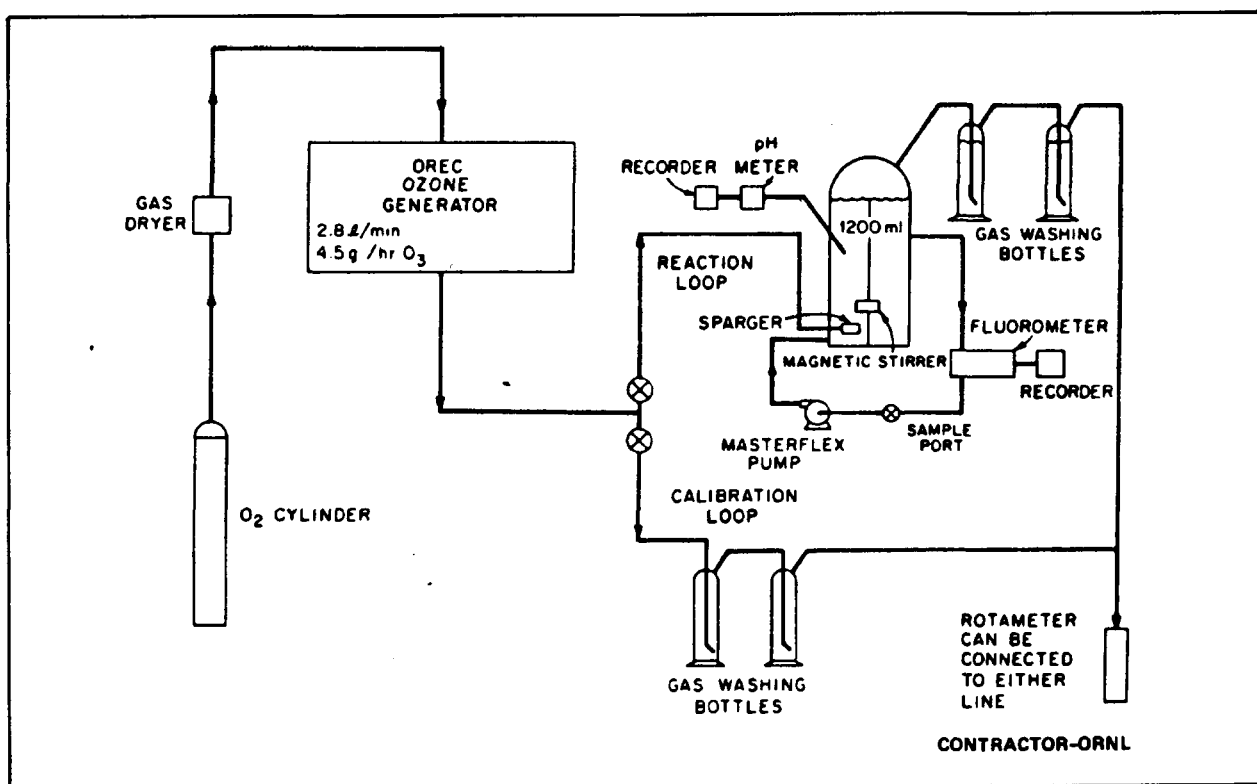


Figure 14. Schematic drawing of batch ozonation system.

plications with respect to effluents and solid wastes. Several programs ongoing within ECT point the way toward control options to meet more stringent standards in a cost-effective manner. As the technical and economic feasibility of these process variations is confirmed, development and scaleup is picked up by FEP, at their option.

One area of concern in coal conversion is, of course, process water contamination. The condensate waters from liquefaction and quench waters from gasification typically contain a high organic loading. While nearly all the organics are biodegradable, a trace fraction of ring-structured compounds (50 to 100 ppb) that resist conventional biological treatment usually remains (Figure 13). Carbon and char adsorption and ozonation are being explored as polishing steps to reduce the level of these trace compounds not

currently regulated (Figures 14 and 15). Biological screening tests are being performed to determine sensitivity thresholds for these materials along with high-sensitivity gas chromatographic analysis to determine actual compounds. An alternative to intensive wastewater post-treatments is water reuse within the process proper. Concentration processes such as freezing and membrane separation are being investigated to maintain water balance and to produce a concentrated contaminated aqueous stream as input to an entrained gasifier (or thermal oxidizer) where the organics are gasified and salts are collected with the slag (Figure 16). Wastewater quality requirements for cooling tower concentration operations are being evaluated.

Another area of more immediate concern is the impact of RCRA on coal conversion wastes (gasifier slag and water treatment sludge disposal). A screening program is underway to determine if gasifier slags would be classified as hazardous under candidate EPA protocols. While preliminary tests indicate slags from entrained gasifiers may not be classified as hazardous under the procedure, DOE does not endorse meaningfulness or relationship of the protocols relative to actual land fill operations. In my judgment, ecological and field characterization studies are in order to verify true environmental acceptability of waste disposal practice. Wastewater treatment sludges will be characterized as quantities of these particular materials become available.

Improved control technology for hydrocarbon control in tail gases and within gasifier sulfur scavenger options is being investigated (Figures 17 and 18). Controls for auxiliary operations such as boiler/power plants are being evaluated under a family of assessments oriented toward power generation.

SUMMARY

DOE incorporates all required compliance environmental, health, and safety safeguard monitoring and assessment within the project proper as the responsibility of the FEP line-division and process operator. As an additional precautionary measure, overview responsibility has been granted DOE's own internal environmental group, ASEV, to advise and assist the line-division in these matters. DOE feels, however,

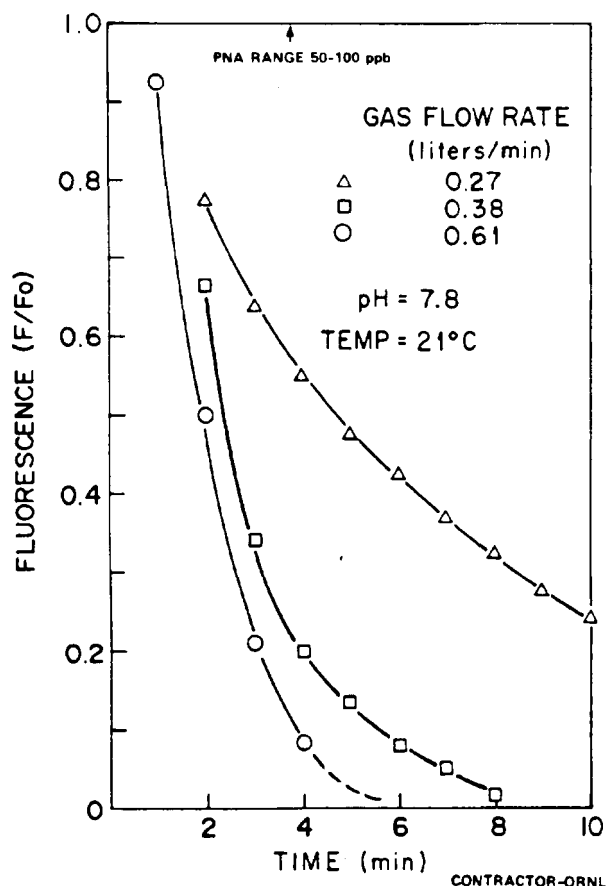
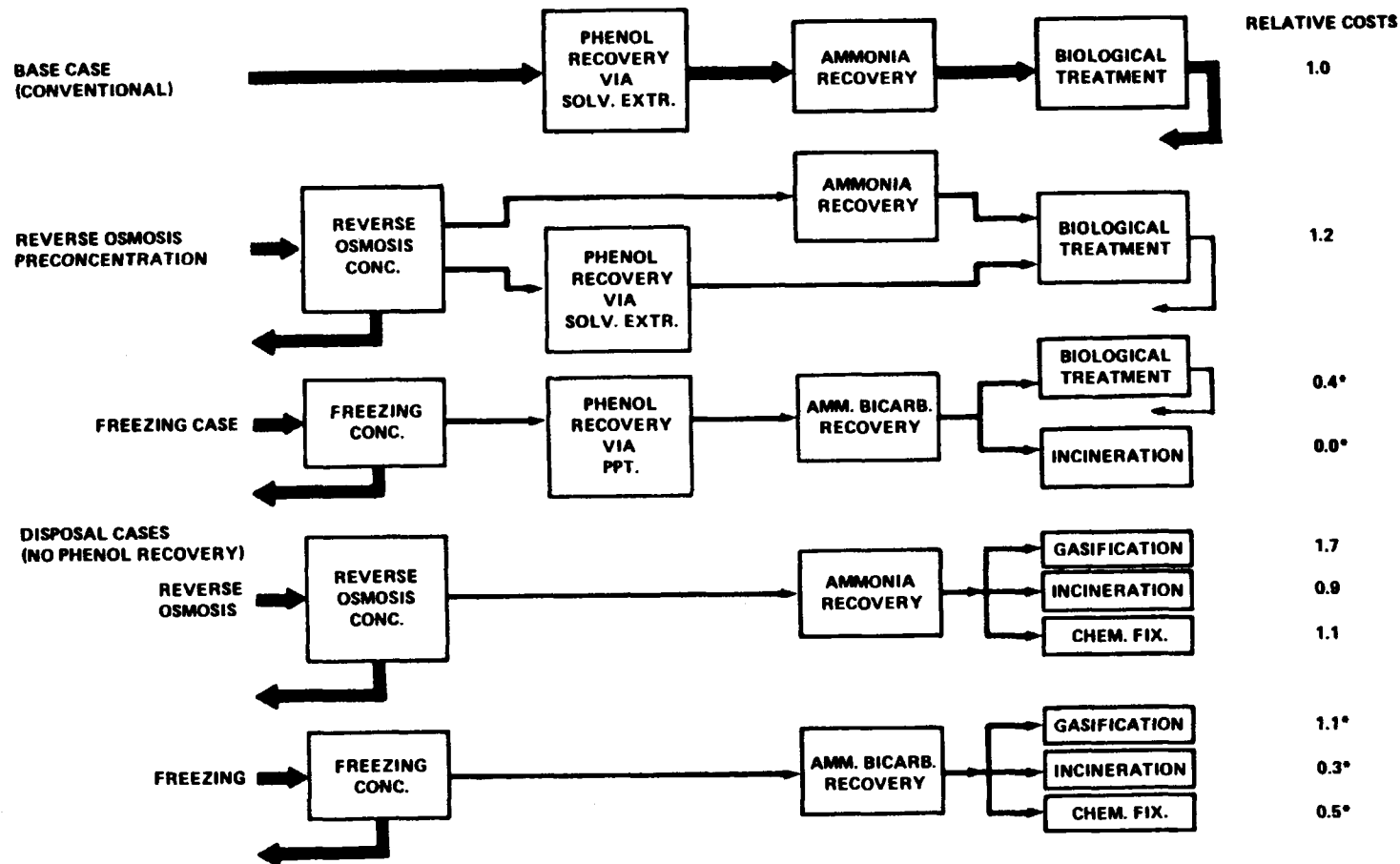


Figure 15. Screening tests—ozonation of hydrocarbonization wastewater (effect of gas flow rate).



*LOW TREATMENT COSTS DEPENDENT ON BYPRODUCT CREDIT OF NH_4HCO_3 (\$50/TON ASSUMED).

CONTRACTOR- CONCENTRATION SPECIALISTS, INC.

Figure 16. Candidate gas-liquor wastewater reuse options.

PROCESS NO.	DESCRIPTION OF PROCESSES	APPROXIMATE COST (¢/10 ⁶ Btu SNG) ^b	TECHNICAL FEASIBILITY FOR THIS APPLICATION
1	INCINERATION IN A COAL-FIRED BOILER	4	GOOD
2	INCINERATION IN A BOILER USING DESULFURIZED MEDIUM-Btu GAS (EPA Reference Case)	11	GOOD
3	CATALYTIC INCINERATION	5	UNPROVED
4	AQUA CLAUS PROCESS	c	UNPROVED
5	HOT CARBONATE SCRUBBING	42	DOUBTFUL
6	COLD WATER SCRUBBING	56	DOUBTFUL
7	CUPROUS AMMONIUM SOLUTION ABSORPTION	18	DOUBTFUL ^d
8	ADSORPTION	c	NO PRACTICAL ADSORBENT KNOWN
9	CRYOGENIC SEPARATION	64	TECHNICALLY FEASIBLE
10	POROUS MEMBRANE SEPARATION	c	DOUBTFUL

^aMOST OF THE PROCESSES LISTED HERE HAVE NOT BEEN DEMONSTRATED IN THIS TYPE OF APPLICATION AND CANNOT BE CONSIDERED AVAILABLE FOR COMMERCIAL USE.

^bCOST INCLUDES BOTH CAPITAL AND OPERATING CHARGES.

^cINSUFFICIENT DATA TO PERMIT COST ESTIMATION IN THIS APPLICATION.

^dTHIS PROCESS REMOVES ONLY CO.

CONTRACTOR-ORNL

Figure 17. Approximate cost of candidate hydrocarbon and CO emissions control for Lurgi-type SNG plants.^a

that "environmental acceptability" of a given energy technology goes beyond meeting here-and-now compliance standards. One must determine the potential environmental impact of a mature industry, operating under future environmental regulations. To support this activity, DOE has initiated a series of detailed process-specific field-oriented environmental character-

izations on advancing synfuel technologies. A multidiscipline systems approach has evolved deploying specialists in conversion technology, control processes, health and safety, plant operations, ecology, and systems analysis. Each of these specialties is being supported by a strong, ongoing generic program.

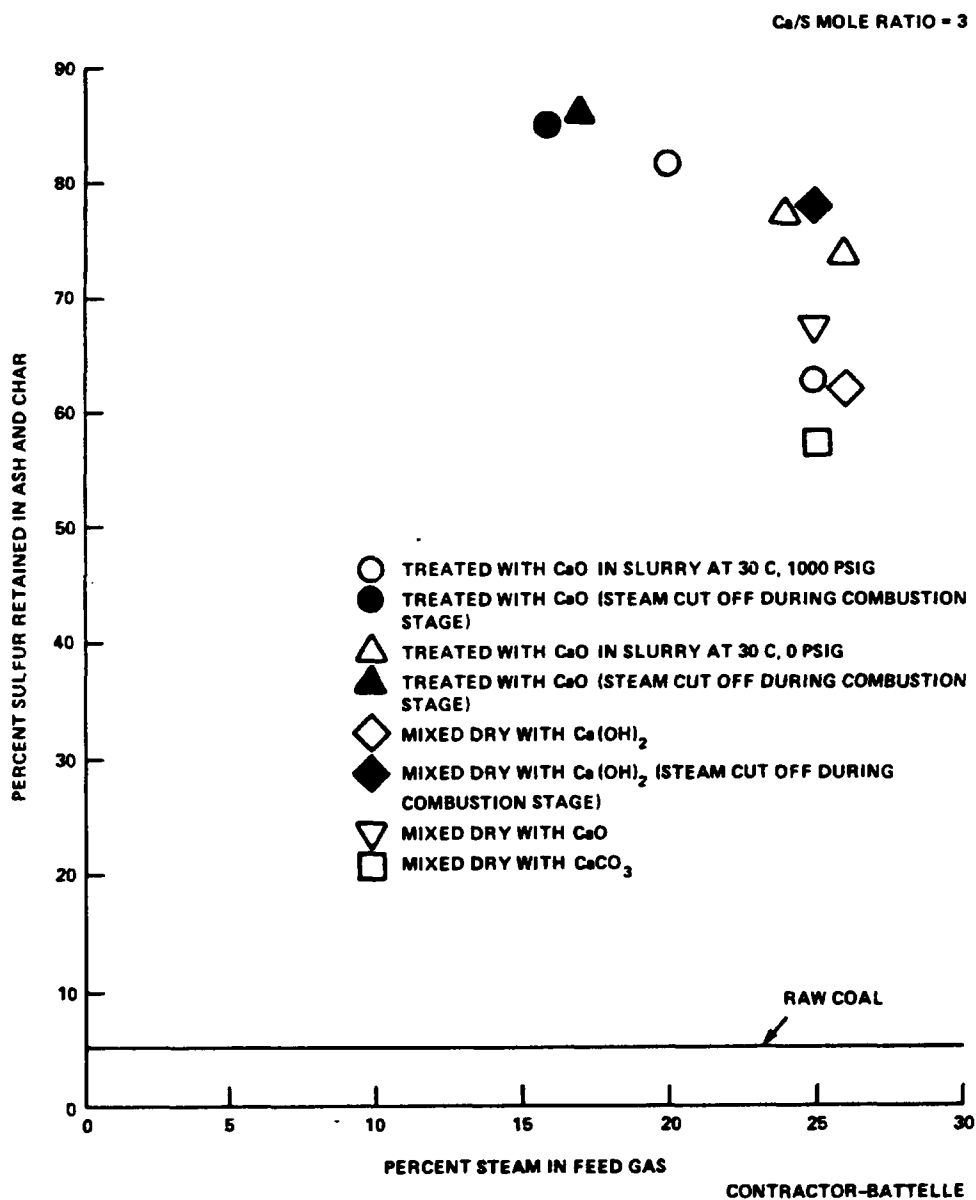


Figure 18. Laboratory screening tests-feasibility of in-gasifier sulfur scavenging (steam air gasification of treated coal in fluidized bed).

NIOSH PROGRAMS FOR EVALUATION AND CONTROL OF INDUSTRIAL HYGIENE HAZARDS IN COAL CONVERSION*

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Enviro Control, Inc., Rockville, Maryland

and

Barry Pallay
National Institute for Occupational Safety and Health, Morgantown, West Virginia

Abstract

It is well known that hazardous chemical substances and physical agents are present in coal liquefaction and gasification and that the potential for occupational exposure is high. To make certain that the workers in this new industry will be protected, NIOSH first had defined practical means of protecting the worker and now has initiated a multidisciplinary, in-depth assessment of occupational health characteristics and control technology for these conversion processes through their principal investigator, Enviro Control, Inc. This paper summarizes the efforts to date.

The first NIOSH work was directed toward protecting the worker from apparent problems. This effort and its results are defined in the documents, Recommended Health and Safety Guidelines for Coal Gasification Plants and Criteria for a Recommended Standard: Occupational Exposures in Coal Gasification Plants. This is currently being followed by three in-depth studies: Industrial Hygiene Characterization of Coal Gasification Plants, Industrial Hygiene Characterization of Coal Liquefaction Plants, and the Assessment of Engineering Control Technology for Coal Gasification and Liquefaction. This paper describes the techniques used for sampling and analyzing in liquefaction and gasification plants and for the ultimate use of the data. The interdependency of the two characterization projects with the Engineering Control Project will also be discussed. While hard data are not included in this paper, sufficient information will be available to show the direction the three projects are taking.

*Unpresented paper.

INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) has been interested in studying coal liquefaction and coal gasification since 1975. The basic objective of NIOSH, and of the studies to be described, is to protect the safety and health of American workers.

NIOSH has implemented programs to achieve this objective through the development of a real understanding of what the workers are exposed to, and through promoting better measures that will avoid occupational exposures.

Hazardous chemical substances and physical agents are known to be present in coal liquefaction and gasification operations, and the potential for occupational exposure is high (see Tables 1 and 2). Because of this potential for occupational exposures, NIOSH undertook to prepare safety and health criteria documents even before the results of longer term detailed technical studies were available. Thus, the criteria documents represent rough cuts at a standard for coal conversion processes based on the best available information at the time. These documents may be revised as other studies including those to be described in this paper are completed.

THE NIOSH STUDY PROGRAM

The first NIOSH study resulted in the document, *Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants*.¹ This was followed by *Criteria for a Recommended Standard: Occupational Exposures in Coal Gasification Plants*.² Both were done by Enviro Control under the direction of NIOSH Project Officer Mr. Murray Cohen. Currently, JRB,

**TABLE 1. POTENTIAL OCCUPATIONAL EXPOSURES IN HIGH-Btu
COAL GASIFICATION^a**

Unit Process	Potential Exposures
Coal handling and preparation	Coal dust, noise, and fire
Coal feeding	Coal dust, noise, gaseous toxicants, and asphyxia
Gasifier operation	Coal dust, high-pressure hot raw gas, high-pressure oxygen, high-pressure steam, fire, and noise
Ash removal	Heat stress, high-pressure steam, high-pressure oxygen under impact conditions, hot ash, and dust
Quenching	High-pressure hot raw gas, hot tar, hot tar oil, hot gas liquor, fire, and noise
Shift conversion	High-pressure hot raw gas, high-pressure hot shifted gas, high-pressure steam, tar, tar oil (naphtha), hydrogen cyanide, fire, catalyst dust, and heat stress
Gas cooling	High-pressure hot raw gas, hot tar, hot tar oil, hot gas-liquor, fire, heat stress, and noise
Gas purification	Sulfur-containing gases, methanol, naphtha, cryogenic temperatures, high-pressure steam, and noise
Methanation	High-pressure Rectisol product gas, high-pressure methanated gas, steam, nickel carbonyl, nickel catalyst dust, fire, and noise
Sulfur removal	Hydrogen sulfide, other sulfides, and sulfur oxides
Gas-liquor separation	Noise, tar oil, tar, and gas-liquor with high concentrations of phenols, ammonia, hydrogen cyanide, hydrogen sulfide, carbon dioxide, and trace elements
Phenol and ammonia recovery	Phenols, ammonia, acid gases, gas-liquor, ammonia recovery solvent, and fire
Byproduct storage	Tar, tar oil, phenols, ammonia, methanol, phenol-recovery solvent, and fire

^aNational Institute for Occupational Safety and Health, *Criteria for a Recommended Standard...Occupational Exposures in Coal Gasification Plants*. DHEW (NIOSH), Publication No. 78-191, September, 1978, pp 32-33.

TABLE 2. POTENTIAL OCCUPATIONAL EXPOSURES IN COAL LIQUEFACTION*

Unit Process	Potential Exposures
Coal handling and preparation	Coal dust, noise, fire, inhalation of combustion products.
Coal slurring	Coal dust, noise, middle distillate.
Coal dissolving	High-pressure hydrogen, high-pressure hot coal slurry, raw gas, fire.
Liquid product flashing and gas recycle	High-pressure hot gas, acid gas, light oils, naphthas, middle oils, hot high-pressure slurry, oil-liquor, noise, steam, fire.
Filtration	Precoat dust, light oil, hot slurry, hot middle oil, hot filtrate, hot filter cake, solvent, dissolved and undissolved coal, steam, noise, heat, fire.
Product distillation	Hot filtrate, hot naphtha, hot middle distillate, hot process solvent, hot solvent refined coal, vapors from SRC cooling, SRC dust, steam, noise, fire.
Solvent Recovery	Filter cake, oil-liquor, hot oil, char dust, combustion gas, inert gas, steam, noise, fire.
Gasification	Ammonia, carbon dioxide, carbon monoxide, hydrogen cyanide, hydrogen sulfide, hot raw gas, trace elements, high-pressure steam, char and coal dust, noise, fire, trace elements.
Shift conversion	High-pressure hot raw gas, high-pressure hot shifted gas, high-pressure steam, hydrogen sulfide, hydrogen cyanide, fire, catalyst dust, heat stress.
Gas cooling	High-pressure hot raw gas, hot condensate, fire, heat stress, noise.

TABLE 2 (continued)

Unit Process	Potential Exposures
Gas purification	Sulfur-containing gases, methanol, oil condensate, cryogenic temperatures, refrigerant gases, high-pressure steam, noise.
Methanation	High-pressure Rectisol product gas, high-pressure methanated gas, steam, nickel carbonyl, nickel-catalyst dust, fire, noise.
Sulfur removal	Hydrogen sulfide, other sulfides, and sulfur oxides.
Hydrotreating	Hot naphtha, hot middle distillates, hot synthesis gas, high-pressure steam, sour water, acid gas, catalyst dust, fire, noise, heat.
Oil-liquor separation	Coal oils, oil-liquor with high concentrations of phenols, ammonia, hydrogen cyanide, hydrogen sulfide, carbon dioxide, trace elements, noise.
Phenol and ammonia recovery	Phenols, ammonia, acid gases, oil-liquor, fire, peroxide compound explosion hazard.
Byproduct storage, handling, cleanup	Tar, SRC-I solid product, hydrogenated oils, phenols, ammonia, benzene-type light methanol, phenol recovery solvent, fire.

* Taken from an interim draft report prepared on NIOSH Contract No. 210-78-0101.

under the direction of NIOSH criteria manager Mr. Lynne Harris, is preparing a criteria document recommending standards for occupational exposures in coal liquefaction plants. NIOSH Medical Officer Dr. William McKay is preparing a medical protocol designed to identify the appropriate means of medical monitoring in present and future coal plants. Arthur D. Little, on a contract directed by Dr. McKay, has prepared some of the material for the medical protocol. And Enviro Control, under the direction of NIOSH Project Officer Mr. William Todd, is conducting a study entitled Respiratory Protection in Coal Preparation Plants. Since relatively little specific information is currently available regarding occupational exposures and health effects of coal conversion, the NIOSH criteria documents on gasification and the liquefaction document being prepared make no attempt to develop permissible levels of exposure to toxic substances specific to coal conversion plants. Rather, they recommend that applicable existing Federal occupational exposure limits (or NIOSH recommendations) be observed. The documents also recommend that specific safety procedures, engineering controls, work practices, workplace monitoring, medical surveillance, personal protective clothing and equipment, sanitation, labeling and posting, and informing employees of hazards and record-keeping be considered. The NIOSH documents include specific information on these recommendations. They also note the need for research efforts to determine and project potential exposures and, in particular, the need for industrial hygiene and control technology efforts.

NIOSH has several coal studies in progress, including the following, which are the subject of this paper:

- A Study of Coal Liquefaction Processes: Coal Liquefaction and Industrial Hygiene Characterizations (Contract 78-0101). NIOSH Project Officer: Mr. Barry Pallay.
- Industrial Hygiene Characterization of Coal Gasification Plants (Contract 78-0040). NIOSH Project Officer: Mr. Barry Pallay.
- Control Technology Assessment for Coal Gasification and Liquefaction Processes (Contract 78-0084). NIOSH Project Officer: Mr. James Gideon.

In order to develop a program of this magnitude at this particular moment when the coal

conversion program in the United States is not past the pilot-plant stage, two questions had to be answered. First, Why bother now? Second (and perhaps the more serious question), Can sufficient information be obtained from the pilot plants to assess potential occupational health exposures in demonstration or commercial operations?

In response to the first question, the time for obtaining this information is now, before demonstration plants or commercial plants have been built, to enable management and labor to focus on the development of better work practices and engineering controls, which will result in a more healthful workplace environment. NIOSH, the U.S. Department of Energy (DOE), the U.S. Environmental Protection Agency (EPA), industry, and labor all agree that it is preferable to have the controls built into the plants in the design and construction stage, rather than to retrofit them at a later date at great expense and after workers have been exposed.

This approach is particularly appropriate to the coal conversion industry, as it now stands. We are interested in identifying what the workers may be exposed to, in determining what the exposure levels may be, and then in identifying cost-effective controls that will reduce or eliminate these exposures, promote productivity, and enhance the feasibility of coal conversion technology being implemented on a commercial scale.

As to the second question, those conducting the study must thoroughly understand the differences between a pilot-plant facility and a demonstration or commercial installation. A pilot plant is designed to obtain engineering data to optimize operating conditions or to provide information on specific process feasibility and practicality. A commercial plant is designed for economical operation. Pilot-plant equipment and operation is not optimized but rather is selected to allow varied test conditions. Often the equipment does not function adequately at the conditions found to exist during the testing. More potential exposure exists in pilot plants, if only because they are continuously going on-stream and offstream, either to change programs, to change layouts, or to repair equipment. In general, the pilot-plant layout is more compact and does not utilize all elements that

would be installed at the commercial or demonstration level. Thus, it is important to remember that pilot plants are not small-scale replicas of commercial plants. They are built to test certain defined parts of the process, using available equipment, and do not represent the complete commercial-scale process.

If this is understood, NIOSH, as well as other agencies and industry, should be able to extrapolate industrial hygiene characterization information and control technology information from the pilot operation to the demonstration and possibly to the commercial plant. If successfully extrapolated, then industry will be able to implement control designs to ensure the safety and health of workers.

INDUSTRIAL HYGIENE CHARACTERIZATION

The two industrial hygiene characterization projects have four primary purposes:

- To determine potential worker exposures from analysis of process streams, byproducts, and workplace levels of toxic materials; the latter by area and personal sampling.
- To identify specific areas within plants where carcinogens and other toxic chemical and physical agents are concentrated by particular unit processes.
- To identify areas where control technology assessment studies are now required or may be required in the future.
- To extrapolate the data thus collected in such a manner that anticipated worker exposures may be approximated at the demonstration plant level and at the commercial plant level.

Studies of coal liquefaction were to be made on four different types of processes, including noncatalytic high-pressure hydrogen transfer, donor solvent process, catalytic hydrogenation, and pyrolysis. Coal gasification characterizations were to include a high-Btu operation and a low-Btu operation. The plants chosen for these characterization studies are shown in Table 3. The first to be studied was the solvent-refined coal (SRC) process at the SRC pilot plant located in Fort Lewis, Washington. The SRC-I process includes a high-pressure noncatalytic hydrogen donor transfer type, while the SRC-II process includes high-pressure natural catalytic hydrogen donor transfer. The second plant chosen

was the Cresap test facility located in Cresap, West Virginia, and operated by the Liquefied Coal Development Corporation. This process includes low-pressure hydrogen donor solvent transfer and catalytic hydrogenation of the solvent-refined coal. The third plant selected was the H-Coal pilot plant located in Catlettsburg, Kentucky, and operated by the Ashland Oil Company; this process includes direct high-pressure catalytic hydrogenation of coal. The location of the fourth process has not been finalized.

For the coal gasification characterization studies, the Synthane plant located in Bruceton, Pennsylvania, was to have been the high-Btu plant, and the Combustion Engineering entrained-bed facility located at Windsor, Connecticut, was to have been utilized for the low-Btu characterization study. In addition, the industrial hygiene characterization data was expected to be available through the Gasifiers in Industry program at the University of Minnesota at Duluth facility. This facility uses a fixed-bed, stoic low-Btu gasifier.

To date, walk-through surveys have been completed at the SRC facility, the Cresap facility, the Synthane facility, and the Combustion Engineering facility. However, the survey at the Synthane plant was not completed when DOE shut down the facility in December 1978. A replacement for Synthane will be selected. Since the H-Coal pilot plant will not be in operation until 1980, no survey has been scheduled there.

The walk-through surveys are made to test sampling and analytical methodology, and to define the range and level of toxicants in the pilot-plant workplace. Pilot plants often do not have predictable operating schedules. Therefore, to facilitate the program, walk-through surveys are sometimes carried out under the conditions at which the pilot plants then happen to be operating. Sometimes conditions are not at steady state. Data taken at nonsteady-state operations are usually adequate for range-finding purposes but might be misleading if used for other purposes. Therefore, DOE and NIOSH agreed that these data would not be published and would be used only for the development of the sampling plan and methodology for the comprehensive studies.

Coal conversion facilities contain at least eight categories of toxic compounds, as shown in Table 4. The walk-through surveys include

**TABLE 3. COAL CONVERSION FACILITIES TO BE SURVEYED ON NIOSH
INDUSTRIAL HYGIENE CONTRACTS^a**

Processes ^b	Developing Company	Location	Nominal Coal Feed Rate	Status
<u>Liquefaction</u>				
Solvent Refined Coal	Pittsburg & Midway Coal Mining Co.	Ft. Lewis, WA	50 t/d pilot plant	600 t/d pilot plant being designed for Morgantown, WV
Cresap Test Facility	Conoco Coal Develop- ment Co.	Cresap, WV	20 t/d pilot plant fa- cility	Project terminat- ed June 79
H-Coal	Hydrocarbon Research, Inc.	Catlettsburg, KY	200-600 t/d pilot plant	Under construction
<u>Gasification</u>				
Synthane Fluid Bed Gasification ^c	Lummus Co.	Bruceton, PA	72 t/d	Project terminated Dec. 78
Combustion Engineering Entrained-Bed Gasifier	Combustion Engineering (C-E)	Windsor, CN	120 t/d	Termination date uncertain

^aContracts 210-78-0101 and 210-78-0400.

^bFourth liquefaction plant not yet selected.

^cSince Synthane terminated, a replacement plant will be selected.

**TABLE 4. TOXIC COMPOUNDS THAT MAY BE PRESENT AT
COAL GASIFICATION PLANTS**

Category	Example			
1. Polynuclear aromatics	Benz(a)anthracene Benzo(a)pyrene Benzo(b)fluoranthene Benzo(e)pyrene Chrysene Dibenzo(a,h)pyrene Indeno(1,2,3-cd)pyrene Dibenz(a,h)anthracene Dibenzo(a,l)pyrene 7,12-Dimethylbenz(a)anthracene			
2. Polynuclear aza-heterocyclic compounds	Benz(c)acridine Dibenz(a,h)acridine Dibenz(a,j)acridine			
3. Aromatic amines	1-Naphthylamine 2-Naphthylamine			
4. Nitrosamines				
5. Trace elements	Antimony Arsenic Barium Beryllium Cadmium	Chromium Copper Iron Magnesium	Manganese Mercury Nickel Phosphorus	Selenium Strontium Tellurium Vanadium
6. Particulates	Organic solubles Particle sizing Respirable and total particulates			
7. Gases	Ammonia Arsine Carbon dioxide Carbon disulfide Carbon monoxide Carbonyl sulfide	Carbonyls Cobalt Hydrogen cyanide Hydrogen sulfide Iron	Nickel Nitric oxide Nitrogen dioxide Sulfur dioxide Thiophene	
8. Other organics	Aldehydes Benzene Cresols Mercaptans Methyl thiophene Toluene Xylenes			

sampling for polynuclear aromatic hydrocarbon (PNA) materials, aromatics, trace metals, particulates including coal dust and benzene solubles, aromatic amines, various gases, and hydrocarbon vapors. Thermal stress and noise levels are also noted.

The walk-through sampling for PNAs is conducted using closed-face 35-mm cassettes (shown in Figure 1) consisting of a silver membrane, a stainless steel screen, chromosorb 102 sorbent, and a cellulose support pad. Mass flow through the cassette is controlled by a critical orifice calibrated at 9.2 L/min. Sampling is conducted at breathing zone level for 8-hr sampling periods. To comply with the need to use intrinsically safe equipment at the pilot plants, air-driven pumps are used. These pumps are relatively small, simple, rugged, and inexpensive. No difficulty has occurred in using this equipment since the pilot plants have plant air piped to all sections. Personal sampling for PNAs is performed during the detailed surveys and uses the train shown in Figure 2 with an MSA Model S high-flow pump run at 2 L/min for 8 hr.

PVC filters are used to collect samples of total particulates, and cellulose acetate filters are used for trace metals. Flow rates are 2 L/min. For respirable dust sampling, the closed-face cassette is preceded in the sampling train by a miniature cyclone to remove nonrespirable particulates. Flow rates are 1.7 L/min

and MSA Model S high-flow pumps are used.

Charcoal tubes are used to collect samples of organics such as benzene and toluene; silica gel tubes are used for aromatic amines, phenols, and cresols. Low-flow MSA C-200 pumps calibrated at 100 mL/min are used for charcoal and silica gel. MSA and Draeger detector tubes are used to check for the presence of toxic gases such as H_2S , SO_2 , CO , CO_2 , NO_2 , HCN , NH_3 , CS_2 , arsine, and mercaptans.

PNA samples were analyzed by the Iowa State Hygienic Laboratory, located at the University of Iowa, under subcontract to Enviro. The analytic methods used are described in the literature. However, the analysis of the pilot-plant PNA material was not straightforward and required developmental work before the complex mixtures found in plant process samples could be characterized. A paper describing the analytical procedures is being developed for presentation. It is sufficient to say that Iowa State Hygiene Laboratory has developed a combination of gas chromatography/mass spectrometry and high-pressure liquid chromatography for the analysis. They are able to back up these analyses by using glass capillary column chromatography as defined by White et al.⁸

After reviewing the sample results from the SRC plant walk-through and current toxicity studies (primarily Ames tests) being carried out

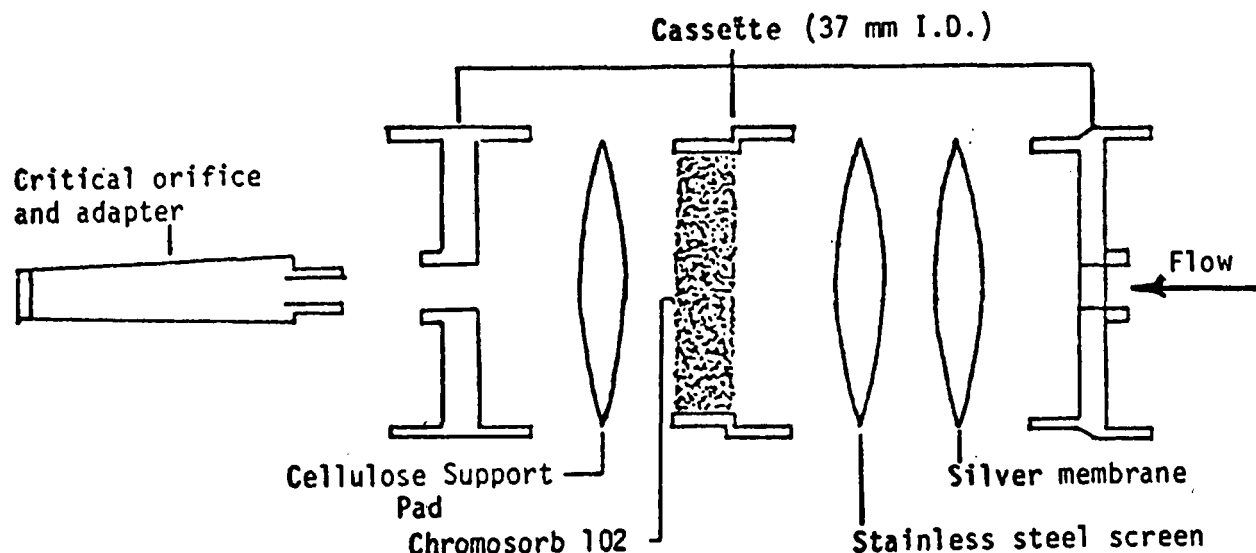


Figure 1. High-volume sampling device for PNA.

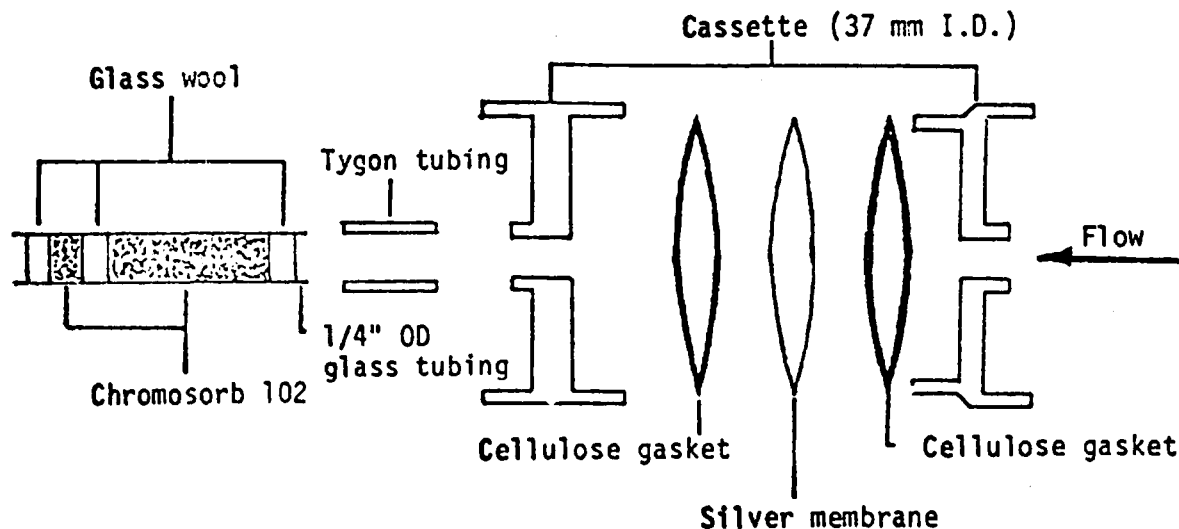


Figure 2. Personal monitoring device for PNA.

at Oak Ridge National Laboratories and at Battelle-Northwest Laboratory, NIOSH and Enviro scientists recommended that the comprehensive sampling studies should concentrate and prioritize sampling and analytical efforts. PNAs were considered highest priority, followed in descending order by aromatic amines; hazardous gases such as CO and H₂S; hydrocarbons such as benzene, toluene, and xylene; particulates; and trace metals.

While NIOSH had originally stated that the presence or absence of nitrosamines should also be investigated, a low priority was placed on this analysis, especially in the complex mixture potentially present at the pilot plants. Research Triangle Institute's technical staff has since pointed out that nitrosamines are not present in their bench-scale reactor and are not expected to be present in other gasification or liquefaction facilities.

The walk-through studies indicate that, although operating pilot plants have a pervasive asphalt-like odor, in general the benzene-soluble content of the atmospheric samples is well below the NIOSH-recommended standards. A first examination of these data also indicates that there is a direct relationship between benzene-soluble material in the atmosphere and house-keeping, leaking equipment notwithstanding.

CONTROL TECHNOLOGY ASSESSMENT

The control technology assessment (CTA) program for coal gasification and coal liquefaction has three prime objectives:

- To bring together as much information as possible on the control technology related to coal gasification and liquefaction.
- To evaluate this information and publish it along with recommendations for further research.
- To use this information as one means of protecting the workers.

To accomplish these ends, we are examining the following categories of control technology:

- Category I: Elimination by substitution of unit process or hazardous material.
- Category II: Application of current technology to specific equipment designed to contain emissions.
- Category III: Devices to control hazardous emissions once they enter the work environment.
- Category IV: Controls used to isolate the worker or prevent contact with the agent.
- Category V: Monitoring systems that warn workers of hazards and initiate corrective measures.

This study attempts to examine all aspects of

the processes that might lead to exposures of the workers and will examine means of preventing these exposures. In short, we will attempt to look at the conditions and chemistry of the process and must examine almost every aspect of equipment design—seals, flanges, packing, valves, rotating equipment, etc. It may be asked how this study differs from the documents that have already been completed, such as the *Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants* and *Criteria for a Recommended Standard: Occupational Exposures in Coal Gasification Plants*. The question is valid and has been raised several times.

For the pilot-plant document, NIOSH attempted to determine where and why workplace emissions occur in order to alleviate such emission sources. The emphasis in the criteria document was on the technology currently available for commercialization (i.e., Lurgi). Those studies also made a thorough investigation into what was currently known about the toxicology and epidemiology of coal conversion products. The control technology assessment program has two central ideas. First, if better equipment design can reduce emissions, there will be less worker exposure. Second, if equipment maintenance requirements can be reduced, there also will be less worker exposure.

The CTA study focuses on the process and, more particularly, on the equipment itself—what the technical problems are, what is being or can be done about these problems to reduce the emissions, what is being developed in the pilot plants, as well as what is commercially available today. We will also attempt to define the problems that may lead to worker exposure and may require further research. The CTA study is not a traditional industrial hygiene survey; few samples will be taken. However, this study and the two characterization studies previously described were designed to complement each other, so that a maximum amount of information could be cross-correlated.

In order to obtain the information required for the CTA study, NIOSH/Enviro investigators plan to make approximately 40 site visits, including coal liquefaction and coal gasification pilot plants, which will be visited in conjunction with the industrial hygiene survey visits. In gathering information for this study, we will visit architectural and engineering firms such as Dravo and Fluor, which have extensive ex-

perience in the design and construction of these plants; we will talk with the designers of demonstration plants such as the Conoco Slagging Lurgi and the SRC-II operation; we will visit several plants operating or being constructed under the Gasifiers in Industry program; and we will visit the ANG Coal Gasification Company, which, in 1980, may begin construction of the first high-Btu coal gasification plant in the world, providing proper Federal Energy Regulatory Commission (FERC) permits are forthcoming this summer.

We will also visit commercial installations with analogous processing systems, such as petroleum refineries and ammonia-manufacturing operations. With the exception of several low-Btu facilities, we will not be able to visit an operating commercial gasification facility in this country; therefore, we hope to visit several operations in Europe that we have not seen before. We also hope to benefit from several projects initiated by DOE, including those that look into the instrumentation needs of demonstration and commercial facilities and into the availability of commercially sized equipment.

When making the site visit, the NIOSH/Enviro team first gathers as much information as possible concerning the site. If we are visiting an operating facility, we generally have the opportunity to inspect the facility in detail and, at the same time, to take a number of samples with direct-reading instruments, primarily for carbon monoxide and organic vapors. (At the three plant sites visited thus far—Combustion Engineering, SRC, and Cresap—we have been unable to find detectable measurements of either the light organic vapors or carbon monoxide, except in a hot well and over an open manhole in a vessel that contained water saturated with carbon monoxide.) We then have the opportunity to talk with supervisors, engineers, and workers at the site about various processing, operation, and mechanical problems. We base our conversations on a pre-prepared site-specific questionnaire, which is generally used to start the conversation and to lead us into areas where little or no information has been reported in the literature.

To date we have made six such visits: Combustion Engineering Entrained Bed Gasifier in Windsor, Connecticut; Solvent-Refined Coal Pilot Plant in Ft. Lewis, Washington; Synthetic Fuels Pilot Plant in Cresap, West Virginia;

Dravo Corporation's Synthetic Fuels Division in Pittsburgh, Pennsylvania; Synthane Pilot Plant in Bruceton, Pennsylvania; and Synthoil PDU in Bruceton, Pennsylvania.

As anticipated, many of the coal conversion operations have similar problems with similar pieces of equipment; for instance, valves passing high-pressure three-phase liquids erode rapidly. Pumps are another area where severe erosion problems occur. Conventional pump impellers and volutes erode out within days. Several of the plants are investigated hard-surface applications on the pump interiors; they are also looking at a number of different solutions to the onnipresent pump seal problem. These efforts do not seem to be tightly coordinated, and information is slow in traveling from one facility to another. In this area alone, we would hope that our efforts will provide a significant contribution, where the net result of our efforts will be an integrated report on all that we have learned, as well as our assessment of the best ideas currently available and the pressing needs for future research.

CONCLUSION

With the integration of the coal gasification and coal liquefaction industrial hygiene characterization studies and the CTA studies, we hope to relate detailed analysis of emissions with process, operating, and mechanical problems. In other words, we now have the opportunity to develop an understanding of the real breadth and depth of the potential occupational health problem in coal conversion.

The information available from the CTA studies will be invaluable to the industrial hygiene studies, particularly for the extrapolation of the sampling data from the pilot plant up to the commercial operation. Industrial hygiene data from the pilot-plant situation has never been extrapolated to a commercially sized facil-

ity. The parameters for obtaining this data have not been established. Thus, if the data are obtained properly and the proper means of extrapolation are used, we should be able to provide sufficient information so plants can be built with emission levels lower than the current anticipated levels.

In summary, it must be recognized that these three programs are a pioneering effort. Never before has NIOSH had the opportunity to take pilot-plant industrial hygiene data and extrapolate it for the protection of future workers in what we see as a future major industry. As this precommercialization effort moves forward, we expect that, through the combined efforts of all of the participating individuals and all of the programs, we will obtain sufficient information regarding potential occupational hazards and their control to not only ensure the health and safety of workers in the coal conversion industry but also to establish it in a cost-effective manner.

REFERENCES

1. *Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants*. National Institute for Occupational Safety and Health. Rockville, Md. DHEW (NIOSH) Publication Number 78-120. January 1978.
2. *Criteria for a Recommended Standard: Occupational Exposures in Coal Gasification Pilot Plants*. National Institute for Occupational Safety and Health. Rockville, Md. DHEW (NIOSH) Publication Number 78-191. September 1978.
3. White, C. N., M. L. Lee, and D. L. Vassilaros. *A New Retention Index System to Program Mid-Temperature Capillary/Column Gas Chromatography of Polycyclic Aromatic Hydrocarbons*. DOE, PETC (submitted for publication, 1979).

EPRI CLEAN FUEL PROGRAM

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Abstract

The EPRI program has been underway for several years. It is aimed at furthering the development of advanced systems that can provide clean synthetic fuels from coal that can be used to generate power. The EPRI program and its technical and economic methodology will be described. A key consideration is the benefit to the environment. The technical and economic attractiveness of technology and the ability of new technology to satisfy existing and projected environmental standards are also considered.

The environmental assessment of the technology with regard to plant siting and fuel utilization is best handled as an essential portion of the R&D contract. Unrelated environmental assessment can be counterproductive and wasteful, especially in situations where assessments are made for technologies that ultimately fail to meet technical and economic goals in pilot plant test programs.

INTRODUCTION

For 5 yr the Advanced Fossil Power Systems Department has been directing and managing the research and development for new advanced systems that have potential application to the production of electric power. These systems need to be cost-competitive and must satisfy increasingly tight environmental standards. Major emphasis has been on flexibility in using U.S. coals in these R&D projects.

This paper describes the EPRI program in coal liquids and gaseous fuels and the methodology used to assess technology and to implement the environmental program associated with the development of advanced systems.

GENERAL OBJECTIVES

Table 1 provides a list of deliverables that

EPRI expects from an integrated R&D program aimed at commercial acceptance in the power industry. In order to receive the attention of the EPRI staff, each of these items needs to be addressed and dealt with in the R&D program that is to be carried out. Table 2 provides a list of factors that need to be addressed in process evaluations and that are optimized during program development.

COAL LIQUEFACTION

In general, orderly program development begins with bench-scale equipment to prove the technological feasibility, moves to operation of integrated process development units, and culminates in large pilot-plant testing at the 100- to 500-ton/day scale to set the design of commercial plants. Two coal liquefaction pilot plants are under construction, each of which represents about 1,000 construction and management personnel. The cost to the participants in these first-of-a-kind facilities is \$100 million. The operation of the pilot plants and the associated support R&D represent a total cost of about one-quarter of a billion dollars. Such programs are expensive and highly risky. Until they are successfully operated for a significant period of time using the design coal that is to be used in a commercial plant, there is a chance of technical failure. Table 3 is an outline of types of synthetic fuels by potential market applications of interest to utilities.

A partial list of key technical issues that remain to be resolved in the R&D program for producing clean liquid and solid fuels is shown in Table 4. I shall not discuss in any detail this simplified list, but it indicates that a number of significant technical issues remain to be solved before coal liquefaction technology reaches a state of readiness wherein we can confidently construct commercial plants.

Incentives For Coal Liquid Fuels

Coal liquefaction offers the utility industry an

*Speaker.

TABLE 1. DELIVERABLES FROM A PROCESS-ORIENTED R&D PROGRAM

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-
- CORRELATIONS AND DATA SUMMARY OF EXPERIENCE
 - A DEFINITION OF OPERABLE AND INOPERABLE COMBINATIONS OF PROCESS VARIABLES
 - SUSTAINED DURATION OPERATIONS AT DESIGN CONDITIONS
 - ENGINEERING DATA ON DESIGN FEED NEEDED FOR SCALE-UP
 - A SERIES OF COMMERCIAL PLANT EVALUATIONS
 - AN OPERATING AND MAINTENANCE MANUAL
 - A SKILLED TEAM OF SPECIALISTS
-
-

TABLE 2. FACTORS REQUIRING OPTIMIZATION IN PROCESSES

PRODUCT VALUE	FUEL BALANCE
PRODUCT SLATE AND MARKETS	WASTE STEAM CLEANUP
CAPITAL COST, OPERATING COST	HYDROGEN, UTILITY GENERATION
THERMAL EFFICIENCY	INTEGRATION OF RECYCLE STREAM
STEAM BALANCE	QUALITY OF RECYCLE STREAMS

TABLE 3. SYNTHETIC FUELS OF INTEREST TO UTILITIES

FUEL TYPE	PROCESS	POTENTIAL MARKETS
METHANOL		● PEAKING COMBUSTION TURBINE
TURBINE FUELS	HYDROTREATED FRACTIONS FROM: ● H-COAL ● EXXON	● COMBUSTION TURBINES ● INTERMEDIATE LOAD COMBINED CYCLE UNITS
DISTILLATE BOILER FUELS	FRACTIONS FROM: ● H-COAL ● EXXON DONOR SOLVENT ● SRC-II	● RETROFIT GAS FIRED BOILERS ● RETROFIT OIL BOILERS FOR PEAKING SERVICE
HEAVY LIQUID BOILER FUELS	FRACTIONS FROM: ● H-COAL ● EXXON DONOR SOLVENT	● RETROFIT EXISTING OIL FIRED BASE LOAD UNITS
SOLID BOILER FUEL	SOLVENT REFINED COAL	● RETROFIT EXISTING INTERMEDIATE LOAD PLANT ● SPECIFICALLY DESIGNED SIMPLIFIED BASE LOAD PLANTS

**TABLE 4. MAJOR AREAS REQUIRING OPTIMIZATION
AND TECHNICAL RESOLUTION**

- PROCESS APPLICATION TO A VARIETY OF COALS
- SOLIDS SEPARATION (SOLID, HEAVY FUEL OIL)
- HYDROGEN PRODUCTION VIA GASIFICATION OF RESIDUES
- FIRED SLURRY HEATER DESIGN
- FEED SLURRY MIXING AND DRYING
- VACUUM TOWER DESIGNS
- LET DOWN VALVES, PUMPS
- PUMPS HANDLING SLURRIED COAL, PRODUCTS

option, based on domestic energy resources, with which to meet its need for liquid fuels. In 1977, generation of electricity consumed 188,000 bbl/d of distillate fuels and 1,469,000 bbl/d of residual oil (see Table 5). The National Electrical Reliability Council projects, in their August 1978 report, that this requirement will grow to 366,000 bbl/d and 1,809,000 bbl/d, respectively, by 1987. In addition, natural gas requirements that can be met by substituting clean liquid fuels will decline from the 1977 level of 1,209,000 bbl/d FOE (fuel oil equivalent) to a still substantial 457,000 bbl/d FOE. This combination calls for 2,632,000 bbl/d of hydrocarbon fuels in 1987 and perhaps 4,000,000 bbl/d by the year 2000.

The same report discusses the potential for additional requirements for liquid fuels because of a 1- or 2-yr delay in completion of coal and nuclear plants. If electricity growth averages 5.6 percent per year compounded, an additional 1,041,000 bbl/d could be required if such a delay occurred. The experience of 1977, when liquid fuels were utilized to cope with the combination of a severe winter that curtailed natural gas supplies used for power generation and a coal

strike, demonstrates that liquid fuels can be quickly utilized to meet emergency situations.

Today, the planned installation of new oil-fired steam boilers is essentially nil. Approximately 96,000 MW of capacity will remain in place in 1987. These units were put into service primarily in the mid-1960's and have 10 to 30 yr of useful life remaining. Installed capacity of liquid-fueled combined-cycle units is expected to grow from 3,000 to 8,000 MW over this time period. These units generate electricity more efficiently than conventional boilers. Combined cycle capacity is projected to be used more extensively than in the past. As a result, the anticipated quantity of power generated from combined-cycle equipment may increase nine-fold from 4 to 36 billion kWh. Unfortunately, the future use of petroleum liquids for this kind of operation has been jeopardized by the recently legislated Fuel Use Act. This act requires coal to be used instead of petroleum for new power stations.

Liquid fuels are attractive to utilities for the following reasons:

- They are clean and satisfy environmental restrictions.

**TABLE 5. ELECTRIC UTILITY INDUSTRY USE
OF GASEOUS AND LIQUID FUELS**

		ACTUAL 1977 <u>000's B/D FOE</u>	ESTIMATED 1987 <u>000's B/D FOE</u>
DISTILLATE OIL -	STEAM	57	70
	COMBUSTION TURBINE	116	152
	COMBINED CYCLE	15	144
RESIDUAL OIL -	STEAM	1,466	1,797
	COMBUSTION TURBINE	1	1
	COMBINED CYCLE	2	11
CRUDE OIL -	STEAM	<u>9</u>	<u>8</u>
SUB TOTAL		<u>1,666</u>	<u>2,183</u>
GAS -	STEAM	1,149	425
	COMBUSTION TURBINE	23	9
	COMBINED CYCLE	<u>37</u>	<u>23</u>
SUB TOTAL		<u>1,209</u>	<u>457</u>
GRAND TOTAL		<u>2,875</u>	<u>2,640</u>

- They are easily stored and transported.
- They have properties that can be tailored to meet user requirements.
- They can be used in new combustion turbines and combined-cycle machines to meet intermediate and peaking power requirements at lower cost than coal-fired plants.

Technology Assessment For Coal-Derived Processing Routes

EPRI's selection of major investment in the Exxon EDS project (\$30 million) and the H-Coal project (\$12 million) was based on a thorough review of the processing route alternatives. Based on the status of technological options, the capabilities of the management and technical teams, and the status of the technology, the EDS and H-Coal routes were selected for major support.

Actually, EPRI has had a similar investment in supporting R&D for clean solid fuel via the SRC-I process. To date the support of the pilot plant at Wilsonville has represented expenditures of about \$17 million on the part of EPRI over the last 5 yr.

Economic Assessments

There is no evidence to indicate that any single liquefaction process offers a significant economic advantage over all others if the desired product slate is fixed. At our current level of understanding, all leading process candidates, H-Coal, Exxon Donor Solvent, and SRC-II, appear to produce a specified slate of products at approximately the same cost from a given coal. The uncertainty in the absolute costs is larger than the difference between processes producing similar product slates and quality. Thus, economic assessments do not aid in selection of technology choices; selection depends on factors such as whether the deliverables can be realized from the project by an experienced organization.

Combustion Testing Programs

Utilization of coal-derived fuels seems to offer no more of a challenge than using any new fuel, such as many low-sulfur fuel oils or low-sulfur western coal. Test results on SRC-I and SRC-II fuels in utility tests are shown in Tables 6 and 7.

The utility industry requires comprehensive, large-scale, and long-term tests in utility equipment prior to accepting any new fuel. As an example, the changeover from eastern coal to western coal was traumatic for many utilities because a large number of new maintenance problems and emission control difficulties were generated. In line with these requirements, EPRI has set up a multitiered synthetic fuel combustion test program to establish acceptable safe handling procedures. Large-scale utility test programs will require 10,000-40,000 bbl/d of fuel. Sustained test programs, which will last approximately 6 mo, must await successful operation of demonstration or pioneer commercial plants, which is not scheduled to occur until after 1985.

Based on EPRI tests performed to date, there are data that indicate that coal-derived solid and liquid fuels can be safely handled and completely combusted in existing utility boilers to avoid exposure of the public to potentially harmful aromatic chemical species.

Although obviously not a coal liquefaction product, shale oil represents another synthetic fuel option. During the last quarter of 1979, the U.S. Department of Defense arranged with Standard Oil of Ohio through the Paraho Development Corporation to refine 100,000 barrels of raw shale oil. EPRI arranged for delivery of 4,500 barrels of the hydrotreated 700° F residue. This product will be used for a utility site combustion test during 1979. Other test work is underway using methanol in combustion turbine equipment at a utility site.

Environmental Tests And Issues

Plant Siting Issues—

A major purpose of the operation of the large coal liquid pilot plants is to obtain information required to design commercial plants that can be sited at specific locations. Thus, each of the major projects has recognized, as an essential objective, the need to provide necessary design data for commercial plants. It is not useful to face the plant-siting issues if the technical hurdles cause development to be abandoned. Table 8 shows a list of recent process failures. It is more efficient to address environmental questions when the basic process is developed.

Air quality will be monitored at the pilot-plant sites. Water samples will be handled in

TABLE 6. SRC-I TEST RESULTS

FUEL	FUEL ANALYSES		EMISSIONS			
	%S	%N	SO ₂	PPM	NO _x	PPM
			<u>LB/10⁶ BTU</u>		<u>LB/10⁶ BTU</u>	
COAL	0.88	1.44	1.01	319	0.47	315
SRC-I	0.71	1.60	0.97	335	0.40	320

TABLE 7. SRC-II TEST RESULTS

FUEL	FUEL ANALYSIS		NO _x EMISSIONS	
	%N	NORMAL BOILER SETTING	LOW NO _x BOILER SETTING	
PETROLEUM DERIVED #6 FUEL OIL	0.23	155	100	
COAL DERIVED SRC-II	1.00	270	175	

facilities either onsite or offsite, and solid wastes will be analyzed and disposed to monitored landfills. The environmental aspects are an essential part of these projects and are the responsibility of the organization carrying out the project.

It is not advisable to separate the environmental plant cleanup from the rest of the project. It is an essential part of the development and cannot be assigned to a separate uninvolved organization.

Fuel-Handling Issues—

Handling coal-derived fuels safely at utility sites with proper protection of plant personnel and the general public does not seem to represent formidable problems. Refineries and chemical plants have a long history of dealing with similar fuels in a satisfactory and acceptable manner. In this instance, the problem is of a general nature and a program of research is likely to be separable from the development of specific technologies.

Timing of Environmental Work

As indicated, there are still technological hurdles in the development of clean fuels de-

rived from coal. The environmental program should be integrated into the R&D program and not performed by outside contractors having no understanding of the technical development.

Elaborate measurement of effluents at the bench scale and at the process development unit scale of operations is useless. For example, the elaborate programs on the Synthoil products and Synthane processes were wasted because they were terminated for a variety of reasons. The detailed reports are filed away. Perhaps the procedures and protocols will be useful, but if the support had been used to solve a number of technical problems, we might have had a better chance of technical success.

GASIFICATION FOR ELECTRIC POWER GENERATION

Gasification is a process of converting a solid fuel, such as coal, into a clean, easy to manage gaseous product containing substantial quantities of carbon monoxide and hydrogen. This gas can be processed further to produce transportable and storable fuels such as SNG and methanol, or it can be burned directly in an environmentally acceptable manner for electric power generation.

There are two fundamentally different ways in which coal gasification can be used for electric power generation. The most obvious method involves a total decoupling of the gasification process from the power generation facility. Examples of such systems are:

- Gasification for SNG production;
- Gasification for methanol production; and
- A remotely located gasification plant supplying intermediate-Btu fuel gas over relatively short distances to be burned in conventional oil or gas-fired steam power plants, combined-cycle equipment, or fuel cells.

All of these options are technically viable. However, studies conducted by EPRI and others have shown that fuels produced in this manner will be expensive and the overall efficiency of converting coal to electric power will be poor. Table 9 provides estimates of delivered fuel costs and coal-to-power efficiencies for some of the above options. Based on the relatively high fuel costs shown in Table 9, and considering current economic dispatch constraints, it is clear that the above options will probably

**TABLE 8. PROCESS FAILURES FOR
PRODUCING COAL LIQUIDS**

COALCON
CLEAN SYNTHETIC FUELS (CSF)
GULF CCL
SYNTHOIL
SOLVENT REFINED LIGNITE

TABLE 9. FUEL COSTS AND EFFICIENCIES FOR DECOUPLED SYSTEMS

	SNG FROM COAL	METHANOL FROM COAL	INTERMEDIATE BTU GAS FROM COAL
COST OF FUEL DELIVERED TO THE POWER PLANT SITE, \$/MMBTU ⁽¹⁾	\$6.00-\$8.00	\$6.00-\$8.00	\$3.50-\$5.00
HEAT RATE, BTU/KWH	16,000	15,500	12,000
EFFICIENCY, PERCENT	21.3	22.0	28.4

(1) MID 1976 DOLLARS; \$1.00/MMBTU COAL, ILLINOIS #6 COAL.

only be considered for intermediate and peak load service in the near future if direct coal firing continues to exist as an environmentally acceptable option for baseload power generation. A possible exception to this conclusion could be utility systems that have a large fraction of oil- or gas-fired baseload equipment that can be retrofitted.

A second option that exists for applying coal gasification technology to electric power generation is the concept of an integrated, dedicated power plant. The gasification plant would be constructed at the power plant site, closely coupled to the power-generating equipment. Studies conducted by EPRI and others have shown that integrated gasification/combined-cycle (GCC) power systems have the potential for extremely efficient operation and for the production of competitively priced baseload electric power while providing an environmentally superior power plant.

Environmental Aspects of Gasification/Combined-Cycle Power Plants

Gasification is a well-known technology for converting coal into an ultra-clean, low- or intermediate-Btu fuel gas that is capable of meeting the increasingly more stringent environmental control requirements dictated by the Clean Air Act Amendments of 1977.

During gasification, the bulk of the sulfur in the coal is converted to hydrogen sulfide, which can be removed from the fuel gas to practically any extent required by any one of a number of commercially proven liquid absorption processes.

Experimental evidence obtained from Texaco's Montebello pilot plant demonstrates that particulate matter carried over from the gasifier into the fuel gas can be removed by water scrubbing, bringing levels down orders of magnitude lower than either existing or particulate emission control requirements.

Nitrogen oxide emissions from a GCC power plant will be mainly a function of combustion conditions in the turbine combustor. Proper combustor design coupled with the relatively low-firing temperatures of currently available combustion turbines will tend to reduce NO_x emissions to levels below those required by current regulations. The contribution from the gasification plant to reduced NO_x emissions will

come from the commercially proven ability to remove all ammonia from the fuel gas by water scrubbing, thereby essentially eliminating the fuel-bound nitrogen.

Solid and liquid effluents from a GCC power plant will be lower in quantity than from other coal-based power generation technology. Solid wastes will be limited essentially to a dry, inert ash and liquid effluents will consist mainly of low-volume purge water streams.

Finally, the total makeup water requirement for a GCC power plant will be approximately 60 percent of that for a conventional coal-fired steam plant because the bulk of the electric power will be generated by the combustion turbines, which do not require condensers.

Economics of Gasification/Combined-Cycle Power Systems

Over the past 4 yr, EPRI has been examining the costs associated with power production from gasification/combined-cycle systems. Much of this work has been conducted by Fluor Engineers and Constructors, Inc. Because of incomplete understanding of the effects of combustion turbine performance on overall system efficiency, much of the initial effort concentrated on GCC plants employing advanced high-temperature turbomachinery. Emphasis has recently been redirected to consideration of the costs of GCC power plant employing current technology combustion turbines.

Also, earlier evaluations were aimed at identifying the gasification technologies offering the greatest economic incentives for development. The general conclusion reached from these initial studies was that the cost of electricity to be expected from a GCC power system based on a variety of second-generation gasification technologies would be somewhat unrelated to the particular gasifier being used. On this basis, the choice of a gasification technology to be employed for the first commercial-scale plants should be based on state of development and downstream processing requirements imposed on the power system rather than on economic considerations alone. Based on this conclusion and the status of various gasifier developments, analytical effort at EPRI has concentrated on the evaluation of Texaco gasification-based systems.

Table 10 presents a performance and cost

**TABLE 10. COST AND PERFORMANCE COMPARISON OF TEXACO-BASED GCC PLANT
WITH A CONVENTIONAL COAL-FIRED POWER PLANT**

	TEXACO BASED GCC PLANT WITH 2,000°F COMBUSTION TURBINE ⁽¹⁾	CONVENTIONAL COAL FIRED PLANT WITH STACK GAS SCRUBBERS ⁽²⁾
COAL TYPE	ILLINOIS #6	ILLINOIS BITUMINOUS
PLANT LOCATION	ILLINOIS	WISCONSIN
EMISSION REGULATIONS	1976 EPA NSPS	1976 EPA NSPS
DESIGN CAPACITY, MW	1,000	1,000
DESIGN HEAT RATE, BTU/KWH	9,100	9,900
TOTAL INSTALLED PLANT COST, \$/KW ⁽³⁾	774	743
TOTAL CAPITAL REQUIREMENT, \$/KW ^{(3) (4)}	903	906 ⁽⁵⁾

(1) BASED ON EVALUATIONS CONDUCTED BY FLUOR ENGINEERS AND CONSTRUCTORS, INC. (RP-239) AND GENERAL ELECTRIC COMPANY (RP-986-3).

(2) EPRI REPORT AF-1011, WORK PERFORMED BY BECHTEL NATIONAL, INC. (RP-1080-1).

(3) MID-1978 DOLLARS.

(4) INCLUDES CONSTRUCTION LOAN INTEREST, INVENTORY CAPITAL, START-UP COSTS, ROYALTIES, INITIAL CATALYST AND CHEMICAL COSTS AND LAND.

(5) DOES NOT INCLUDE THE COST OF LAND AND EQUIPMENT FOR SOLID WASTE DISPOSAL.

TABLE 11. ECONOMIC COMPARISON OF ELECTRICITY COSTS FROM
GASIFICATION/COMBINED-CYCLE PLANTS
(1976 DOLLARS)

PROCESS	COAL FIRED POWER PLANT WITH F.G.D.	LURGI*	BGC SLAGGER	COMBUSTION ENGINEERING	TEXACO
CAPITAL, \$/KW	838	906	711	860	816
COST OF SERVICES, MILLS/KWH					
COAL @ \$1/MM/BTU	40.9	41.2	32.8	39.0	37.2
COAL @ \$2/MM/BTU	51.2	51.4	41.6	47.6	46.5
*WESTERN COAL					

comparison of a Texaco-based GCC plant employing currently available combustion turbines with a conventional coal-fired power plant using nonregenerable limestone scrubbers for SO₂ emission control. Because these two cost estimates were prepared by different contractors with designs based on somewhat different coals, they are not strictly comparable. However, they do demonstrate that the Texaco-based GCC plant with available turbomachinery will be more efficient than and cost-competitive with conventional coal-fired technology based on 1976 environmental control requirements.

If environmental regulations become more stringent (as they already have, based on EPA's proposed regulations stemming from the Clean Air Amendments of 1977), studies have shown that the cost differential between GCC systems and coal-fired plants will increase; i.e., the economic incentives to build GCC plants will become greater.

Economic Evaluations

The EPRI economic evaluations have been extensive in order to direct the selection of gasification technologies to be supported. Table 11 summarizes costs of power from conceptual plants based on a variety of coal gasification processes. As can be seen, the second-generation processes offer competitive costs for electric power. In part, such economic analyses are used to guide the projects in which EPRI has in-

vested R&D funds. We have supported the three technologies indicated in the last three columns and have test work underway on these three coal gasification processing routes.

Table 12 summarizes the steps underway, with EPRI support, to further develop these second-generation coal gasification processes.

Environmental Considerations

A large incentive for applying coal gasification/combined-cycle gasification technology to the production of electric power is the ability to cope with increased requirements for reducing emissions to the lower levels mandated by regulatory agencies. In the opinion of EPRI, the status of second-generation gasification of coal is now at a point where 100-MW capacity plant handling 1,000 tons/day of coal could be designed, constructed, and operated. Major objectives of such a project are the acquisition of data required for siting even larger plants and the complete assessment of the environmental effects of electric generation by such advanced techniques.

Based on the status of Texaco gasification, which has been operated at a scale of 150 tons/day both in the United States and in Western Germany, support of a demonstration plant at a California location is under negotiation. The assessment of the environmental impact is one of the major objectives of the demonstration plant. While typical laboratory environmental

TABLE 12. SECOND-GENERATION COAL GASIFICATION PROGRAMS

PROCESS	PROGRAM
COMBUSTION ENGINEERING	OPERATION OF 5-TON/HR. P.D.U. ON EASTERN COAL, VARIETY OF COALS, ENRICHED AIR OPERATION
BGC SLAGGER	DYNAMIC TESTS USING U.S. COAL (300 T/D)
TEXACO	DYNAMIC AND ENVIRONMENTAL DATA (15 T/D)

data, as shown in Table 13, provide some information, actual demonstration plant operations are better data sources. Data from other gasification technologies, such as conventional fixed

bed, are of little importance or relevance. Here again, environmental information is an essential part of the project and cannot be separated from the necessary R&D.

TABLE 13. TYPICAL WATER BLOWDOWN QUALITY

<i>pH</i>	<i>8.7</i>
<i>TOTAL ORGANIC CARBON</i>	<i>230 ppm</i>
<i>TOTAL INORGANIC CARBON</i>	<i>445 ppm</i>
<i>AMMONIA</i>	<i>1020 ppm</i>
<i>FORMATE</i>	<i>492 ppm</i>
<i>CHLORIDE</i>	<i>432 ppm</i>
<i>SULFIDE</i>	<i>264 ppm</i>
<i>SULFATE</i>	<i>166 ppm</i>
<i>CALCIUM</i>	<i>140 ppm</i>
<i>MAGNESIUM</i>	<i>100 ppm</i>
<i>SODIUM</i>	<i>80 ppm</i>
<i>THIOCYANATE</i>	<i>70 ppm</i>
<i>THIOSULFATE</i>	<i>69 ppm</i>
<i>FLUORIDE</i>	<i>39 ppm</i>
<i>CYANIDE</i>	<i>31 ppm</i>
<i>ALUMINUM</i>	<i>20 ppm</i>
<i>SILICON</i>	<i>5.0 ppm</i>
<i>IRON</i>	<i>3.7 ppm</i>
<i>C₆+VOLATILE ORGANICS</i>	
<i>TOLUENE</i>	<i>20 ppb</i>
<i>BENZENE</i>	<i>10 ppb</i>
<i>ALL OTHERS</i>	<i>< 10 ppb</i>

Ref

MONITORING AND TESTING PROGRAM OF LOW-Btu GASIFIERS

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Abstract

Demonstration of low-Btu gasifier technology includes an extensive environmental and health study as part of the Gasifiers in Industry Program sponsored by the U.S. Department of Energy (DOE). Monitoring and testing plans have been developed to investigate the gasifiers located on the campus of the University of Minnesota-Duluth and in a planned community development at Pike County, Kentucky.

Four general areas of study are emphasized in the plans including on-line studies, in-plant studies, and local area studies to be integrated through multidisciplinary assessments. This paper provides a description of the processes and facilities, of the rationale for the environmental and health study, and of the principal program components. Results are limited to startup experience at the UMD gasifier.

INTRODUCTION

The Gasifier in Industry Program (GII) of the U.S. Department of Energy (DOE) is part of a broader activity to develop and improve technologies for converting coal to synthetic gas and liquid fuels.¹ Specifically, this program involves demonstrating the integration of existing low-Btu gasification technology in various operational environments. State-of-art technology is to be applied in six selected gasifier projects, one located on the campus of the University of Minnesota-Duluth (UMD) and another included in a planned community development at Pike County, Kentucky (PCK).

Information to be gathered during the demonstration period will consider questions of environmental acceptability as well as those related to technical and economic uncertainties.

DOE requested that the Oak Ridge National Laboratory (ORNL) develop for their consideration comprehensive, environmental, and health plans to study the UMD and PCD gasifiers.^{2,3} The final version of each plan incorporates U.S. Environmental Protection Agency (EPA) and National Institute for Occupational Safety and Health (NIOSH) comments made through an Environmental Working Group, GII. Following is a description of the monitoring and testing activities involved in developing the environmental and health data base.

Characteristics of Program Plan

A number of environmental and health concerns in coal gasification were identified previously by DOE and listed in an Environmental Development Plan.⁴ The issues and information requirements to satisfy these concerns for coal gasification were subsequently enhanced by staff of the Assistant Secretary for Environment, DOE. It was the latter determination of environmental and health tasks that was used to guide plan development.

Design of the program plans is based upon several premises:

- The study period will be limited to 3 yr;
- State-of-the-art capabilities in monitoring and testing will be applied wherever practicable;
- The first-year program will emphasize scoping and screening activities to delineate the requirements for more detailed investigations; and
- Program activities will be conducted without interrupting normal plant operation.

Although efforts will be made to utilize methods and instruments already available, some development in monitoring and testing protocols may be required to address unexpected problems. Screening activities during the first year will be

*Speaker.

followed by detailed investigation of the major concerns and important constituents, and by initiating monitoring and testing efforts into potential problem areas identified in the screening studies.

Four general areas of study are emphasized in the study plan: on-line studies, in-plant studies, local area studies, and multidisciplinary assessments that encompass the entire effort.

- On-line studies, or process characterization, provide guidance for sample testing and information for control technology evaluation;
- In-plant studies provide information for occupational health controls and for correlations of potential to actual personnel exposures;
- Local area studies identify pollutant fate and potential effects and confirm projections based upon effluent monitoring; and
- Local impact assessments are concerned

with the potential impacts on health and environment and with the adequacy of environmental and engineering controls.

Because the study plans for the two gasifiers are similar, subsequent descriptive material focuses on the UMD facility. Discussion of the PCK plant is limited to description of the process.

PROCESS MEASUREMENTS AND CONTROLS

Process conditions at the two projects will differ in that different gasifiers, feed stock, and environmental control systems will be used.

UMD Project

An existing oil-fired heating plant at UMD has been converted to burn low-Btu gas pro-

ORNL-DWG. 78-13526

UNIVERSITY OF MINNESOTA HEATING PLANT DULUTH CAMPUS STOIC TWO-STAGE GASIFIER

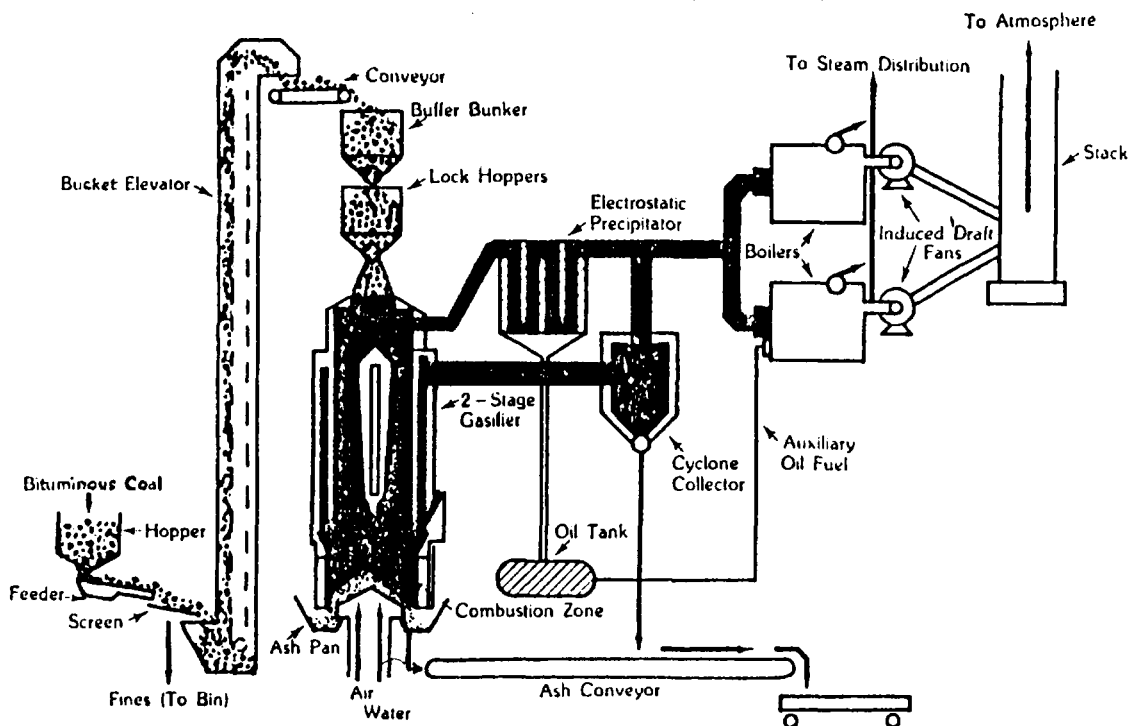


Figure 1. Schematic diagram of University of Minnesota-Duluth heating plant.

duced by coal gasification.⁵ Tar byproducts from the gasifier will be collected and used for peak heating requirements in an existing oil-fired boiler. The major components of the heating plant, illustrated in Figure 1, include a coal handling section, the gasifier, environmental control devices, and the boiler-steam-off gas section.

A Wyoming bituminous coal from the Elkol Mine, containing 6.6 percent ash and 0.5 percent sulfur, will be the initial feed stock. Coal will be received at the Duluth docks as 90 percent 1 1/4 in x 3/8 in, then screened and trucked to the heating plant. Several other lignite and bituminous coals have been proposed for testing.

After tramp iron removal and another screening for fines removal, coal will be dropped through purged lock hoppers into the gasifier. The gasifier is a Foster-Wheeler, Stoic two-stage design. Gas and tars are produced as the coal falls through the 250° to 1,100° F devolatilization zone and are removed from the top of the gasifier. Combustion and gasification of the devolatilized coal in an 1,000° to 1,800° F zone, fed by air and steam, produce bottom gas. Ash is removed beneath the gasifier from a water-filled pan, which serves to quench the hot ash and seal against operating pressure (less than 50 in H₂O).

Top and bottom gases must be cleaned of tars and particulates before combination into boiler feed. Because bottom gas at 1,100° F is primarily laden with particulates, a hot cyclone removes the dust for storage or disposal. In contrast, top gas (250° F) will contain tars and some particulates, which will be removed in a hot electrostatic precipitator and stored in heated underground tanks for use as boiler feed during the winter months.

Two modified 25,000-lb/hr steam boilers will burn low-Btu gas. Tars collected from the underflow of the electrostatic precipitator will be burned directly in an existing 50,000-lb/hr Combustion Engineering boiler. Gas-fired boiler flue gases vent to the main heating plant stack, while tar-fired boiler flue gases vent to a stub stack. Figure 2 shows the recently completed addition of the gasifier to the heating plant, on which shake-down test began October 24, 1978.

PCK Project

The gasifier plant now under construction at

the Douglas site in Pike County, Kentucky, will support a multiuse community composed of residences, a hospital, a school, municipal buildings, and industries. As such, it will initially provide both hot and chilled water, and in the future, low-Btu producer gas. The project, scheduled for completion by early 1980, is shown schematically in Figure 3.

Two standard design, air blown, agitated fixed-bed Wellman-Galusha gas producers will be installed in this facility. Each has been designed to handle 3,000 lb/hr of Pike County coal selected to meet air effluent standards for sulfur emissions. The producer gas will be individually piped to two steam-producing boilers. Each gasifier system is capable of being operated independently or in parallel. A standby supply of fuel oil will be used to meet excess demand. Steam from the boilers will be used to produce hot and/or chilled water by the use of three steam hot water convertors and two steam absorption chilled water generators.

Kentucky bituminous coal from local Pike County mines will supply the feedstock for the plant. This relatively low-sulfur coal (0.8 to 2.0 percent) is in good supply and will be delivered directly to the site by truck. A 30-day supply of coal will be stored in a covered and floored storage area and conveyed by front-end loader to a coal feed pit outside the plant.

After screening and crushing, the coal will be conveyed to storage bins, one for each gas producer. Coal will be injected into the gasifiers through coal valves and will travel downwards through a coal devolatilization stage, a reducing zone, an oxidation zone, and an ash zone. Air will be introduced through an annular water jacket, become saturated with water vapor, and enter the gasifier just below the slowly revolving eccentric grate.

Gas will exit the reactor at 1,000° to 1,200° F into a cyclone where large particles of ash will be removed. Gas can then be piped to two boilers to produce steam used to heat water or operate a steam absorption refrigeration unit or sent to the gas cleaning system. Initial plans call for the reactor gas to be utilized directly in the boilers, with a gas desulfurization system coming on-line in the future. A secondary cyclone separator will be utilized to remove the majority of the remaining particulate matter escaping from the boilers with the combustion gases.

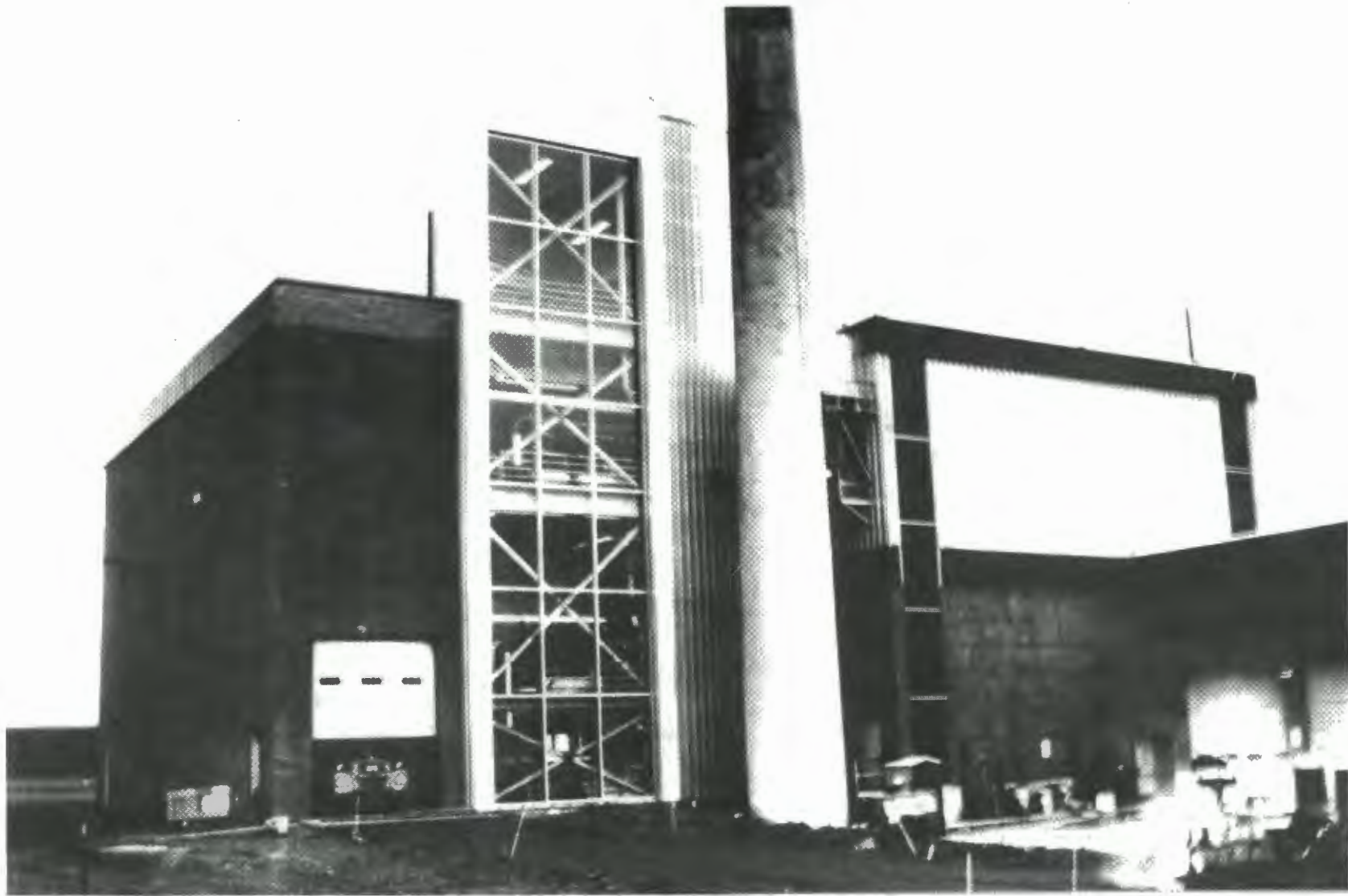


Figure 2. University of Minnesota-Duluth heating plant and coal gasifier.

PIKE COUNTY PROJECT PIKEVILLE, KY

TWO WELLMAN-GALUSHA GASIFIERS

SINGLE STAGE

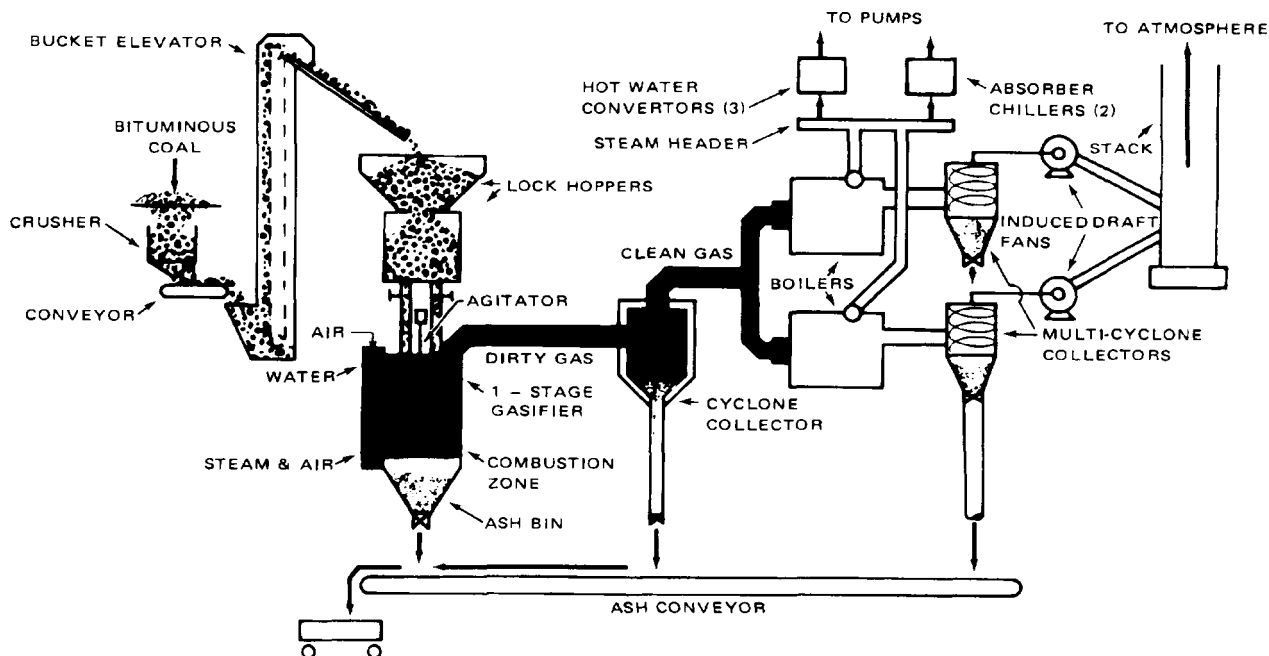


Figure 3. Schematic diagram of Pike County coal gasification facility.

Process Sampling and Characterization—UMD

Numerous sampling points have been designated to achieve the requirements of process measurements. Locations of each sampling point at the UMD project are identified in the flow schematic of the heating plant (Figure 4). The details of process sampling and analyses are described in the UMD product plan.² In general, process sampling strategy provides for characterizing materials introduced into the process, the intermediate or final product, and the recycle or waste streams.

The sampling schedule, analytical procedures, and constituents or parameters to be measured were chosen to allow early measurement of traditionally monitored or suspected materials, and to maximize the probable detection of unexpected and hazardous constituents. Results must be adequate to document process

conditions, to evaluate the efficiency of environmental control technology, to identify limitations in sample size or analytical methodologies, to identify possible biological hazards in potential fugitive emissions, and to establish priorities for subsequent bioassay.

On-line instrumentation required for process sampling and monitoring is summarized in Table 1. Gas chromatographs will monitor the primary gases (N_2 , CO, CO_2 , H_2), water vapor, and sulfur compounds (H_2S , COS, CS_2) at the electrostatic precipitator, cyclone, and stack effluents. SO_x and NO_x will be monitored initially in the main stack effluent. Grab samples and samples classified by use of four special sampling trains will also be used in process and effluent characterization. Table 2 includes a general description and the intended application of each sampling train. Twenty-three chemical and physical tests will be used initially in characterizing some 400 process samples collected the first year.

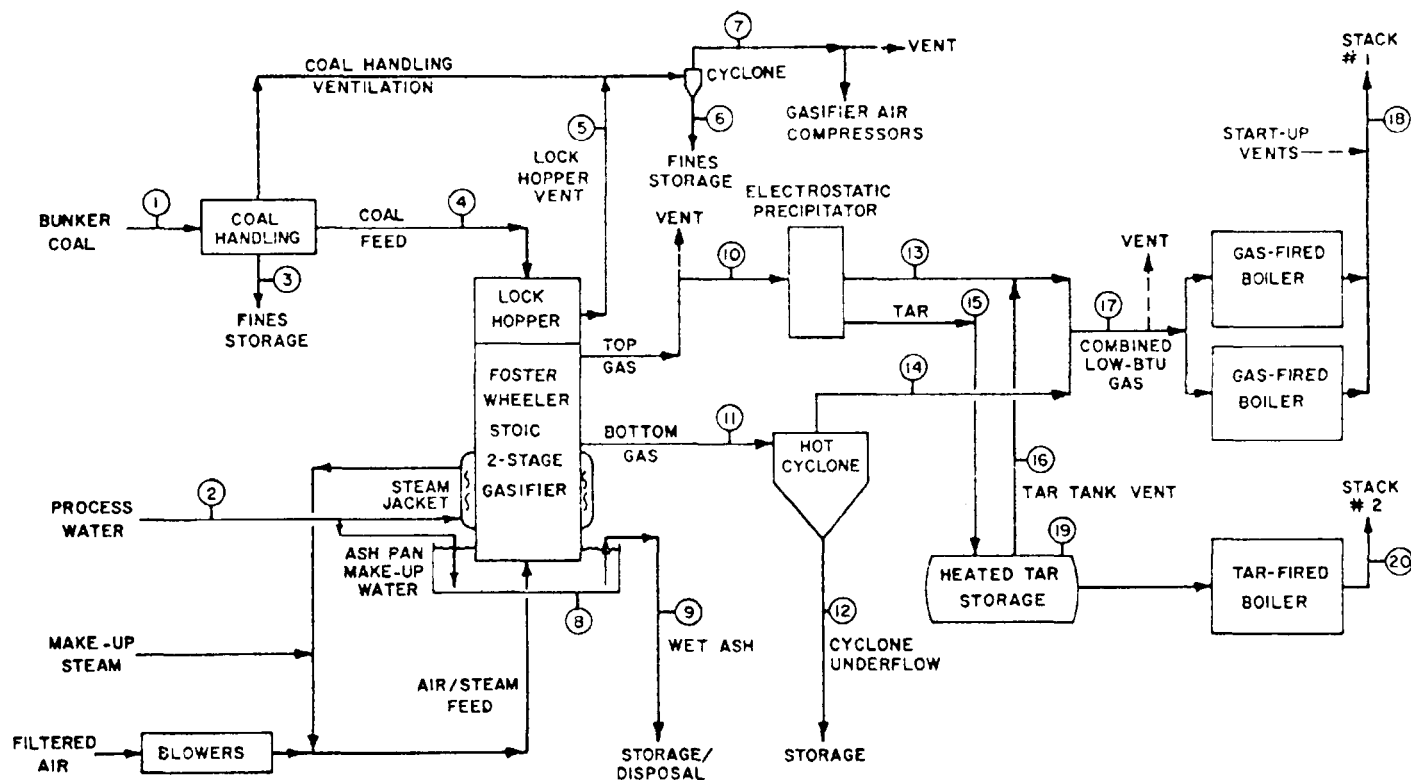


Figure 4. Flow schematic and sampling points for University of Minnesota-Duluth heating plant.

TABLE 1. ON-LINE INSTRUMENTATION FOR CONTINUOUS PROCESS MONITORING

Instrument	Monitored streams	Analysis
Gas chromatograph	13, 17 18, 20	N ₂ , CO, CO ₂ , C ₁ , C ₂ , C ₃ N ₂ , O ₂ , CO ₂
Gas chromatograph	13, 17 18, 20	H ₂ O, H ₂ H ₂ O
Gas chromatograph	13, 17 18, 20	H ₂ S, COS, CS ₂ , methyl mercaptan, ethyl mercaptan, thiopene SO ₂
Continuous monitor	18	SO _x
Continuous monitor	18	NO _x

(ORNL-DWG.)
(78-13533)

OCCUPATIONAL EXPOSURE AND EFFECTS

Potential exposure of man in the working environment includes consideration of plant area controls and effects on man if exposures occur. Monitoring and testing activities thus involve the requirements of worker protection and the potential effects of exposure to primary effluents and fugitive emissions.

Plant Area Sampling and Characterization—UMD

The primary objective of an industrial hygiene program is to recognize, evaluate, and control exposures that may be capable of producing overt health effects. An industrial hygiene and medical surveillance program has been established in cooperation with the University. The University has prime responsibility for protecting the health of its employees, and we have participated to complement the University requirements and to provide information for occupational health control assessments.

Two types of monitoring for potential exposures are provided. Area monitoring for CO, PAH, NH₃, NO_x, fugitive emissions, heat, noise, and various chemical stresses indicates possible exposures and will be accomplished by various

instruments providing real-time monitoring. A partial listing of area monitors and their functions is provided in Table 3. Personnel monitoring defines the actual exposures. A variety of standard industrial hygiene techniques employing filter cassettes and gas badges will be used to define the time-weighted exposures to gaseous and particulate contaminants.

Medical surveillance is necessary to ensure full protection of all personnel involved in operating and maintaining the gasifier. Information recorded by such surveillance will be correlated with results of personnel monitoring and become part of the assessment activity. The University provides for complete physical examinations, with special attention given to skin abnormalities and sputum cytology tests for employees at the gasifier.

Occupational Toxicology

The principal focus of occupational toxicology is the testing of primary effluents and fugitive emissions for potential effects on man. Information will be developed in response to questions of relative toxicity of byproducts and effluents, toxicity variation with process conditions, and toxicity potential of fugitive emissions.

A two-level bioassay program is designed to test effluents and potential fugitive emissions. Level one, or cellular bioassays, will be used to ascertain how the relative toxicity of effluents,

TABLE 2. SAMPLING TRAINS FOR UMD GASIFIER

Gas sampling train	In-stack particle sampler	Heated isokinetic probe ^a	Heated 3-cyclone series ^{a,b}	Knock-out drum, electrostatic precipitator ^a	Heated filter ^a	Gas cooler/ condenser	XAD-2 organic sorbent	Ice-cooled impingers			Vacuum pump and dry test meter	Purpose
								Reagent solutions	Empty	Drierite		
1		X		X	X	X			X	X	X	Measurement of tar loading.
2	X	X			X				X	X	X	Measurement of particulate loading and sizes.
3		X		X	X	X	X	X		X	X	Assessment of tar loading; collection of samples for organic, aqueous, and trace element analyses.
4		X	X		X	X	X	X		X	X	Assessment of particulate loading and size; collec- tion of samples for organic, aqueous, and trace element analysis.

^aHeated to 300°F to prevent water condensation.

^bAlternative staged particle separators could be used.

TABLE 3. AREA MONITORS

ORNL-DWG. 78-13539

Control pollutant	Type of instrument and capability
CO	Multipoint, continuously operating sensor station for CO analysis with visual and audio alarm
NH ₃ , NO _x , SO ₂ , C ₆ H ₆ , C ₆ H ₅ OH, naphthalene and its derivatives	Second derivative, UV absorption spectrometer with multipass gas cell for real-time monitoring of selected effluents
Respirable aerosol and dust particles (coal dust, tarry fumes and ash particles)	Piezobalance, portable monitor for measuring respirable aerosols with mass concentrations readout each minute; analyses for particulate polycyclic aromatic hydrocarbons (as benzene solubles) to determine integrated exposures will be conducted as part of the conventional industrial hygiene program; attempts will then be made to correlate the mass concentration and benzene soluble fraction for specific locations in the gasifier plant. If such correlations are found to exist then one would have indirect, but near real-time method for measuring benzene solubles

byproducts, and fractions thereof vary with process changes, to screen for further testing, and to correlate with whole animal, somatic effects. Tests in this category use a variety of biological systems, including bacteria, yeast, and mammalian cells, to investigate mutagenic effects. These shorter term tests will provide guidance and be complemented by longer term validating assays using drosophila, cultured mammalian cells, and whole animal (mouse) systems. Not all tests will be run on all samples collected at a given point, but priorities will be established based on the biological activity detected in the screening assays.

Level two, or mammalian somatic toxicity tests, complement mutagenic and cytotoxic testing. These assays use whole animals to characterize the acute, subacute, and chronic toxicity of products and effluents. Initially, only selected samples will be used in the more expensive toxicity tests, with selection based on the probability of direct or indirect human exposure and on current information of potential emis-

sions. Additions to the toxicity testing program are anticipated as the information base on biological activity develops.

ENVIRONMENTAL FATE AND EFFECTS

Environmental area monitoring includes sample collection and analyses, operation of continuous monitors, and application of appropriate ecological toxicity tests. Information derived from these activities is used to characterize and quantify air, water, and solid effluents that may impact the immediate environs of the plant.

Design of the monitoring program for the UMD environment considers the ambient environmental conditions and the expected operating characteristics of the gasifier. The following information guided development of the monitoring program:

- The Duluth-Superior urban area is industrialized, and operation of the heating plant is not expected to modify the ambient air to a discernable level;

- Water use at the gasifier is expected to be primarily consumptive and not result in any liquid effluents; and
- The principal solid waste is ash from the gasifier.

Two instrumented monitoring stations will primarily monitor criteria air pollutants (CO, NO_x, hydrocarbons, SO₂, oxidants, and particulates) with periodic sampling for total organics and organic speciation. The monitoring scheme and sampling frequency are listed in Table 4. If stack monitors indicate sufficient efflux of noncriteria pollutants (e.g., COS, NH₃, HCN), additional measures will be adopted to monitor for these pollutants.

Water quality measurements will be limited to samples taken from wells in a sanitary land fill used for ash disposal. In the event of unusual plant operating conditions, liquid effluents and surface streams will be monitored. Gasifier ash will be leached to investigate this important environmental parameter, and the water samples and leachates will be analyzed for a variety of organic and inorganic constituents. Screening activities will be used, as appropriate, to test the toxicity, transport, degradation, and bioaccumulation characteristics of either whole ef-

fluent streams, selected chemical fractions, or specific model compounds.

ASSESSMENTS

Site-specific assessments will be used to ensure maximum integration and utilization of information developed by the program elements of sample collection, analytical characterization, biological and environmental testing, and occupational control and medical surveillance.

Analyses of potential impacts include consideration of:

- Human health-related assessments, including the industrial worker and the general public;
- Ecologically related assessments, both terrestrial and aquatic systems in the site area; and
- Operational assessments involving: environmental control equipment, its efficiency and reliability; and occupational health control and the engineering systems used to reduce fugitive emissions.

Information developed through these assessments will be combined with information from studies of other low-Btu gasifiers and will be

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TABLE 4. ON-LINE ENVIRONMENTAL MONITORING

Analyses	Instrumentation	Sampling frequency
<u>Gases:</u>		
CO	Infra-red spectrometer	Continuous
NO _x	Chemiluminescence detector	Continuous
Hydrocarbons	Gas chromatograph	Continuous
SO ₂	Flame photometric detection	Continuous
Oxidants	Chemiluminescence detector	Continuous
<u>Particulates:</u>		
Total particulates ^a	High volume sampler	24-hr sampling, collection weekly

^aGravimetric analyses carried out by sampling personnel.

used to investigate potential impacts of anticipated industry growth.

Sample and Data Management

Successful execution of this program requires that a large number of samples be characterized by many investigators, and that the data and information developed be of high quality and readily accessible in assessment activities. Several thousand samples subjected to numerous analyses and tests and the on-line monitoring equipment output must be handled the first year. Both sample and data management are required.

Initially, all samples other than those characterized onsite will enter the Sample Management Center at ORNL. Samples will be treated as required, forwarded to project leaders responsible for various discipline-oriented tasks, and distributed to individual investigators. The Center will serve as the interface between the UMD sampling staff, the discipline task groups, and the Data Management Center.

The Data Management Center will provide a computerized data management system for storage and retrieval of data and information and will include: structure for data base development; procedures to ensure proper identification and recording of data; network to provide user access to the files; and data analyses routines.

PROGRAM IMPLEMENTATION AT UMD

All on-line instruments to monitor process streams, stack effluents, areas within the plant, and environmental air quality have been installed. Several modifications were made in the original plan. For example, the process gas chromatographs were equipped with an additional cleanup system consisting of electrostatic precipitators and perma-pure dryers, with the latter installed to permit optional use of a drying step during GC operation. Preliminary test results by Radian Corporation indicate that removal of aerosols from the sample stream should reduce GC maintenance requirements without affecting the concentration of the components monitored. A data acquisition system has been provided to monitor process variables, and computer programs were developed to per-

mit visual display of these variables on a real-time basis.

Plant operators and environmental monitoring personnel have completed initial tests as part of the medical surveillance program. The program under University direction consists of complete physical examinations and laboratory studies including routine blood analyses, pulmonary function tests, audiograms, electrocardiograms, chest X-rays, and color photography of the skin. Sputum cytology testing has also been recommended. All records become part of the UMD Health Service file.

Our original plan provided only general guidance for in-plant worker protection. Subsequently, in collaboration with University officials, an industrial hygiene monitoring strategy was developed specifically for the UMD Gasifier. Program details were identified after completion of the major components of the facility and were the results of a site visit by a team of industrial hygienists and engineers. Major consideration was given to monitoring requirements for carbon monoxide, particulate polycyclic aromatic hydrocarbons (PPAH), heat, noise, miscellaneous chemical stresses, fugitive emissions, and personnel sampling. Eleven locations were identified for continuous CO monitoring and sample collection for PPAH analyses, portable CO monitors and UV light were specified for fugitive emission surveys at potential points of leakage, and CO dosimeters and personnel air sampling devices were recommended for worker application. This strategy will be reviewed after 3 mo of plant operation.

The gasifier has been operated during two separate periods, primarily to determine operating characteristics and the need for modifications in the coupled equipment. Coke was the fuel used most often although several short-term runs were made with a coke and coal blend. Not unexpectedly, a number of leaks occurred at flanges, valves, gaskets, and seals; their repair required immediate recommendations by the industrial hygienist for worker protection.

Many of the detected leaks were of small volume and did not cause acute exposure to carbon monoxide. However, several major emissions took place, which required a change in gasifier operation and a clearing of the area until levels were reduced to less than threshold limit values (TLV). Three types of CO monitor-

ing were employed: fixed area monitors, hand-held portable analyzers, and personnel dosimeters. Sixty man-days of dosimeter data from the first shake-down period showed that no 8-hr time-weighted average (TWA) was over 20 ppm and that most were less than 10 ppm (TLV/TWA = 50 ppm).

The value of an industrial hygiene capability especially during startup operations is well documented by the above example. This experience will provide a useful guide to personnel protection not only when the UMD Gasifier becomes operational but also for other similar facilities. Details of this experience will be discussed in subsequent reports.

CONCLUDING REMARKS

Design of the monitoring and testing program for UMD involves all of the uncertainties in the characteristics of a gasifier only recently operational, and consequently in the nature of the process streams, byproducts, and effluent streams. Parameters and tests were chosen initially to focus on screening methodologies as opposed to only selected constituents. Program changes can be expected after the first full year of study, with emphasis on investigating the more significant components.

REFERENCES

1. *Gasifiers in Industry: a Program of Coal Conversion and Utilization*. U.S. Energy Research and Development Administration. ERHQ-0015. August 1977.
2. Cowser, K. E. (ed.). *Proposed Environmental and Health Program for University of Minnesota Gasification Facility*. Oak Ridge National Laboratory. January 23, 1978.
3. Cowser, K. E. (ed.). *Proposed Environmental and Health Program for Pike County Coal Gasification Facility* (draft). Oak Ridge National Laboratory. December 18, 1978.
4. *Environmental Development Plan (EDP): Coal Gasification Program FY 1977*. U.S. Department of Energy. DOE/EDP-0013. March 1977.
5. Soderberg, W. E. *Coal Gasification Duluth Campus Heating Plant, Program Opportunity Notice for the Integration and Evaluation of Low-Btu Coal Gasification Technology in Operational Environments*. University of Minneapolis. July 9, 1976.
6. Rutherford, W. T. *Coal Gasification for a Utility Heating/Cooling Plant, Douglas Site, Pike County, Kentucky, Volume I, Technical Proposal*. Pike County, Kentucky. July 6, 1976.

THE USE OF LOW-Btu GAS FOR IRON OXIDE PELLET INDURATION: AN INTERIM REPORT

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Abstract

The U.S. Department of the Interior's Bureau of Mines is conducting a pilot-plant test program to evaluate low-Btu gas generated from the gasification of bituminous, subbituminous, and lignite coals. The program explores the technical feasibility of utilizing the gas as an alternate fuel for high-temperature induration of iron oxide pellets. A 2-m diameter single-stage, atmospheric, fixed-bed gasifier has been erected at the Bureau's Twin Cities (Minn.) Metallurgy Research Center adjacent to its pilot pelletizing facility. The gasifier provides a hot, raw, low-Btu gas for firing iron oxide pellets in an 0.85-m diameter by 10.7-m long rotary kiln. Pellets were made from commercial magnetic taconite concentrations and were processed at a rate of 450 kg/hr. Gasifier operating data at fuel rates of 900 to 1,200 kg/hr are presented for coke, eastern Kentucky bituminous coal, Colorado-Wyoming subbituminous coal, and a North Dakota lignite, along with corresponding coal and gas analyses, Btu content, and thermal efficiency. Approximately 90 to 140 Mg of raw coal was processed in each of the 5-day around-the-clock tests. Pellet induration with low-Btu gas is described, and some preliminary information on pellet quality is presented.

INTRODUCTION

The U.S. iron ore pelletizing industry provides about 60 percent of the nation's iron ore consumption and relies heavily upon natural gas for pellet induration, consuming an estimated 1.7 km³ annually. During the past few years, the industry has seen its gas supplies interrupted while costs have tripled. In the short term, supplies are likely to become even more restricted, interruptions longer and more frequent, and costs may be further increased. In the long term, natural gas may not be available to the in-

dustry. Presently, fuel oil is the only proven alternative that is similarly restricted, costly, and unreliable as a future base fuel because of declining supplies.

To face the challenge of dwindling premium fuel supplies to an industry so basic to the nation's economy, the Federal Bureau of Mines and others had previously examined direct coal-burning methods as an alternate energy source.¹ Pulverized coal-firing tests at both the pilot plant and commercial scale have shown that no single coal type is compatible with the three commercial pelletizing systems. For the grate-kiln process, only the premium quality eastern coals with high ash fusibility temperatures have shown real promise. Coals having ashes with low fluid temperatures are required for the straight-grate process because the prototype design consists of external "wet bottom" combustion chambers. The shaft-pelletizing furnaces have not yet been adapted to direct coal firing. The major problems are the distribution of powdered coal to a large number of combustion chambers and the potential for blockage with coal ash of the inaccessible refractory passageways. The general conclusions regarding coal firing for iron ore pelletizing are that although it can be used, coal selection will be restrictive, premium coals may have to be used, and with the required plant modifications and increased refractory costs, it may be no more economical than some form of coal gasification.

A recent study², funded by the Bureau and conducted by the Arthur G. McKee Company, pointed out that with currently available technology, production of a hot, raw, low-Btu gas generated by an atmospheric producer would offer a viable, economical alternative to natural gas or oil. An onsite facility would provide a high overall thermal efficiency and minimize the capital costs of the coal gasification plant. This system of gas production would give the pelletizing industry a wider selection of coals and would be even more cost-effective if the low-rank western subbituminous and lignite

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coals could be used. Although the study indicated that the use of low-Btu gas for pellet induration appears technically feasible, the practical aspects of using this fuel must first be demonstrated on a pilot-plant scale.

The research program conducted by the Bureau in its pelletizing pilot-plant facility is a cooperative effort with the U.S. Department of Energy (DOE) and a consortium of 17 companies with interests in iron ore, coal, gas, and industrial engineering. The Bureau's goal is to determine whether pellet firing with coal gas of low heating value is technically feasible and practical, while DOE is interested in gasifier operations and technology. The U.S. Environmental Protection Agency (EPA) is monitoring the tests to characterize various gaseous and liquid streams in the process. Coal gas to be used in the pelletizing program will be derived from gasifying bituminous, subbituminous, and lignite coals.

The data presented in this paper represent the initial test campaign. It is expected that the project will be completed by the fall of 1979.

PROCESS AND PLANT DESCRIPTION

The Bureau's pelletizing facility is a fully integrated pilot plant capable of taking concentrate through all pelletizing steps of balling, drying, preheating, induration, and cooling. Plant capacity is nominally 500 kg/hr dry feed. The balling circuit consists of a table feeder for concentrate, a screw feeder for bentonite, a belt-type paddle mixer for blending the bentonite binder with the concentrate, and a 1.5-m diameter pelletizing disk to form the nominal 1.2-cm diameter green pellets. The green pellets are first dried and then preheated to approximately 1,270 K on a 0.3- by 3-m long traveling grate with one updraft drying zone and two downdraft preheat zones. Then, pellets are indurated in an 0.85-m diameter by 10.7-m long rotary kiln operating at 1,570 K to 1,620 K and discharged through a shaft-type cooler. The pellet cooler supplies preheated air to the kiln. The low-Btu kiln burner is a scroll-type unit with adjustable register vanes for flame shaping. Combustion air supplied to the burner can be preheated to 720 K.

Pellet plant instrumentation and controls are centrally located in a control room. Tempera-

ture and most pressure and flow data are obtained with a data logger and later processed in a computer. The low-Btu kiln burner control system was designed to adapt quickly to changes in gas composition. The gas flow is controlled by kiln temperature, and the air flow is controlled by a fully electronic flow ratio control scheme. Producer gas flow to the kiln is measured with a "low loss" venturi flow element and a mass flow computer.

The gasification pilot plant, shown in Figure 1, is adjacent to the pelletizing plant and includes a 2-m diameter, fixed-bed, atmospheric producer with a water-cooled agitator arm and has a nominal capacity of 1.35 Mg/hr of bituminous coal. Steam is self-generated by passing the air over water heated by the gasifier cooling jacket, whereby the air becomes saturated at some desired temperature. The producer gas flows through a refractory-lined dry cyclone and is then transmitted via a 61-cm I.D. duct to a combustion chamber and a 20-cm I.D. duct to the pelletizing kiln. Both ducts are lined with 10 cm of refractory. The combustion chamber is designed to match the full capacity of the gas producer because, at maximum output, the pelletizing kiln would use only 10 to 15 percent of the producer gas. A scroll-type burner is also installed on the combustion chamber and includes adjustable register vanes to control flame shape. Exhaust gases from the combustion chamber are cleaned with an impingement tray-type scrubber with pH control. A combination ignitor-incinerator is installed on the gasifier cent stack to ignite the gases during flaring or completely combust the small amount of gases generated during banking. The gasifier building was constructed to satisfy an electrical classification of Class I, Group B, Division II, and includes a building exhaust fan, open grating floors, and a hooded vent over the coal feed bin. Carbon monoxide monitors are present at three locations with alarm capability between 0 and 100 ppm.

Instrumentation and controls for the gasifier are centrally located in a control room adjacent to but isolated from the main operating floor of the gasifier building. In addition to the normal complement of instrumentation for such a producer, the 9-Mg capacity coal storage bin is supported on precision load cells, and the producer gas flow is measured with a "low loss" venturi

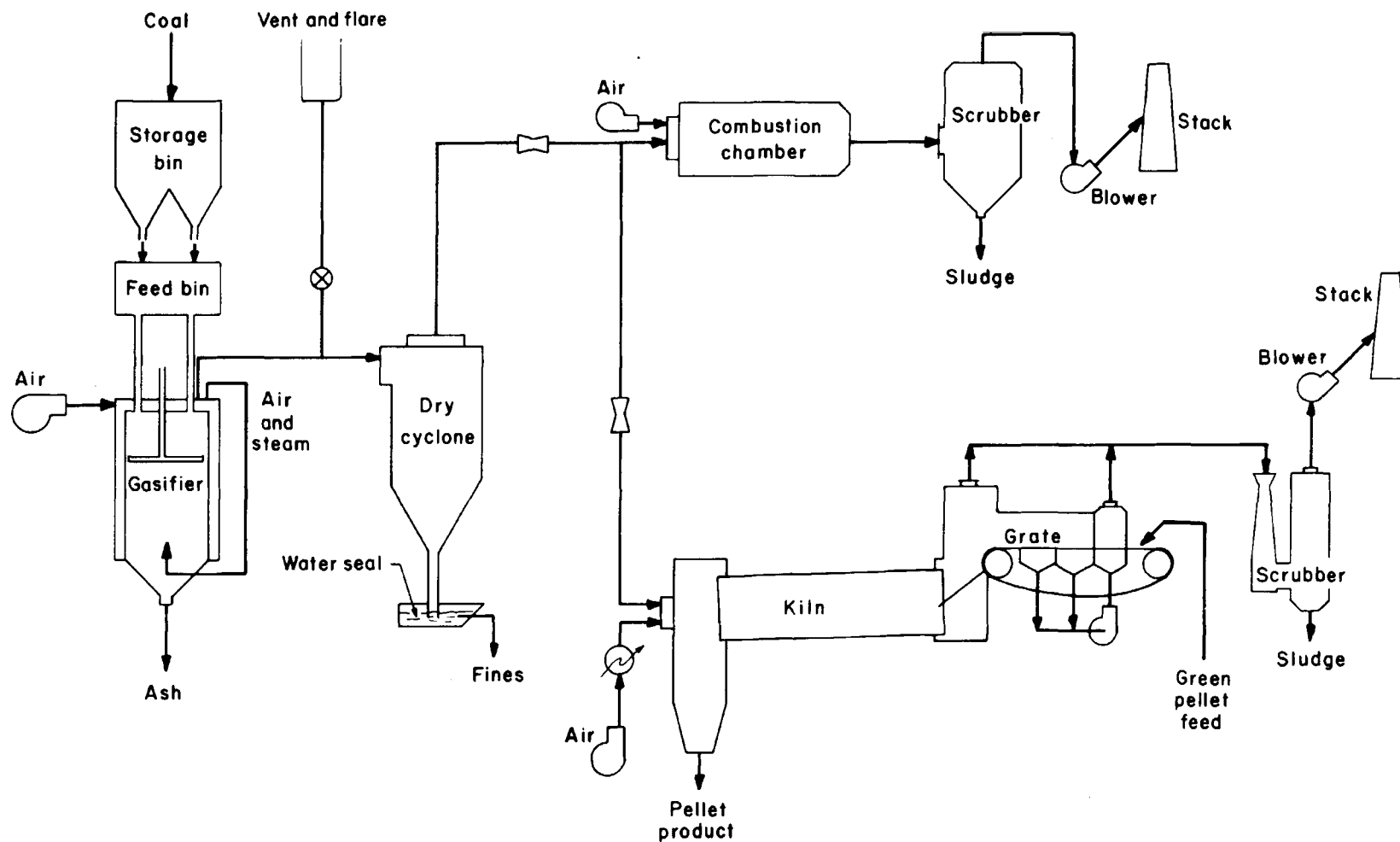


Figure 1. Process flow diagram of Bureau of Mines Gasification and Pelletizing Pilot-Plant, Twin Cities Metallurgy Research Center.

flow element. The air flow is measured with an Annubar* flow element and controlled by the producer offtake pressure. The system is designed to operate with a maximum offtake pressure of 1.25 kPa; the ducts, flow elements, etc., were designed to contribute no more than 0.5 kPa permanent pressure loss at two-thirds rated capacity. Temperature, pressure, and flow data are obtained with a data logger and later processed by computer. Combustion chamber instrumentation is minimal, and most controls are local and manual. The chamber pressure is automatically controlled and a temperature profile is recorded. Flame supervision at the combustion chamber burner includes interlocks to shut down and vent the gasifier when the 61-cm gas safety shutoff valve to the burner closes. A fully automated gas chromatograph with a thermal conductivity detector provides the producer gas analyses. The gas sampling and conditioning system, which was built in-house, was designed to obtain tar, oil, and moisture contents and to deliver a dry, clean gas to the chromatograph.

DESCRIPTION OF INITIAL TEST CAMPAIGN

The initial campaign consisted of one 7-day and three 5-day continuous tests conducted from November 13 to December 15, 1978. All tests contained downtime of one to three shifts. The gasifier was banked between tests.

The test program was based on the assumption that the producer would gasify bituminous, subbituminous, and lignite coal under reasonably stable conditions and would produce gases typical of atmospheric producers for these fuels. The producer was originally designed for tar-free coke and anthracite, and it was expected that some modifications would have to be made to the unit for it to operate successfully with this wide range of fuels. The first few tests would yield information on the required modifications.

Radian Corporation, Austin, Texas, representing EPA, was onsite during the entire test campaign and obtained gas analyses of the combustion chamber exhaust and producer gas during the last three tests. Radian's analyses were obtained with three gas chromatographs on

*Reference to specific trade names does not imply endorsements by the Bureau of Mines.

each sampling system; producer gas samples were obtained independently of the Bureau's samples. There was some overlap in the suite of constituents analyzed to allow better coordination of the results between the two systems. During the test with lignite, a full-scale sampling program was run to fully characterize the producer gas, all gasifier effluents, and combustion chamber exhaust. Sampling included isokinetic sampling of the producer gas and combustion chamber exhaust gas streams. Samples of water discharges were also obtained. Results of Radian's sampling program are not included in this report.

The operating philosophy for all tests was to bring the entire pilot plant on-stream as quickly as possible and to stabilize each section of the plant later. After the gasifier was running, the pelletizing plant and combustion chamber were brought on-stream with natural gas prior to switching the producer gas from the flare to the combustion chamber. After the combustion chamber and gasifier were on-line, the low-Btu gas flow was started to the pelletizing kiln, and pellet making commenced shortly thereafter. System malfunctions, however, prevented the startup sequences from proceeding smoothly. Numerous equipment and system failures occurred during the test campaign, and repairs had to be made almost continually during the operation. The abnormally cold weather caused most problems because the ambient temperature decreased steadily throughout the campaign. Because the plant was not fully winterized, water lines, air lines, and valves required an inordinate amount of attention. Consequently, the stable test periods, especially in the pellet plant, were too short to attain steady state. All coals, however, were gasified, and pellets were indurated with gas from each coal.

Coke was used to start the gasifier and was run for periods long enough to stabilize the fire and heat the refractory-lined ducts. The first coal to be gasified was a high-quality, closely sized bituminous coal from eastern Kentucky. The second and third coals were a Colorado-Wyoming subbituminous coal and a North Dakota lignite. All coals were screened at 1.9 cm just prior to loading into the storage bin via a bucket elevator. Analysis and sizing of the "as fed" coal are given in Table 1 and Table 2. The data were developed from composite analyses of samples taken four times per shift.

TABLE 1. ANALYSIS OF FUELS "AS FED"

Solid fuel tested	Coke	Bituminous	Subbituminous	Lignite
Source	-	E. Kentucky	Colorado-Wyo.	N. Dakota
Proximate analyses, ¹ wt-pct				
Moisture	4.8	3.3	10.8	30.6
Volatile matter	0.9	37.2	36.2	28.3
Fixed carbon	87.1	54.1	46.2	33.4
Ash	7.2	5.4	6.8	7.7
Ultimate analysis, ¹ wt-pct				
Hydrogen	0.9	5.1	5.4	6.3
Carbon	74.1	79.0	63.8	44.7
Nitrogen	0.5	1.6	1.3	0.6
Oxygen	16.7	8.1	22.0	39.8
Sulfur	0.6	0.8	0.7	0.8
Ash	7.2	5.4	6.8	7.7
Heating value, kJ/kg	28,428	31,520	25,660	17,582
Ash fusibility, ² °K				
Initial deformation	1,444	1,716	1,644	1,322
Softening	1,505	1,744	1,672	1,350
Fluid	1,566	1,810+	1,744	1,377
Free Swelling Index	0	4	0	0

¹"wet basis" as received.

²ASTM reducing conditions.

RESULTS AND DISCUSSION

Because of the nature of the initial campaign, the tests yielded results primarily of a "mechanical" nature, although significant process information was also collected. The detailed equipment modifications found to be required are not reported here. Instead, observations are presented along with a small amount of process data.

A subjective observation was made that the gasifier operation was just "settling out" at the end of a 5-day test. Because all operators agreed on this point, it has been decided that 10 days will be the minimum operating period for future tests. This "settling out" period is a combination of many factors, not the least of which is learning the behavior of the specific coal being used. At 900 kg/hr of coal feed with 7 percent ash (which is typical of the coals of interest to the

Bureau's test program), the coal residence time is approximately 4 hr, while the ash residence time is an additional 24 to 48 hr, depending on ash bed depth. It can be easily seen, therefore, that changes to the gasifier operation may not fully show up for 2 days.

Gasifier operating difficulties were expected with subbituminous coal and lignite because of the friable nature of the fuels and the ash characteristics. Low-rank coals generally have a lower ash fusion temperature, and clinker formation is considered a major problem. Gasifier air saturation-temperature (i.e., stream consumption) is the major method for controlling clinker formation. Maintenance of ash bed depth is affected by clinker formation, grate speed, and the size of the grate openings. A variable speed drive was installed on the grate; however, this modification did not appear sufficient to compensate for the wide differences in ash be-

TABLE 2. COAL SIZING "AS FED"

Solid fuel tested	Coke	Bituminous	Subbituminous	Lignite
Size, mm	Cumulative wt-pct passing			
57.2.....	100	100	100	100
50.8.....	100	99.9	99.9	99.4
45.3.....	95.6	99.5	97.8	98.5
38.1.....	75.3	97.5	85.2	94.4
32.0.....	41.2	93.7	64.9	77.0
25.4.....	10.9	72.3	43.9	42.6
19.0.....	3.1	32.6	28.7	15.0
16.0.....	1.9	14.1	21.1	6.7
12.7.....	1.6	6.1	13.6	3.4
9.51.....	1.4	3.5	8.0	2.0
6.35.....	1.1	2.5	3.8	1.2

havior among the three coals. Although serious clinkering problems were not encountered with the subbituminous coal, the operation was not smooth. Auxiliary steam was necessary at one point because the fire zone became very thin and the jacket water temperature was not high enough to saturate the air to the desired level. The operators were able to stabilize the operation after 8 hr, and self-generation of steam became possible again. During the test with lignite, however, clinkering was a serious problem, although the gasifier did not appear to operate as poorly as expected. At the end of the test, 80 percent of the 12.4-cm wide grate openings were found to be solidly plugged with ash fines, and very large clinkers were found floating near the top of the ash bed. During all tests, the air saturation-temperature was unsteady, and the control scheme proved to be inadequate for this test program. This contributed to the

generally unstable gasifier operation and the clinkering problems with lignite.

Numerous other observations were made during plant operations. It was noted that control and safety shutoff valves in the producer gas lines should have oversized actuators for reliable operation. Coal and char fines entrained in the producer gas increased dramatically with the low-rank coals as opposed to bituminous coal. Quantitative measurements were not obtained; however, a higher dust loading was noted in the combustion chamber scrubber water and gasifier cyclone water seal. Gasifier operating data are given in Table 3, which shows that the pressure drop across the bed increased for the low-rank fuels. Also, as expected, the offtake temperature decreased for low-rank fuels, but the temperatures obtained were lower than expected.

Operation of the venturi flow elements was

TABLE 3. GASIFIER OPERATING DATA SUMMARY

Solid fuel tested	Coke	Bituminous	Subbituminous	Lignite
Saturated air, m ³ /hr.....	1,388	2,355	2,740	1,789
Saturation temperature, °K.	335	334	334	332
Coal burn rate, kg/hr.....	ND	657	1,179	1,161
Bed pressure drop, kPa.....	.87	1.19	4.53	2.71
Offtake temperature, °K....	624	692	559	416
Gas yield, m ³ /hr.....	ND	3,058	3,993	3,143

better than expected. The flow element in the 20-cm ID gas duct to the pelletizing kiln remained operable until the last test with lignite. During the lignite test, the low gas temperature, which caused tar, oil, and moisture condensation, along with the high dust loading, combined to build a 3-mm thick coating of coal fines on the converging cone of the flow element and a 1.5-mm thick coating on the venturi throat. The pressure taps were coated over but were not internally plugged. The flow element in the 61-cm gas duct became inoperative during the first test because of plugging of the pressure taps and would plug up again within minutes after cleaning. Because both venturies were well insulated, the difference in performance was attributed to the orientation of the flow elements. The small flow element was installed in a horizontal duct, and its pressure taps were installed vertically at the top, allowing condensate to flow back to the process. The large flow element was installed in a vertical duct (flow downward), and its pressure taps were horizontal, causing any condensate to stay in the taps. The 61-cm venturi had not yet been removed for inspection; there may be other problems associated with its orientation.

Gasifier process data and material balances are summarized in Table 4. The data shown are for short periods during the tests and are based on average rates for periods that were most stable. The producer gas flow meter on the gasi-

fier outlet was inoperative, so the flow was estimated and selected to yield the best total weight and carbon balance. Carbon, hydrogen, oxygen, nitrogen, and total weights were balanced independently. For all balances presented, the output/input ratios were within the range of the 0.9- to 1.1-range. Also, during the test with subbituminous coal, the gas sampling system was not operating well enough to provide a water vapor content in the producer gas. Gas moisture content for this test was calculated with a hydrogen balance; dry gas analyses for this test were also limited but are considered acceptable for characterizing the short test period. Ash balances were exact because they were based entirely on the known ash feed rates. Because the carbon in the ash varied significantly during the tests, the values used in the balances were based on residence time estimates and were not modified to produce better material balances.

Total thermal efficiency was calculated for the hot, raw gas at the cyclone outlet and was approximately 90 percent for all coals. Transmission heat losses were an additional 1.8 percent to the kiln and 2.9 percent to the combustion chamber for bituminous coal with a 1.0-percent total loss in the cyclone. For the subbituminous coal, there was a 2.1-percent transmission heat loss to the combustion chamber with a 1.2-percent total loss in the cyclone.

Representative gas analyses are presented in

TABLE 4. GASIFIER MATERIAL BALANCE AND PROCESS DATA SUMMARY

Solid fuel tested	Bituminous	Subbituminous	Lignite
Input, kg/hr			
Coal.....	657	1,179	1,161
Steam.....	360	425	239
Air.....	2,298	2,663	1,800
Output, kg/hr			
Dry gas.....	2,961	3,717	2,602
Tar.....	53.5	62.6 ^{e/}	44.9 ^{e/}
Water.....	186	345	464
Bottom ash.....	40.8	88.5	98.0
Cyclone solids.....	6.8	11.8	13.6
Input ratios, kg/kg			
Steam/coal.....	.55	.36	.21
Air/coal.....	3.51	2.26	1.56
Total thermal			
Efficiency, pct.....	92	89	89
Gas yield			
m ³ /kg coal.....	4.68	3.43	2.68
Heating value, MJ/m ³			
Dry basis (tar free).....	5.55	6.67	6.33
Wet basis (tar free).....	5.18	5.70	5.10
Tar contribution (wet basis).....	.63	.60 ^{e/}	.63 ^{e/}
Sensible heat (wet basis)....	.48	.22	.15

^{e/} Estimated.

Table 5. The analyses do not necessarily represent the same operating periods that were used for the balances shown in Table 4. The analyses were corrected to air-free values and were obtained from raw gas analyses having less than 3 percent oxygen with most oxygen contents in the 1- to 2-percent range. Oxygen in the producer gas analysis was assumed to come entirely from leaks in the sampling system. The sampling system performed very well during the last test with lignite. Oxygen values of 1 percent or less were consistently obtained during the last test after correcting for argon superimposed on the oxygen peak. Tar and oil in

the gas from lignite were measured but were an order of magnitude lower than values typically reported. It was felt that the tar fraction condensed into droplets in the gas duct and the sampling geometry prevented obtaining a representative sample. Gas temperature at the sampling point was above the dew point, so moisture measurements were considered representative.

Results of the pelletizing test with magnetic taconite concentrates and the three coals are encouraging, but they are limited because of mechanical difficulties and a generally unstable gasifier operation. Desired pelletizing tempera-

TABLE 5. PRODUCER GAS ANALYSES

Solid fuel tested	Coke		Bituminous		Subbituminous		Lignite	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Constituent, volume pct. ¹								
H ₂	10.7	10.1	18.3	16.7	16.9	14.7	17.5	14.1
CO	23.8	22.4	26.7	24.4	28.5	24.9	28.9	23.3
CH ₄	.001	.001	1.7	1.6	2.0	1.7	1.5	1.2
C ₂ H ₄	.0	.0	.10	.09	.43	.37	.15	0.12
C ₂ H ₆	.0	.0	.20	.18	.14	.12	.10	0.08
CO ₂	9.0	8.5	6.2	5.7	6.5	5.7	6.2	5.0
N ₂ +A	53.6	50.4	46.8	42.8	46.9	40.9	45.6	36.7
H ₂ O		6.0		8.6		12.8 ²		19.4
Tar, g/m ³	ND	ND	17.7	16.2	ND	ND	ND	ND
Gas heating value, kJ/m ³								
Gross	4,136	3,875	6,260	5,738	6,558	5,701	6,297	5,067
Net	3,949	3,726	5,812	5,328	6,148	5,365	5,924	4,769
Tar contribution, kJ/m ³								
Gross	ND	ND	633	578	ND	ND	ND	ND
Net	ND	ND	604	551	ND	ND	ND	ND
Sensible heat at cyclone exhaust, kJ/m ³	ND	376	ND	458	ND	347	ND	149

¹ Corrected air free.² By hydrogen balance.

ture were not sustained as a result of short-test duration. Pelletizing data for all tests are summarized in Table 6. The pellet strengths listed were the best obtained during the tests. Although the strengths were 25 to 40 percent too low for a commercially acceptable product, they were increasing in all cases. The strengths are typical of induration at these lower than normal temperatures.

Pellet chemistry is given in Table 7. The analyses are also shown normalized to zero Fe⁺⁺ by "adding" the required oxygen. The analyses indicate there may have been some minor ash pickup by the pellets in the kiln during the tests with the western coals. The high sulfur content in the grate discharge pellets indicates a recirculating load of sulfur between the grate and kiln during all tests. These data can be used qualitatively only because the analyses represent short operating periods and only a few samples. High ferrous iron in the pellets is

indicative of "underburning" and is consistent with the low strengths attained.

SUMMARY AND CONCLUSIONS

Four 100- to 160-hr around-the-clock tests were completed during November 13 to December 15, 1978, in the Bureau's iron ore pelletizing and coal gasification pilot plant. Pellets were indurated in the 10.7-m long rotary kiln at rates of 400 to 544 kg/hr using hot, raw, low-Btu gases generated from an eastern Kentucky bituminous coal, a Colorado-Wyoming subbituminous coal, and a North Dakota lignite. The minus 50.8-mm plus 19.0 mm sized coals were gasified at rates of 900 to 1,180 kg/hr in a 2-m diameter single-stage, fixed-bed atmospheric gas producer originally designed for tar-free anthracite and coke. The ability to gasify these widely different solid fuels in this gasifier, generate good quality gas, and obtain or approach the

TABLE 6. PELLETIZING DATA SUMMARY

Solid fuel tested	Bituminous	Subbituminous	Lignite
Concentrate feed rate dry basis, kg/hr.....	456	424	544
Average grate hood temperature, °K.	995	955	895
Maximum kiln temperature, °K.....	1,625	1,520	1,515
Crushing strength, kN.....	1.62	1.49	1.80

TABLE 7. PELLET CHEMISTRY SUMMARY

Constituent, wt pct	Grate feed		Grate discharge		Kiln product	
Bituminous coal						
Fe	66.0	(64.5) ¹	65.7	(64.4)	65.7	(64.9)
Fe ²⁺	21.8	(0)	14.1	(0)	7.6	(0)
SiO ₂ +Al ₂ O ₃	6.63	(6.47)	6.56	(6.44)	6.50	(6.43)
CaO+MgO	.40	(.39)	.41	(.41)	.42	(.42)
Na ₂ O+K ₂ O	.079	(.077)	.067	(.065)	.055	(.055)
S	.016	(.015)	.032	(.032)	<.005	(<.005)
Subbituminous coal						
Fe	67.0	(65.0)	66.8	(65.2)	65.5	(65.4)
Fe ²⁺	21.6	(0)	16.8	(0)	1.8	(0)
SiO ₂ +Al ₂ O ₃	5.55	(5.39)	5.57	(5.44)	5.69	(5.68)
CaO+MgO	.46	(.45)	.46	(.44)	.48	(.47)
Na ₂ O+K ₂ O	.05	(.048)	.053	(.052)	.043	(.042)
S	.011	(.011)	.022	(.021)	<.005	(<.005)
Lignite						
Fe	66.2	(64.2)	65.9	(64.7)	65.3	(64.8)
Fe ²⁺	21.8	(0)	13.0	(0)	5.3	(0)
SiO ₂ +Al ₂ O ₃	5.79	(5.58)	6.13	(6.02)	6.29	(6.24)
CaO+MgO	1.11	(1.07)	1.06	(1.04)	1.19	(1.18)
Na ₂ O+K ₂ O	.05	(.048)	.07	(.07)	.06	(.06)
S	.015	(.015)	.038	(.037)	.004	(.004)

¹ Analyses in parentheses are normalized to zero Fe²⁺ to show trends. Numbers are independently rounded.

necessary pelletizing temperatures in the kiln is considered a major accomplishment of the initial startup campaign. Although pellets were indurated with the raw, low-Btu coal gas, frequent interruptions in gas flow to the kiln as a result of erratic gasifier operations prevented achieving the fully stabilized kiln temperature profile required to produce pellets of commercially acceptable quality. The pelletizing results obtained from these initial tests indicate that acceptable quality pellets probably can be made from magentic taconite concentrates in a rotary kiln with raw, low-Btu coal gas. However, further demonstration tests under more stable gasifier and pelletizing operations are needed before this approach can be considered for a full-scale pelletizing facility. Future tests must also be run on hematite concentrates because both the maximum induration temperature and total heat requirements are greater than those requirements for magnetite.

Problems in gasifier operation and in transporting and burning the raw producer gas became more prevalent with the decrease in coal rank. It is now apparent that some modifications will have to be made to the gasifier to allow safe and stable operations when high moisture and friable western subbituminous coal and lignite are treated. Some of the more important future modifications will include:

- Changing the cooling water piping and

replacing the air saturation-temperature controller for closer and more stable control over steam consumption;

- Increasing the revolving grate spacings to account for the different ash characteristics of the low-rank western subbituminous coals and lignites; and
- Installing traps in the gas ducting to prevent buildup of tar and condensate at low points in the distribution mains. The necessary modifications to the plant are now underway, and testing is expected to be resumed in the summer of 1979.

REFERENCES

1. Nigro, J. C. Alternative Coal-Firing Methods for Indurating Iron Ore Pellets. *Mining Congress J.* 64(6): 19-26. June 1978.
2. Ashworth, R. A., K. C. Byas, and D. G. Bonamer. *Utilization of Low and Intermediate Btu Gas from Coal for Iron Ore Pelletizing*. Bureau of Mines, U.S. Department of Interior. Open File Report 36-77. 1977. 283 pp. (Available for consultation at each of the Bureau of Mines Metallurgy Research Centers; at the Natural Resources Library, U.S. Department of the Interior, Washington, D. C.; and from National Technical Information Service, Springfield, Virginia, PB 264-702/AS.)



**Session II: ENVIRONMENTAL ASSESSMENT:
GASIFICATION**

**Charles F. Murray, Chairman
TRW
Redondo Beach, California**



SYNTHETIC FUELS IMPLEMENTATION

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Abstract

The need is urgent to start building large synthetic fuel plants. Supply side action is essential to meet social expectations that rest on energy. New energy supplies will help counter international inflationary pressures. Synthetic fuels offer us a significant mobilization alternative and, in sufficient quantities, can provide a cap for world oil prices.

Of the many implementation alternatives, three suffice to show the range of opportunity available: shale oil tax credit, competitive bidding for Federal support, and The Petroleum Substitutes Requirements Program (PETSUB).

INTRODUCTION

It is a real honor for me to be with you in this symposium, for your work here is vital. There are problems to be identified and resolved, but the need for synthetic fuels is critical. There may be little we can do to avoid brownouts during this summer and successive summers. There will be other energy shortages, for as a society we have remained unconvinced about the energy crisis for too long. Synthetic fuels will have to fill part of the void, but the void is huge.

The void will be created by nuclear generating plants that are and will be closed, by other plants—coal, hydroelectric, and nuclear—that will not be built. To maintain a per capita zero rate of energy growth for the growing world population we need new electric utility plants faster than they are now being planned or built. But we need to increase our electric energy growth rate to shift (indirectly) to coal. At a construction rate we cannot maintain, we are already over 2 years behind. We will not succeed in building all the electric plants we need, but somehow, we need to fill the void—or at least part of it—with synthetic fuels.

This energy shortage—and it is not only in electricity—cannot be made up solely by orderly conservation. The difference can only be

made up by *new investment* or *denial*. The problem with denial is America's social promise: that denied minorities can expect their share of what only energy can provide. President Carter said clearly that our energy crisis has the "moral equivalent of war." To me, the moral aspect incorporates these social expectations. So I emphasize this basic energy need, heightened and sharpened by social expectations for real goods and services. It is easy for me to assert the need, but I have two documents here—the Commerce Department's forecasting effort—that attempt to prove it.^{1,2}

Beyond a basic energy need and growing social expectations, a need exists for an emergency supply capability. Synthetic fuel plants can give us this additional mobilization, or emergency capability, in addition to below-ground storage.

Finally, synthetic fuels produced in sufficient volume offer a cap on world oil prices. Successful work on the supply side of energy may relieve international inflationary pressures. Because we are limited to what we can accomplish by disciplining demand, we need to devote renewed effort to the supply side, perhaps the answer to many of our productivity problems.

How do we go about it? You know the environmental problems, and I leave the technical solutions to you. But, from a management view, there are many implementation alternatives. Three, however, will suffice to show the range of opportunities open to us.

First, the Administration is working on a draft bill entitled "Shale Oil Tax Credit of 1979." Because a 50,000-bbl/d plant is expected to cost \$1.2 billion to build, and because shale oil is expected to sell profitably only at \$5 or \$6 more than world oil, considerable incentive is needed. This bill would provide a \$3-credit against tax liability that would shelter from \$5 to \$6 per barrel and provide the needed incentive. This kind of legislation could be applied to other synthetic fuels.

Second, an earlier Department of Commerce

proposal suggested that prospective producers bid to produce units of 50,000 barrels of oil—or the equivalent in Btu content of synthetic gas or other fuel—with the bid including those aspects of Federal assistance that the producers wanted. This would encourage competition but would not limit the kind of support any firm could seek: front end grants, per barrel tax credits, guaranteed loans, guaranteed prices, etc. This proposal is not active today, but it is representative of the range of implementing plans that have been considered.

Finally, PETSUB, The Petroleum Substitutes Requirement Program,³ is under active consideration by the Administration. Under that program, natural gas distributors, importers, and other large users of oil and gas would be required to purchase a specified amount of substitute fuels. The amount would be a small fraction of their earlier consumption of oil and/or gas. Producers of substitutes would issue certificates of quantities delivered to prove customer compliance.

The certificates would be salable so certain specialized firms could escape use of the substitutes where other firms had surplus certificates to sell. All users would bear the program costs as the synthetic fuel cost differentials were passed through by refineries and others. Since synthetic producers would not be limited in price, market entry would be encouraged. Active competition would be expected.

In closing, let me repeat that your job is vital; technical solutions to identified problems are needed now. The benefits are three:

- Social expectations can be met,
- Our mobilization capability can be expanded for emergencies, and

- International inflationary pressure can be countered.

To reach these benefits, significant implementation alternatives are available to permit your work to be brought to fruition.

But everyone must work quickly—our energy supply and distribution system are tenuous. We need to make significant changes swiftly and carefully.

REFERENCES

1. Forecast of Likely U.S. Energy Supply/Demand Balances for 1985 and 2000 and Implications for U.S. Energy Policy. PB 266 240.
2. Preliminary Forecast of Likely U.S. Energy Consumption/Production Balances for 1985 and 2000 by States. PB 287 486.
3. Petroleum Substitutes Requirement Program. Sobotka & Co., Inc. March 12, 1979.

BIBLIOGRAPHY

Gustaferro, J. F., M. Maher, and R. Wing. Forecast of Likely U.S. Energy Supply/Demand Balances for 1985 and 2000 and Implications for U.S. Energy Policy. National Technical Information Service. PB 266 240.

Gustaferro, J. F., C. S. Warlick, A. M. Maher, and R. Wing. Preliminary Forecast of Likely U.S. Energy Consumption/Production Balances for 1985 and 2000 by States. National Technical Information Service. PB 287 486.

Sobotka & Co., Inc. Petroleum Substitutes Requirement Program. March 12, 1979.

POLLUTANT EVALUATIONS FOR A LABORATORY SEMI-BATCH COAL GASIFIER

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Abstract

Nine U.S. solid fuels have been gasified in the RTI laboratory unit. Gasifier streams have been extensively and quantitatively defined in terms of process and chemical pollutant parameters. Experimental results have received preliminary analysis on the basis of:

- *Coal-associated influences on pollutant production,*
- *Stream pollutant level comparisons,*
- *Comparison with similar pollutant and process operations data reported in the literature,*
- *Correlation of process parameters with pollutant production, and*
- *Cross-correlations of pollutant data.*

Integrated results from the semibatch gasifier have evidenced good simulation of fixed-bed, full-scale, continuous units in terms of product composition, throughputs, and effects of operational variables. Mass balances have been improved, and consistent chemical analyses of potential environmental hazards have allowed evaluation of production trends. Specific compounds consistently contributing to significant potential environmental hazards have been identified. Compounds posing threats to health (on the bases of both quantity and toxicity/carcinogenicity) appear to be limited to a reasonable number, allowing routine quantitation. Analysis of this limited number of compounds is being augmented by bioassay research to encompass total materials and synergistic effects.

INTRODUCTION

The gasification reactor is the primary, unique source of pollutants in this type of coal conversion plant. A large amount of information is already available on such subsidiary processes as coal storage, water processing, utility

stack gas contamination, and control and treatment.

In attempting an environmental assessment applicable to various types of coal gasification reactions, RTI has been operating a small semi-batch reactor along with extensive sampling and analysis of reactor streams. This approach has proved reasonable for fixed-bed gasifier simulation, where the complications of wall effects and slugging, present in fluidized beds, are minimized. We have concentrated on evaluating various U.S. solid fuels to determine the pollutant loads that control systems must handle. This screening is substantially complete with nine different fuels (Pittsburgh #8, Illinois #6, western Kentucky #9, Montana Rosebud, Wyoming subbituminous, North Dakota lignite, North Carolina humus peat, a western Kentucky char, and Bottom Red anthracite) characterized in more than 35 tests.

Typically, tests have included air-blown auto-thermic operation, making a low-Btu producer gas. Figure 1 illustrates the reactor and sampling systems. Five main streams are characterized: input coal, gas product, tar, aqueous condensate, and ash or char. Data acquisition and analysis have been augmented by a PDP 11/34 with RSX11M operating system. As shown in Table 1, pollutant data are typically arrayed.¹ All data are presented in integrated form for each stream, although time-dependent data are recorded where possible to take advantage of the information available from the batch reactor. Integrating pollutant output allows approximating steady-state continuous gasifier operation, while the distinct phases of drying, devolatilization, and steam/char reaction can also be defined.

Important process variables such as reaction temperature, process gas composition and volume, water gas shift predictability, combustion characteristics, and fuel heating values compare with those of other processes, as seen in Table 2. The consistency of process variable control and comparisons with other gasifiers have been pre-

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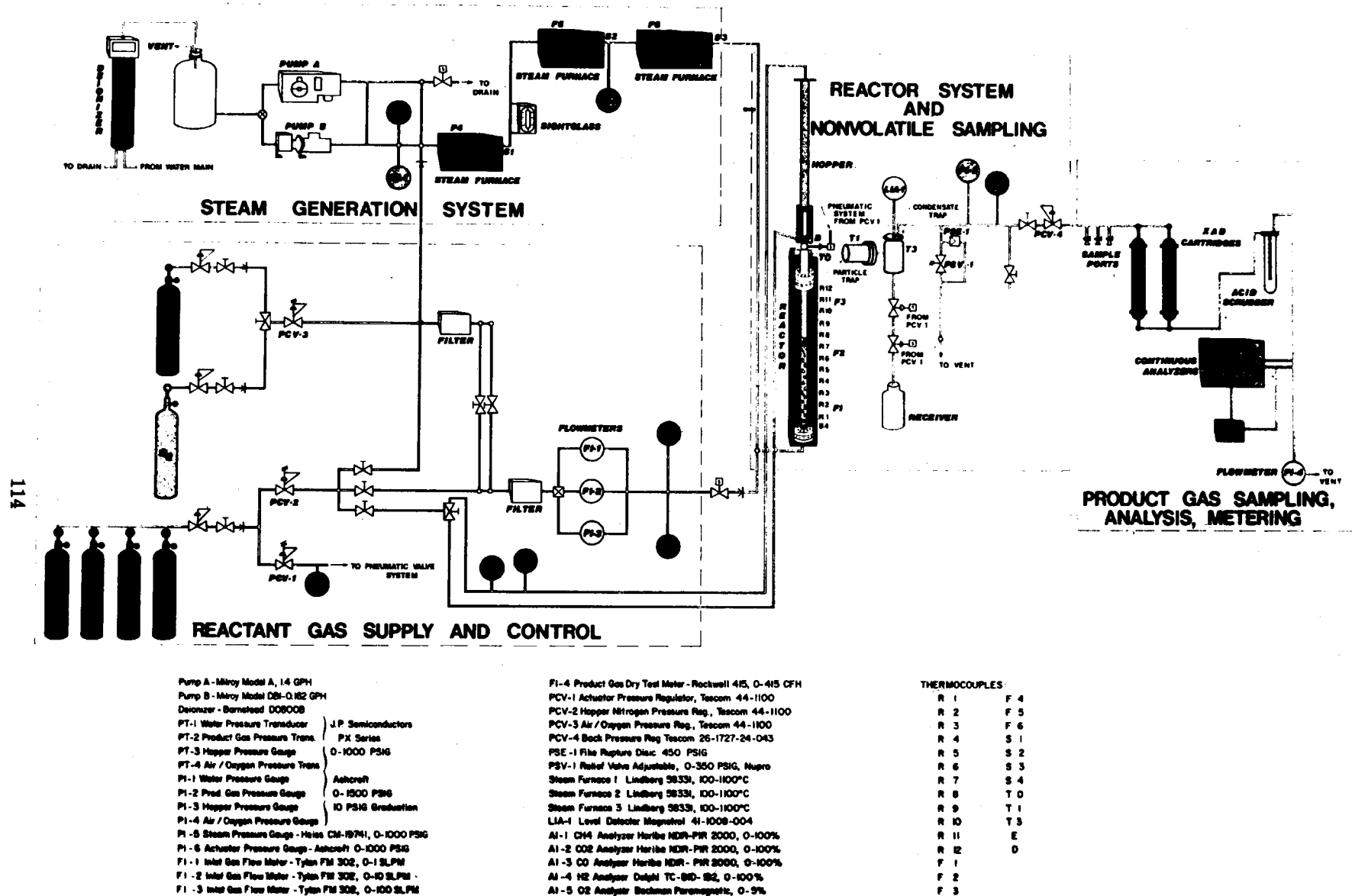


Figure 1. Reactor and sampling systems.

TABLE 1. TYPICAL DATA ARRAY

CONCENTRATION OF POLLUTANT (MICROGRAMS/CUBIC METER)

COMPOUND	MEG NUMBER	DATE	TEST NUMBER										
			6	16	20	21	23	25	26	31	32	33	35
BENZALDEHYDE	07A140	5.9E+04		2.0E+00						1.2E+04			
ACETOPHENONE	07B120	4.1E+04		2.7E+04									
ACETIC ACID	08A040	2.5E+04								3.9E+04			
BENZENE	15A020	3.0E+03	7.7E+03	1.1E+06						6.4E+05			
TOLUENE	15A040	3.8E+05	5.7E+03	7.8E+06						3.2E+05			
ETHYLBENZENE/C2-BENZENE	15A060	4.4E+05	2.2E+04	8.2E+03		8.8E+04	8.6E+04	5.8E+04	1.9E+05	8.0E+02	4.9E+04	5.1E+04	5.2E+04
STYRENE	15A080	4.2E+05	2.9E+03	1.4E+03									
BIPHENYL	15A160	1.0E+03	4.4E+02	4.0E+02		1.9E+03	2.7E+03	6.2E+02	2.0E+04	3.0E+01	1.2E+03	2.9E+03	1.2E+03
DIPHENYLMETHANE	15AN01	2.2E+05				3.1E+02	2.7E+03	3.1E+02	3.9E+03		4.9E+02	1.3E+03	6.0E+02
C4H7-BENZENE	15AF03	7.7E+04	1.1E+04	3.8E+03									
C4-BENZENE	15AP30	7.7E+04	4.6E+04	2.0E+03									
C5-BENZENE	15AP31	7.7E+04	1.5E+04										
INDAN	15B020	2.3E+05	5.4E+03	1.3E+04		4.9E+03	5.9E+02	1.5E+03	4.1E+04	2.0E+02	2.0E+03	3.5E+04	7.8E+03
INDENE	15B040	4.5E+04	8.1E+04	9.1E+04		1.9E+03	6.3E+04	3.3E+04	4.0E+05	1.0E+02	2.4E+04	2.5E+05	5.6E+04
XYLENES	15B080	4.4E+05	2.2E+04	2.0E+04		8.8E+04			1.8E+05				
DIETHYLBENZENE	15B100	2.3E+05		2.4E+03									
TRIMETHYLBENZENE	15B180	1.2E+05		9.6E+02									
METHYLBENZENE	15BP01	4.5E+04	7.1E+04	9.0E+04									
C3-BENZENES	15BP21	2.2E+05	6.2E+04	2.8E+05								1.1E+05	4.8E+04
DIMETHYLBIPHENYL	15BP22	1.0E+03		2.0E+03									
PHENOL	18A020	1.9E+04	2.9E+04	5.2E+03		2.8E+04	3.9E+04	3.1E+04	4.3E+05		6.4E+04	5.6E+05	2.4E+05
CRESOLS	18A040	2.2E+04	1.2E+05	4.4E+03		6.9E+04	9.0E+04	1.1E+04	2.1E+05		3.5E+04	1.5E+05	1.1E+05
C2-PHENOLS	18A080	2.5E+04	3.8E+05	5.0E+03									
XYLENOLS	18A140	1.3E+04				6.9E+04		2.2E+04	7.8E+05		6.4E+04	6.5E+05	2.8E+05
NAFTHALENE	21A020	5.0E+04	6.2E+04	2.8E+04		1.7E+05	5.9E+05	4.0E+04	2.6E+05	3.1E+03	1.4E+05	1.2E+05	3.4E+04
ALPHA-METHYLNAPHTHALENE	21A041	2.3E+05		1.0E+03					4.0E+04				
BETA-METHYLNAPHTHALENE	21A042	2.2E+05	4.4E+02	5.0E+03					5.9E+04				
ACENAPHTHENE	21A100	1.6E+04	4.4E+02	5.2E+02					8.0E+03				2.0E+02
ANTHRACENE	21A140	5.6E+04	7.4E+01	5.7E+02		1.6E+03	1.2E+03	6.2E+02	7.6E+03	7.0E+00	4.0E+02	1.1E+03	4.7E+02
PHENANTHRENE	21A180	1.6E+03				6.9E+02	7.8E+02		2.0E+01				
PROPENYLPHENANTHRENE	21AF03	2.4E+04		7.7E+00									
C15H12: 3 RINGS	21	2.4E+04											8.0E+01
C16H10: 4 RINGS	21	9.0E+02											1.7E+02
PYRENE	21B180	2.3E+05		1.0E+02									
FLUORENE	22A020	9.0E+02		7.0E+00									
FLUORANTHENE	22B040	9.0E+05		7.0E+01					3.1E+03				
PYRIDINE	23A020	1.5E+04											
BENZOFURAN	24A040	5.3E+06		1.3E+05		2.1E+04	5.5E+04	1.0E+04	1.3E+05		7.9E+03		4.2E+04
METHYLBENZOFURAN	24A140	5.3E+06	1.0E+04	4.8E+00									
DIMETHYLBENZOFURAN	24AF01	5.3E+06	1.2E+03										
DIBENZOFURAN	24B020	5.3E+06	2.0E+03			9.8E+03	1.2E+04	9.2E+02	1.8E+04		1.3E+03	8.4E+03	2.9E+03
METHYLTHIOPHENE	25A040	2.2E+04	1.0E+04	7.0E+04		2.0E+05	1.9E+05	2.3E+03	7.8E+04		9.3E+03	4.6E+04	1.2E+04
DIMETHYLTHIOPHENE	25A060	2.6E+04	4.4E+04	1.7E+03					1.6E+04				
C2-THIOPHENES	25AF02	2.6E+04	2.3E+03			7.8E+04	9.4E+04	1.0E+03	3.0E+04		1.6E+03	1.3E+04	9.3E+03
C3-THIOPHENE	25AF20	1.3E+03	6.5E+03										
C4-THIOPHENES	25AF04	2.6E+04	3.3E+04										
BENZOTHIOPHENE	25B040	2.3E+04	3.7E+03	2.7E+03					1.6E+04				
NITROGEN (BY DIFFERENCE)			-4.8E+07	3.4E+08	3.6E+08	3.9E+08	5.1E+08	6.4E+08	-1.0E+08	5.7E+08	5.1E+08	5.7E+08	7.1E+08
POLLUTANTS AS PERCENTAGE OF TOTAL GAS													
STREAM (BULBS, TENAX, XAD2, SCRUBBER)													
MASS FRACTION W/ CO			3.4E-01	2.1E-01	2.8E-01	2.0E-01	1.6E-01	2.6E-01	6.6E-01	1.4E-01	3.2E-01	3.3E-01	1.6E-01
MASS FRACTION W/O CO			4.3E-02	2.5E-02	9.3E-03	1.2E-02	1.9E-02	2.9E-03	1.3E-02	7.8E-03	6.4E-03	5.8E-03	3.3E-03
MOLE FRACTION W/ CO			1.8E-01	2.0E-01	3.0E-01	2.3E-01	2.5E-01	4.9E-01	4.3E-01	2.2E-01	4.5E-01	5.0E-01	3.5E-01
MOLE FRACTION W/O CO			1.8E-02	1.5E-02	8.4E-03	1.1E-02	2.1E-02	3.1E-03	3.6E-03	8.1E-03	3.9E-03	3.3E-03	2.3E-03

**TABLE 2. EXPERIMENTAL TEST PARAMETERS AND COMMERCIAL GASIFIER
OPERATING CONDITIONS**

	RTI TESTS								WELLMAN GALUSHA	WOODALL DUCKHAM
	21	23	25	32	33	35	MERC	LURGI	3.5	2.3
Air/Coal g/g	1.1	2.2	1.7	1.5	1.5	1.7	2.3	3.0		
Steam/Coal g/g	3.1	1.2	0.50	0.37	0.36	0.37	0.31	1.5	0.4	0.25
Carbon Conversion %	97	96	99.7	99.5	98.9	97	98.7	95	99+	99
Coal Residence Time (Min.)	340	300	180	110	110	110	120-540	60	120-540	N/A
Tar Produced g/g	.035	.033	.018	.011	.012	.029	.022	N/A	0.06	0.075
Gas Produced SCF/lb	48	56	41	32	35	40	47	52	N/A	N/A
HHV Btu/SCF	106	96	142	183	201	128	153	195	168	175
Thruput lb/hr ft ²	16	19	30	44	45	46	107	248	899	70
Coal Type	Ill. #6	Ill. #6	Montana Sub.	Wyoming Sub.	Wyoming Sub.	Wyoming Sub.	Ill. #6	Sub. C N.M.	Bitum	HVCB
Pressure psia	200	200	200	200	200	200	315	300	ATM	ATM
Mesh Size	8x16	8x16	8x16	8x16	8x16	8x16	2"x0	1.75"x0.08"	2"x1.25"	1.5"x.25"
Max Temp °C	1015	1050	1060	1050	1040	910	--	--	1300	1200
Heatup Time to 800°C (Min)	20	11	3	5	8	23	--	--	--	--
Gas Composition										
CO	16	10	24	29	32	16	21.8	17.4	28.6	28.3
CO ₂	18	18	9.1	9.1	4.9	12	6.9	14.8	3.4	4.5
CH ₄	5.4	3.1	2.4	5.7	5.7	3.7	2.0	5.1	2.7	2.7
H ₂	30	13	13	20	20	14	17.8	23.3	15.0	17.0
N ₂	30	55	52	36	37	54	51.5	38.5	50.3	47.2
H ₂ S	0.4	0.8	0.06	0.07	0.07	0.08	0.2	N/A	N/A	0.3
HHV Btu/SCF	200	100	140	210	210	130	150	200	170	170

1. Gilmore, D.W. and A.J. Liberatore, "Pressurized, Stirred, Fixed-Bed Gasification," Morgantown Energy Research Center Presented at Texas Symposium on Environmental Aspects of Fuel Conversion Technology, EPA-600/2-76-149, June 1976.
2. Cavanagh, E.C., et.al, Technology Status REport: Low/Medium Btu Coal Gasification and Related Environmental Controls, Radian Corporation, 1977.
3. Cleland, J.G., et.al, "Pollutants from Synthetic Fuels Production: Facility Construction and Preliminary Tests," EPA-600/7-78-171.

viously discussed.^{1,2,3} Confidence in the approximation of pollutant production from actual gasifiers is supported by comparison with results of others reported in the literature. Table 3 shows some chemical compounds analyzed in the RTI producer gas stream and also in the streams of other reactors that have been environmentally evaluated under U.S. Environmental Protection Agency (EPA) funding.

Tables 4 and 5 examine RTI tar compositions compared to other coal tars. It should be noted that typically less than 20 percent of total tar is quantitated as specific compounds in our analyses. In the case of tar and other streams, a low-percent quantitation is partially owed to restricting quantitation to compounds that represent high-priority hazards. In the case of tar, however, it is also owed to difficulties in specifically defining the heavier fraction of the tar. Outside research^{7,8} indicates that from 10 to 75 percent

of a coal conversion tar fraction may lie in the boiling point range above 400° C. Currently applied RTI techniques on gas chromatography/mass spectrometry restrict elution temperatures to about 260° C, but some compounds whose boiling points slightly exceed 400° C and whose vapor pressures are sufficient have been detected. Methods in high-performance liquid chromatography and other analytical techniques are being developed to extend RTI's range of analysis in this area.

It is also notable that RTI has detected few of the five-ring and above compounds such as benzo(a)pyrene. This could result from analytical limitations, although these compounds have been routinely found and quantitated in other RTI programs, including coal tar analyses. It is also possible that low throughputs, slow heating rates, and high fixed-bed length/diameter ratios promote secondary reactions that reduce the

TABLE 3. REACTOR GAS STREAM

RTI Detected Compounds	Found in ⁽⁴⁾ MERC Cond.	Found in ⁽⁴⁾ MERC Tar	Found in ⁽⁵⁾ C-W Vent Gas	Found in ⁽⁵⁾ C-W Cond.	Found in ⁽⁵⁾ C-W Tar
Methylthiophenes	X				
C ₂ -thiophenes					
C ₂ -benzenes	X	X	X		
Benzofuran	X	X			
Indan	X	X			
Indene	X	X	X	X	X
Phenol	X	X	X	X	X
Cresols	X	X	X		
Xylenols			X		
Naphthalene	X	X	X	X	X
Biphenyl		X			
Diphenylmethane					
Dibenzofuran	X	X			
Anthracene			X		X
Phenanthrene					
C ₃ -Benzenes	X	X	X		
Acenaphthene	X	X	X		X

C-W = Chapman-Wilputte

TABLE 4. TAR AROMATICS (μg PER GRAM TAR)

Aromatic Group	"Coal Tar" ⁽⁶⁾	RTI Tar III. #6	RTI Tar* III. #6
Naphthalenes	1.2E5	6.7E4	1.7E5
Phenanthrenes	1.6E5	2.3E4	5.9E4
Chrysenes	5.0E4	8.0E3	2.1E4
1-2 Benzanthracenes	3.E4	2.2E4	5.6E4
3-4 Benzphenanthrenes			
Pyrenes	3.1E4	9.0E3	2.3E4
5-ring compounds	1.3E4	2.7E4	6.9E4
% of total tar	40	17	40

*Normalized to 40% to account for nonquantitated compounds.

TABLE 5. TAR COMPOSITION (WEIGHT PERCENT)

Compound	Coal Tar 1 ⁽⁹⁾	Coal Tar 2 ⁽¹⁰⁾	RTI Tar*	MERC ⁽⁴⁾	Chapman ⁽⁵⁾ Wilputte
Naphthalene	10.0	—	5.2	2.1	0.2
Phenanthrene	5.0	4.8	2.3	—	—
Fluoranthene	3.3	1.8	1.3	—	0.1
Pyrene	2.1	1.1	0.9	—	—
Fluorene	2.0	—	0.7	0.5	0.2
Chrysene	2.0	0.3	0.8	—	0.3
Anthracene	1.8	0.4	0.7	—	0.6
Dibenzofuran	—	—	0.7	0.4	—
2-Methyl- naphthalene	1.5	—	0.9	—	—
Cresols	0.9	—	1.0	1.8	—
Acridene	0.6	—	0.2	—	0.09
Phenol	0.4	—	0.3	0.04	0.2
Quinoline	—	—	0.3	—	1.9
Xylenols	0.2	—	0.3	—	—
Indole	0.2	—	0.01	—	—
Perylene	—	0.08	0.4	—	0.08
Benz(a)anthracene	—	0.6	—	—	—
Benzo(a)pyrene	—	0.2	—	0.4	0.08

*III. #6 Coal

heavier tar fractions.

The occasional pronounced variations (between processes in the tables) in tar composition are primarily caused by the differences pertaining to what gasifier stream is defined as "tar." A large amount of contaminated water may be mixed in streams sampled onsite at pilot or full-scale units.^{4,5} Relative levels of the components are consistent. The extrapolation of the RTI aromatic values in Table 4 is reasonable because the total aromatics determined by fractionation for this test comprised about 55 percent of the total tar. The linear extrapolation of each group may be somewhat inconsistent, of course.

Many of the best analyses for such liquids have been conducted on the synthesis products from such processes as Synthoil. The differences between these reaction processes and gasification make comparison difficult, however.

Aqueous condensate compositions are compared in Table 6. The characteristics of a process, especially steam-to-carbon ratio, will influence water concentrations. Because the separation of tars and aqueous condensate may not be well defined, major water contaminants are shown both with and without tar inclusion. The major tar contribution is increased xylenols concentration.

While benzene, toluene, and xylene can be considered useful byproducts, their potential toxic and carcinogenic hazards as fugitive emissions require attention. These substances are measured in the reaction gas stream through-

out testing. Integrated tests results for a maximum production case are presented in Table 7. While the pilot units compared are fluidized bed types, results are quite similar, possibly reflecting the constancy of lighter devolatilization products under varying conditions. Production of BTX is highly dependent upon coal type, with eastern or other highly volatile coals producing the highest levels.

Sulfur balances for the reactor have presented problems. These have ranged from 30 to 140 percent. Closures are typically best for high-sulfur coals. Some sulfur is lost during pressure letdown of the condensate trap stream, but predicted solubility levels for H₂S in water do not explain the sulfur losses indicated. Efforts are being made to characterize more extensively the early rapid devolatilization of sulfur species.

An interesting effect in H₂S (and COS) output has been noted in the batch reactor, especially for the more reactive coals. Production of the sulfur species often increases near the end of testing where the combustion reaction begins to dominate and steam/char reactivity has nearly ceased. In this phase, concentration curves very closely parallel those of increasing carbon dioxide. The liberation of additional sulfur as SO₂ (finally reduced in the upper bed) appears to be the mechanism for the phenomenon. The behavior is unique to sulfur compounds.

Table 8 compares some RTI sulfur distributions with data from other processes. Ash sulfur is notably higher in subbituminous and lignite coals at oxygen breakthrough (approximate to-

TABLE 6. CONDENSATE COMPOSITIONS (ppm)

Compound	Lurgi ⁽¹¹⁾	PERC ⁽¹²⁾ III. #6	Synthane ⁽¹³⁾	RTI Water	RTI (Max) Water + tar
Phenol	1200-5650	3400	1000-4480	400-4100	4600
Cresols	480-1965	2840	530-3580	340-1100	1400
Xylenols	100-450	1090	140-1170	65-230	670
Trimethylphenol	—	110	20-150	18	72

tal carbon conversion). H₂S, COS, and thiophene levels are typical for coals tested. Mercaptans appear to be higher for lignite, as found in larger scale units.¹⁸

Attempts to summarize the large amounts of pollutant data have included formulation of composite values for total reactor-stream hazard factors per test. This allows both reactor stream and coal-type comparisons on an environmental basis. Each chemical substance quantitation in a reactor stream is expressed as:

- Concentration in terms of $\mu\text{g}/\text{m}^3$ gas, $\mu\text{g}/\text{L}$ tar or water, and $\mu\text{g}/\text{g}$ ash;
- Potential hazard level expressed as (stream concentration)/(MATE); and
- Micrograms of pollutant produced per grams of carbon converted in a reaction test.

Here, the MATE value for each substance is a minimum acute toxicity effluent¹⁹ level to which pollutants should be controlled in the environment to prevent detrimental health effects. MATEs are estimates based on available toxicity data and current environmental regulations and criteria.²⁰ These values, along with extensive chemical information, have been stored in the RTI synfuels data processing system.

Table 9 outlines the various approaches to total stream evaluation for each gasification test. Pollutants expressed as a mass fraction of the total stream include those substances rou-

tinely quantitated and presenting hazard potentials. Fuel gas products (e.g., CO) are not included here as pollutants. Gross variations in pollutant mass fraction may reflect limited stream analyses rather than actual stream composition.

The stream hazard factor calculation is derived from the EPA SAM/IA²¹ (source analysis model) scheme. This summation calculates relative stream environmental problems but is a function of the stream flow volume and therefore system operating conditions. For example, air and steam flow rates and percent conversion levels vary from test to test, changing the nitrogen, unconverted water, and tar levels in which pollutants are diluted.

Calculation of pollutant loading based on mass production per mass of coal or carbon conversion eliminates stream volumes from consideration. Summation of pollutant masses divided by MATE levels results in the amount of ambient diluent (air, water, soil) required to reduce environmental pollutant concentrations to safe levels (assuming dispersion of the entire stream into the environment). Percent decreases in a minimum required diluent are directly proportional to the efficiency of control technologies. The term "minimum" is applied because pollutant quantitations are limited.

An example of coal environmental compari-

TABLE 7. BENZENE, TOLUENE, XYLENES (RECOVERED FROM GAS STREAM)

PROCESS	BTX (Liquid Liters/Kg Coal)
Hygas Pilot Plant (Ill. #6)	0.01-0.02 ⁽¹⁴⁾
Synthane	0.006 ⁽¹⁵⁾
Synthane PDU	Benzene: 10^{-4} – 0.01; Toluene: 0.001 (max) ⁽¹⁶⁾
RTI (maximum values)	Benzene: 0.02 Toluene: 0.006 BTX: 0.03 Xylene: 0.003

TABLE 8. SULFUR BALANCES (PERCENT)

Stream	RTI TESTS				OTHER PROCESSES		
	Ill. #6 (21)	Montana (25)	Wyoming (33)	N.D. Lig. (43)	Lurgi	Hygas	Synthane
Ash	1.95	15.3	20.7	9.00	5 ^a	0.9 ^c , 1.0 ^d	1.5 ^e
Condensate	4.06	7.5	—	—	—	—	6.9 ^e
Tar	2.10	2.1	—	—	1.4 ^b , 2.9 ^a	—	1.4 ^c , 7.8 ^e
Gas	91.9	75.1	33.9	38.8	—	—	84.0 ^e

^aWESCO ESTIMATES⁽¹⁷⁾

^bN.D. LIGNITE⁽¹⁴⁾

^cIL. #6⁽¹⁴⁾

^dMONTANA SUB-BITUMINOUS⁽¹⁴⁾

^ePITTSBURGH #8—NORMALIZED TO 100% CHAR CONVERSION⁽¹⁶⁾

TABLE 9. POLLUTANT STREAM SUMMATIONS

POLLUTANT COMPOSITES PER TEST		RANGE OF VALUES—ALL TESTS			
		GAS	TAR	WATER	ASH
FRACTION OF TOTAL STREAM = (% mass)	$\frac{\sum_1^n C_i}{\text{STREAM DENSITY}}$	0.2– 4.0	0.7– 19.0	.008– 1.1	.04– 2.9
HAZARD FACTOR OF STREAM =	$\sum_1^n \frac{C_i}{\text{MATE}_i}$	300– 2200	1×10^5 – 2×10^7	7×10^4 – 1×10^6	10– 120
MINIMUM DILUENT FOR STREAM = (M ³ air; liters water; grams soil–per gram ΔC)	$\frac{1}{\Delta M_C} \sum \frac{M_i}{\text{MATE}_i}$	1.4– 12.0	10– 800	100– 900	1.4– 120

C = Pollutant Concentration
M = Pollutant Mass
MATE = Minimum Acute Toxicity Value

ΔM_C = Mass of Carbon Converted
n = Total Number of Pollutants

sons on this minimum diluent basis is shown in Figure 2. Ranges of minimum diluent (or pollutant mass production divided by MATE, on the basis of carbon converted) are given for the most relevant experimental gasification tests for seven coals. The required dilution of pollutant streams in the ambient environment has been normalized on a "mass required" basis for air, water, and soil. Rough significance can be attached to these results by considering two hypothetical cases:

- A plant with 10,000 tons per day carbon conversion and a gas stream minimum diluent value of 7,500 vents this gas stream to the atmosphere. If the gas uniformly diffuses throughout a hemispherical volume, the radius of diffusion reaches 1.8 mi before 1 day's gas output is sufficiently diluted.
- If the same plant, with a condensate minimum diluent value of 1.5×10^5 , dumps its raw condensate stream to surrounding waters, about 1 trillion gal of diluting water is required per day.

No surprising hazard variations among the coals are noted on this generalized basis of Figure 2. High-sulfur coals naturally present highest gas stream hazards. Tars and condensate ranges are strong functions of the amount of phenol, cresols, and xylenols produced. In such composite evaluations, the contribution of some constituents may be masked by those with high concentrations or MATEs. This is evident in Table 10, where it is obvious that phenols dominate the hazard level evaluation for condensed streams, primarily because of their low MATE values (based on EPA and NAS/NAE Water Quality Criteria, and Public Health Service Drinking Water Regulations).¹⁹

Compounds with associated relative hazard values of less than 1 have not been quantitated at stream concentrations that exceed their MATE values. Relative values of more than 1 are based on a mass of minimum diluent values for each compound or element, averaged over all relevant test cases. Within analytical limitations, the table summarizes the RTI evaluation of potential environmental hazards on a "per substance" basis.

Tar fractions have also been routinely separated through a solvent extraction process. Mean distribution of the polynuclear aromatic, nonpolar neutral, polar neutral, organic base, organic acid, and insoluble fractions are shown

in Figure 3. Average tar levels, as a percent of coal mass input, are included for each coal. Tar densities typically range from 1.05 to 1.20 g/cc.

It should be emphasized that operational conditions, such as maximum temperatures or gas velocities and pressures, influence pollutant production and must be considered on a test-by-test basis. Parametric test conditions are being investigated for possible reactor design controls of pollution.

Research into reactor parameter effects on contaminants has been initiated through statistical correlations of coal screening tests results (the first phase of research) and continued laboratory experimentation.

Simple linear statistical correlations were begun by first dividing the data into four groups: test variables (e.g., steam/air ratio, maximum temperature), coal characteristics (e.g., percent volatiles), tar fractions (organic bases, PNAs, etc.), and pollutant levels by stream. Two examples of correlating these groups are shown in Figures 4 and 5. Coefficients of correlation, precision of fit, and number of correlated values are evaluated and best correlations plotted.

Some preliminary results include:

- Phenols in condensates inversely correlate with percent tar and coal rank (see Figure 4).
- The percent of organic bases in tar increases with higher steam/air ratio.
- Carbonyl sulfide production is higher when air/coal is high.
- Coals producing more tar also produce more sulfur gases and increased PNA and organic base fractions in tar. The gas stream hazard factor for these coals is higher and the tar hazard lower (reduced phenols).
- Organic acids, polar neutrals, and nonpolar neutrals in tar directly correlate. This group inversely correlates with the related polynuclear aromatic and organic base fractions.
- Extending the time period to reach maximum temperature reduces the tar hazard factor.
- For high-sulfate sulfur in a coal, more sulfur remains in ash following reaction.
- Percent of PNAs in tar correlates poorly with coal rank and only slightly with tar mass produced.
- Known correlations are reverified; e.g., gas heating value and coal rank, gas hydrogen percent and steam/air ratio, and heating rate and volatile production (see Figure 5).

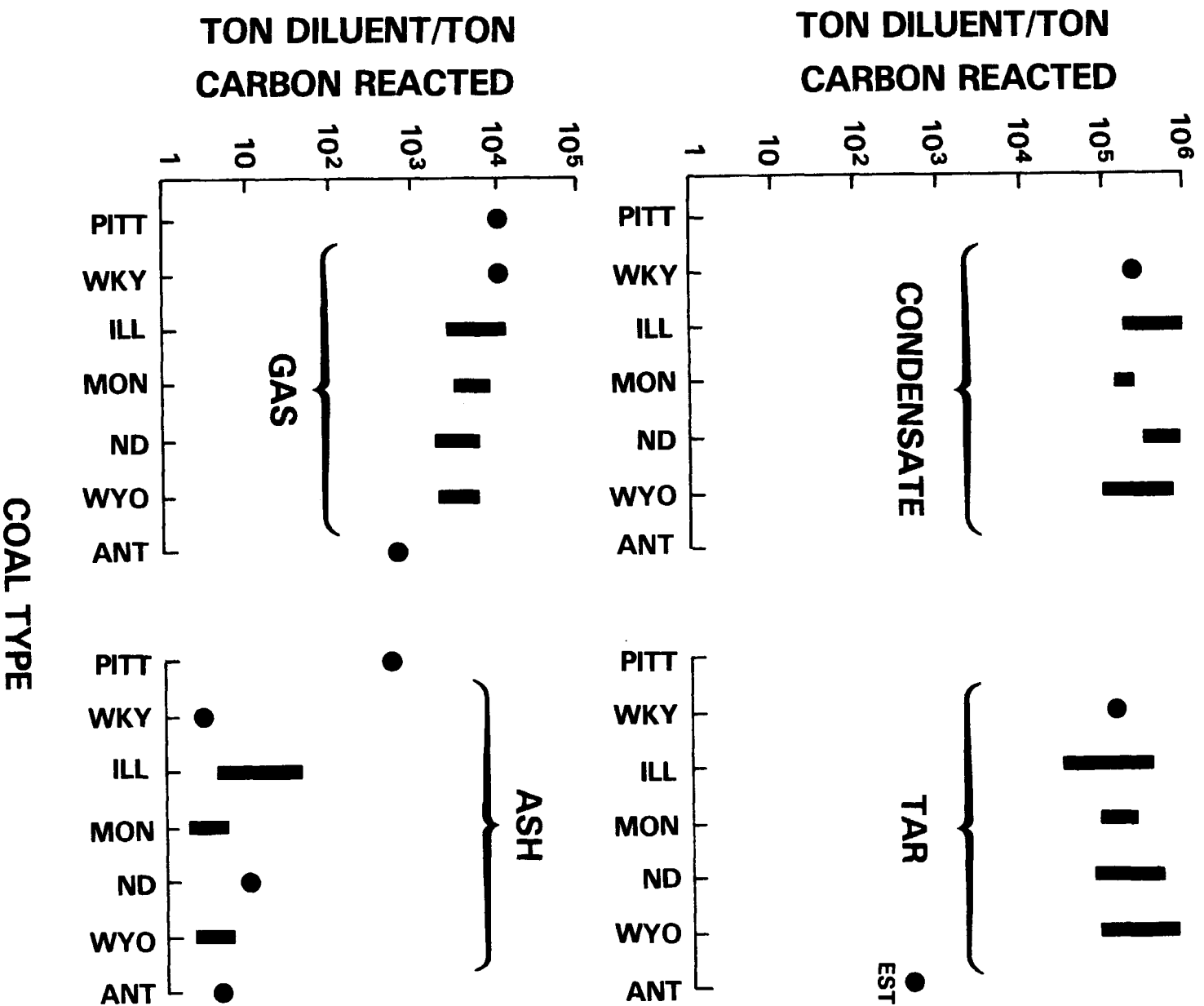


Figure 2. Coal-type comparisons.

TABLE 10. POLLUTANT RANKING—POTENTIAL HEALTH EFFECTS

TAR

Xylenols (10^6)*
 Cresols (10^5)
 Phenol (10^5)
 Trimethylphenol (10^5)
 O-isopropylphenol (10^5)
 Phenanthrene (10^3)
 Chromium (10^3)
 Benzidine (10^3)
 Fluorene (10^2)
 Perylene (10^2)
 9-méanthracene (10^2)
 Chrysene (10^2)
 Sulfur (10^2)
 Naphthalene (10^1)
 Anthracene (10^1)
 Arsenic (10^1)
 Fluoranthene (10^1)
 Lead (10^1)
 Quinoline (10^1)
 Pyrene (1)
 2-ménaphthalene (1)
 Cadmium (< 1)
 Dibenzofuran (< 1)
 Acridine (< 1)
 Aniline (< 1)

GAS

Carbon monoxide (10^4)
 Benzene (10^3)
 Hydrogen sulfide (10^3)
 Hydrogen (10^2)
 Carbon dioxide (10^1)
 Thiophene (10^1)
 Xylenols (10^1)
 Ammonia (10^1)
 Methanethiol (10^1)
 Ethanethiol (10^1)
 Methane (10^1)
 Phenols (10^1)
 Cresols (10^1)
 Methylthiophene (1)
 Naphthalene (1)
 Biphenyl (1)
 Hydrogen cyanide (1)
 Indene (1)
 Toluene (1)
 C₂-thiophenes (1)
 Carbon disulfides (< 1)
 Carbonyl sulfide (< 1)

CONDENSATE

Phenol (10^7)
 Cresols (10^6)
 Xylenols (10^5)
 Ammonia (10^4)
 Thiocyanate (10^2)
 Cyanide (10^2)
 HCN (10^2)
 Sulfur (10^1)
 Chromium (1)
 Lead (< 1)
 Arsenic (< 1)
 Cadmium (< 1)
 Phosphorus (< 1)
 Antimony (< 1)
 Nitrates (< 1)

ASH

Arsenic (10^3)
 Sulfur (10^2)
 Lead (10^1)
 Mercury (10^1)
 Cadmium (1)
 Chloride (< 1)

*Relative hazard, equals 1 where stream hazard is zero.

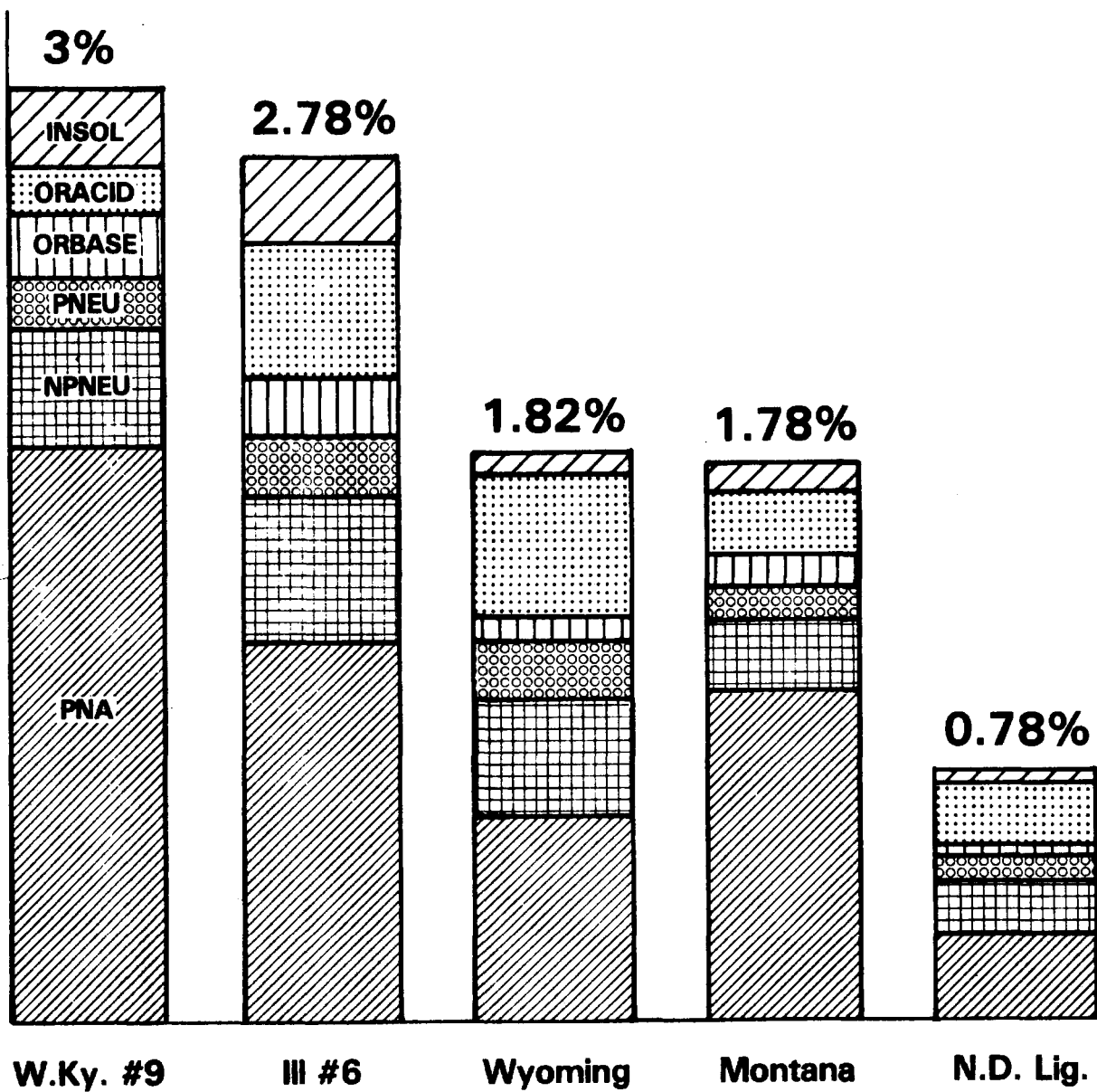


Figure 3. Tar partitions.

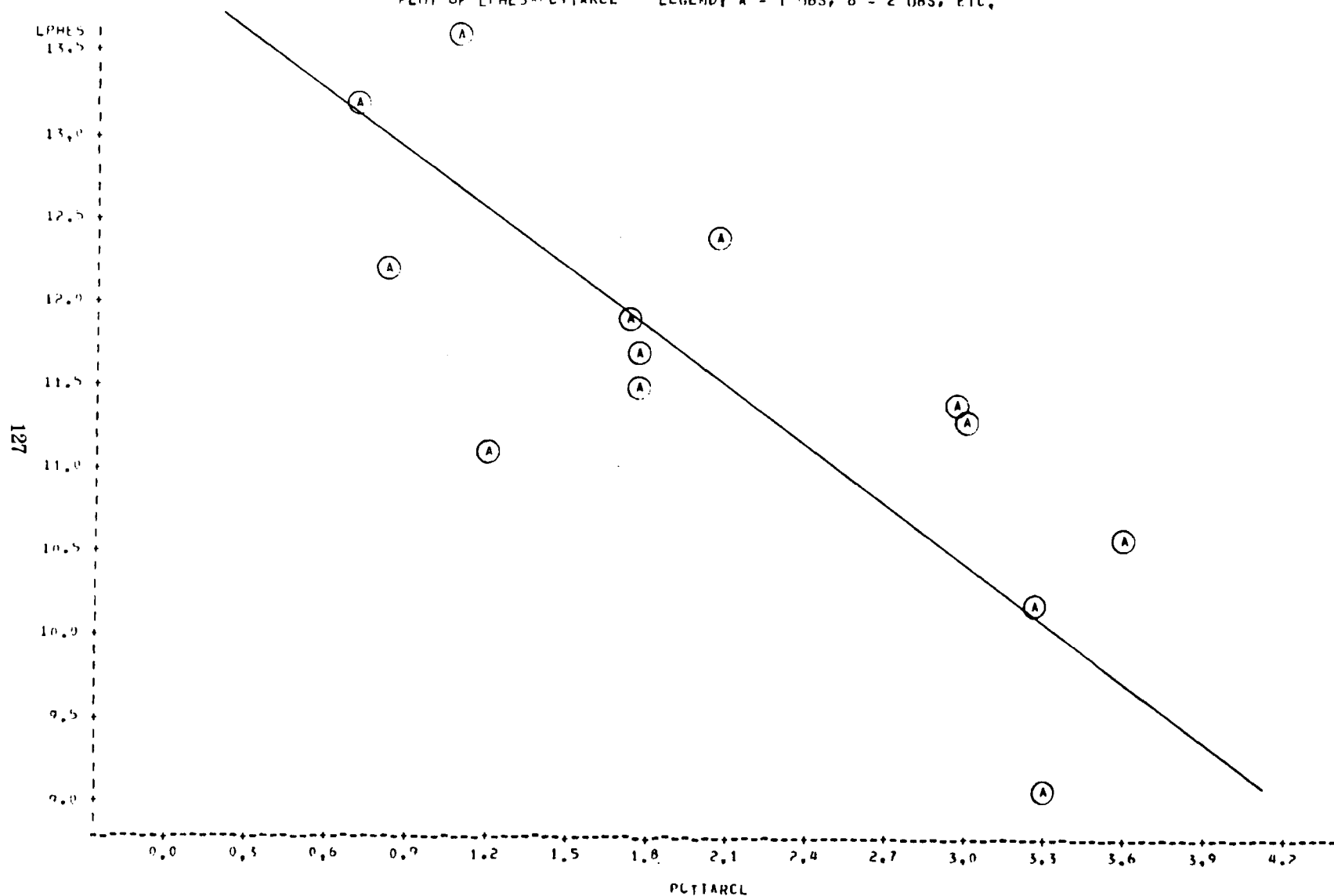


Figure 4. Tar/coal (weight percent) vs. phenol condensate concentration (log $\mu\text{g/L}$ [MATE]).

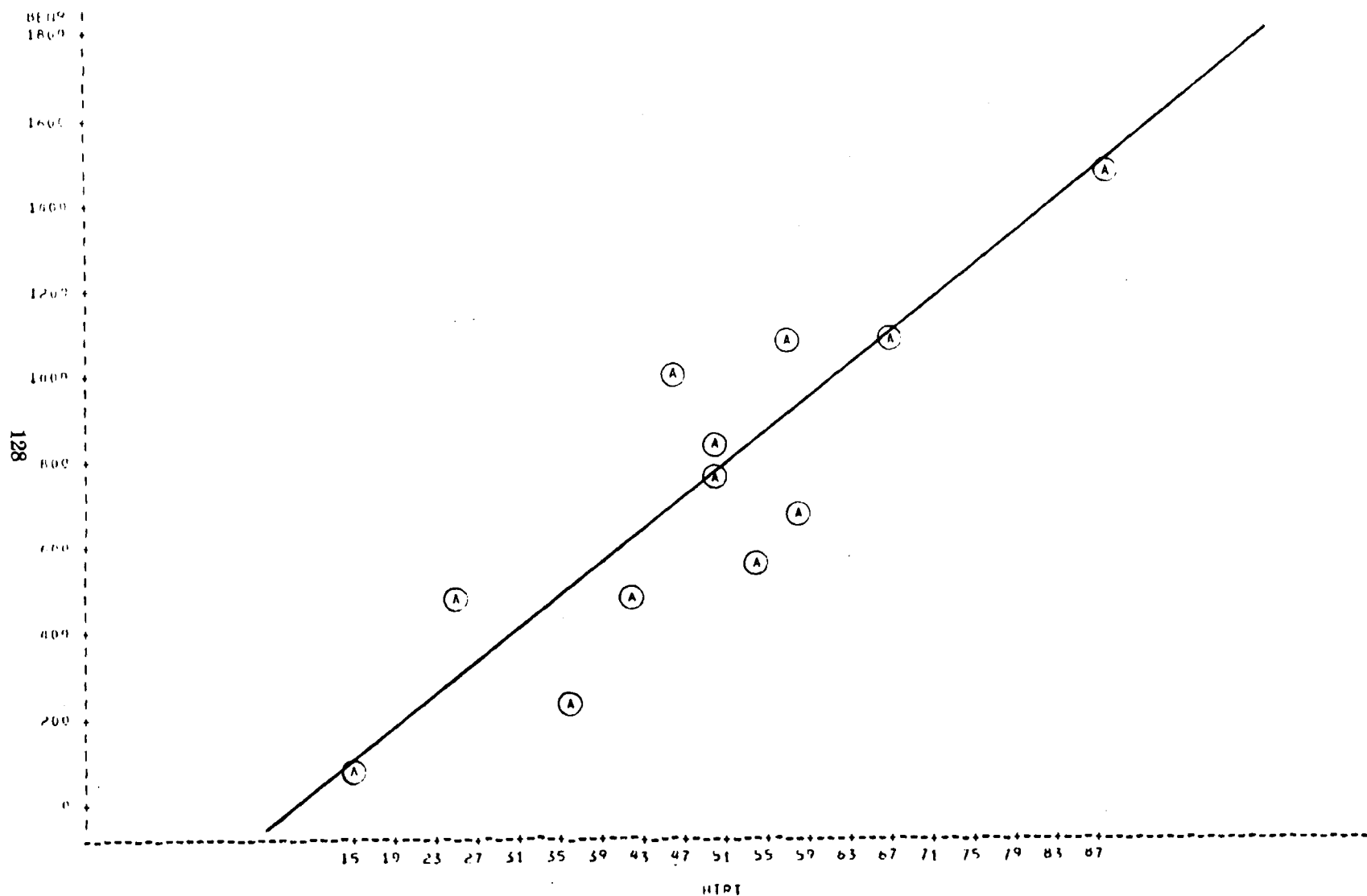


Figure 5. Devolatilization heating rate ($^{\circ}\text{C}/\text{min}$) vs. benzene concentration in gas stream ($\mu\text{g}/\text{m}^3/[\text{MATE}]$).

While few of the results are definitive, certain trends are indicated. Multiple regressions may improve some results.

As mentioned, a slow heating rate has been characteristic of the system. Figure 6 illustrates a typical temperature history. The entire coal load for each test is added cold to the preheated reactor. Autothermic heat addition by air combustion is immediately begun. The period following is critical for pollutant production because the coal temperature now moves slowly through the range of pyrolysis temperatures (300°-700° C) within which 90 percent of the volatiles may appear.

Heating rates through devolatilization average about 50° C/min, low compared to those obtained in most pyrolysis studies.²² Reactor throughputs of steam have been typically low, although recent tests have emphasized an approach to optimum reaction rates by increasing air and steam flows.

Low heating rates should decrease both tar and total volatile production. This does not obviate the important results obtained during these test periods. Integrated pollutant outputs have been demonstrated closely comparable to those of commercial units, and indeed (for fixed-bed reactors that are fed by lock hoppers) dis-

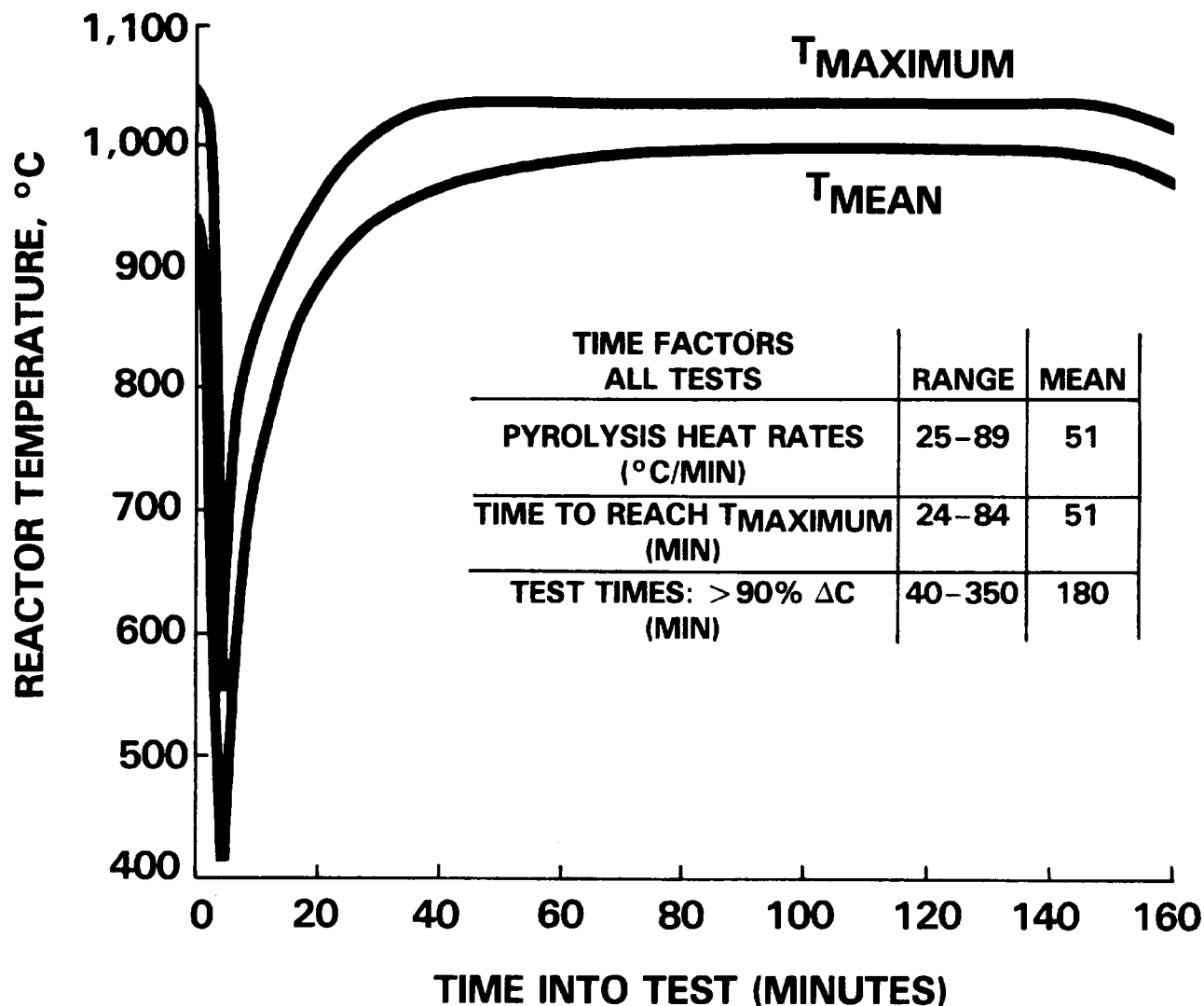


Figure 6. Reactor heating.

continuous feed and slow heatup may be a more realistic approximation.

The batch reactor permits investigation of the time-dependent evolution of pollutants, as shown in Figures 7 and 8. The typical rate expression for devolatilization is first order,

$$dV/dt = k(V_i - V)$$

where $V \rightarrow V_i$ as $t \rightarrow \infty$. The simplest integrated form is

$$\frac{V_i - V}{V_i} = e^{-kt},$$

or

$$\ln\left(\frac{V_i}{V_i - V}\right) = kt.$$

This expression for volatiles production as a function of time is given in the figures, where a linear curve should approximate first-order devolatilization with the rate constant, k , as the slope. It may also be seen that for a zero-order expression, where

$$\ln\left(\frac{V_i}{V_i - V}\right) = -\ln\left(1 - \frac{kt}{V_i}\right), \text{ the kinetics}$$

may be approximated by the first-order expression for low rates, if

$$\frac{kt}{V_i} \ll 1.$$

The kinetics may also be examined with respect to the time derivative of volatiles produc-

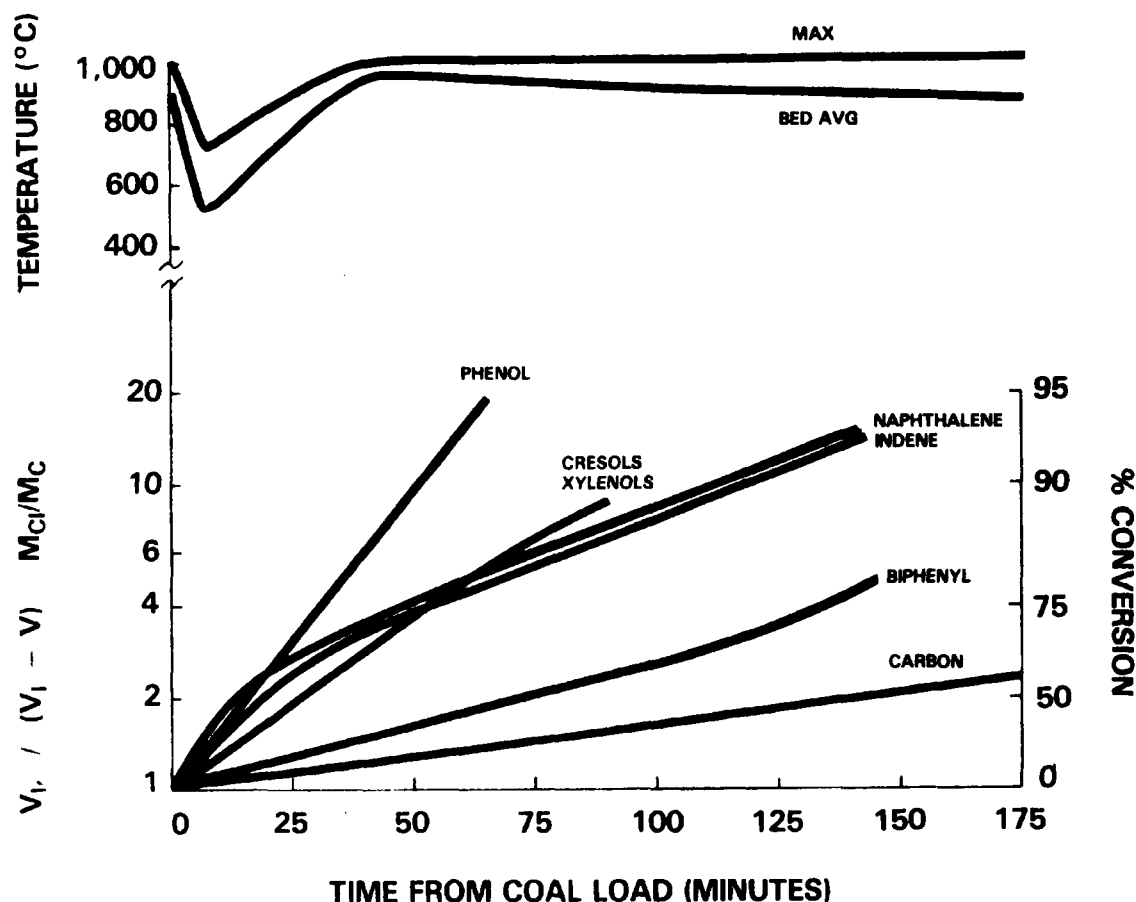


Figure 7. Pollutant kinetics.

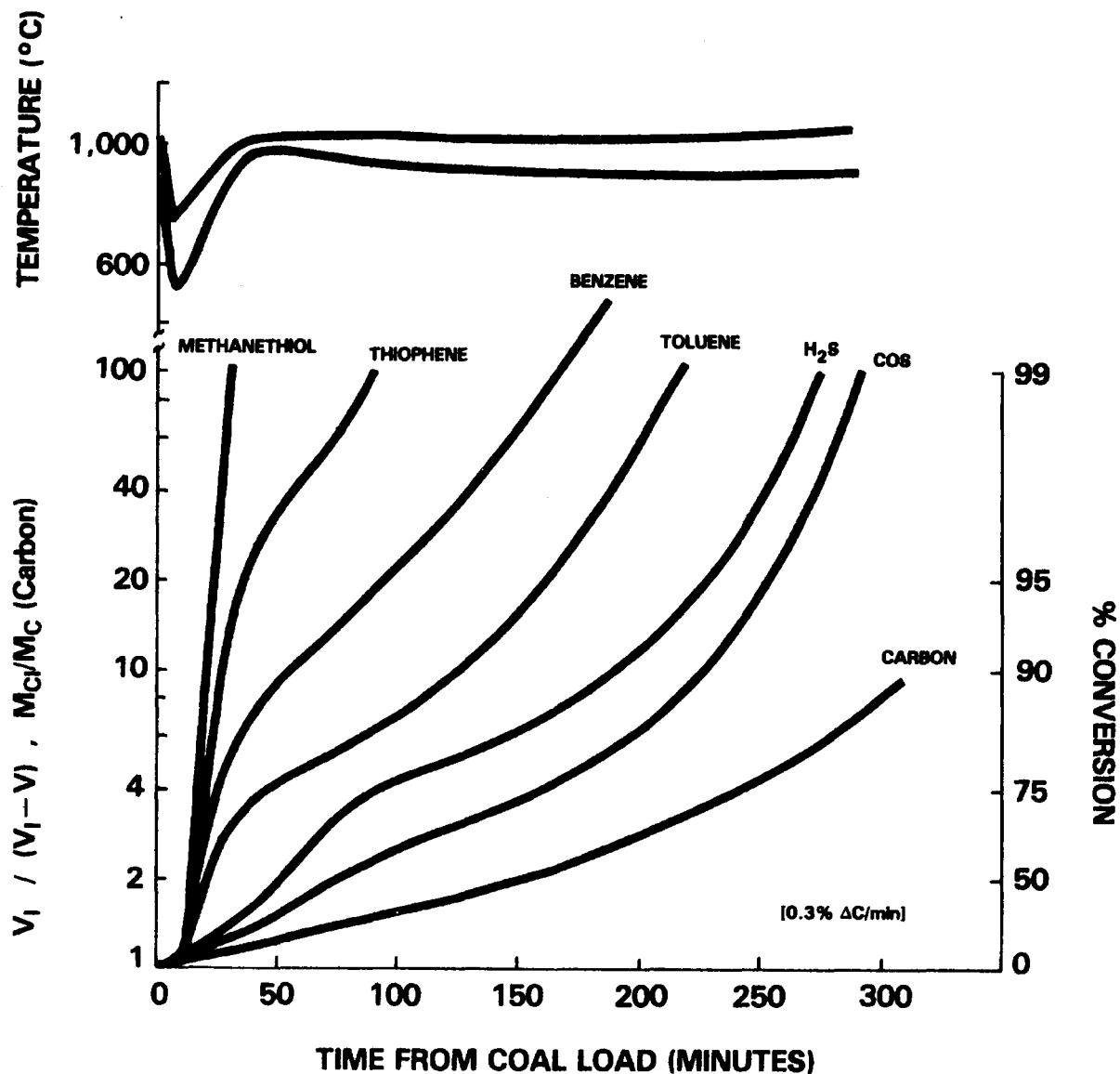


Figure 8. Pollutant kinetics.

tion; i.e., dV/dt vs. $(V_i - V)/V_i$. This approach and that above indicate that many compounds tend to devolve in a second-order manner through the nonisothermal phase of heatup. Then the kinetics become first order at temperature stability. This approach agrees to some extent with the results of Wiser, et al.²³ Nonisothermal pyrolysis, for the case where temperature is a linear function of time, has been discussed previously.²⁴ Commonly, more than 75 percent of the pollutant species will have been produced before 20 percent of the gasification

test has been completed. H_2S and COS often react relatively slowly, while mercaptans are expended quickly. Carbon conversion past the heatup phase is essentially zero order, as expected for reaction under conditions of constant steam partial pressure. A summary of the sequence of gas stream pollutant production of five coals is given in Table 11. The percent of conversion may be taken from the figures.

It has been noted that the major reaction sequence during devolatilization for this reactor closely adheres to that commonly promulgated;

TABLE 11. REACTIONS SEQUENCE

#43 (N.D. Lignite)		#41 (W. Ky. #9)	
50%	90%	50%	90%
Methanethiol	Methanethiol	Methanethiol	Methanethiol
Benzene	Benzene	Thiophene	Thiophene
Toluene	Toluene	Benzene	Benzene
H ₂ S	COS	Toluene	Toluene
Thiophene	H ₂ S	COS	H ₂ S
COS	Thiophene	H ₂ S	COS
Carbon	Carbon	Carbon	Carbon

#23 (Ill. #6)		#25 (Montana Sub)		#33 (Wyoming Sub)	
50%	90%	50%	90%	50%	90%
Naphthalene	Thiophene	Cresols	Methanethiol	Methanethiol	Methanethiol
Phenol	Phenol	Naphthalene	Benzene	H ₂ S, COS	Benzene
Benzene	Benzene	Methyl	Thiophene	Benzene	Toluene
Thiophene	Cresols	Thiophene	Methyl	Toluene	Indene
Indene	Xylenols	Indene	Thiophene	Indene	Biphenyl
Toluene	Naphthalene	Benzene	Methylthiophene	Phenol	Naphthalene
Cresols	Indene	Toluene	Indene	Cresols	Xylenols
Xylenols	Toluene	Thiophene	Naphthalene	Naphthalene	Cresols
Biphenyl	Biphenyl	Xylenols	Cresols	Biphenyl	Phenol
H ₂ S	H ₂ S	Methanethiol	Xylenols	Xylenols	COS
COS	COS	Phenol	Phenol	Carbon	H ₂ S
Carbon	Carbon	Biphenyl	Biphenyl		Carbon
		H ₂ S	Toluene		
		COS	COS		
		Carbon	H ₂ S		
			Carbon		

i.e., the appearance first of water vapor, followed by CO₂, CO, tars, ethane, methane, and hydrogen.²⁵

The possibilities of reaction rate control other than by chemical kinetics have been investigated. It appears from available criteria²⁶ that internal particle heat transfer is not limiting. However, external heat transfer (gas diffusion to particle surface) and mass transfer do seem to play a role. The common particle sizes util-

ized vary from about 32 to 4 mesh, and there is evidence of particle size influence on reaction rate. The primary control of rate at this point is, as stated, the time required to satisfy the heat capacity of the entire coal charge to bring the coal to reaction temperature (basically through convective heat transfer).

Briefly, some conclusions and recommendations include:

- The gas stream essentially contains pollut-

ants that are well recognized. Major pollutant factors in the gas stream result from carbon monoxide, benzene, hydrogen sulfide, and other sulfur species. Removal of benzene, xylenols, ammonia, and sulfur species should prevent problems. The removal of pollutants to the ranking level of methane (see Table 10) could, on a toxic hazard basis, leave the producer with only the same control requirements placed on natural gas pipelines.

While there is little positive evidence of important levels of heavy hydrocarbons found in the gas stream, certain trace constituents may deserve increased attention. This would require examination beyond acute effects, where synergistics and persistence in the environment are considered in terms of chronic health effects. A definite need exists for better characterization of aerosols and gas-stream-suspended particulates. Nevertheless, it can be stated with assurance that if ambient carbon monoxide, hydrogen sulfide, and benzene concentrations are monitored at a coal gasification plant, the primary fugitive emissions from the product gas stream will have been accounted for.

- Tar presents a more consistent environmental hazard. While phenol and cresols dominate the hazard picture, elimination of these reduces the hazard factor to only 10^3 . The presence of fused aromatic hydrocarbons such as phenanthrene, chrysene, and 9-methylanthracene disallows obvious elimination of the hazard problem. Preliminary bioassay work has also shown that RTI gasifier tars are mutagenic.²⁷ More extensive study of the heavier tar fraction is needed. It is interesting to note that western coal tars present as high a hazard as eastern coals because of the comparable levels of organic acids (e.g., phenols) produced in gasifying these coals. More research is required on the storage, handling, and utilization of the coal tars. It is in these areas of plant operation that tars become an environmental hazard.
- It has been noted that the overall pollutant potential for various coals varies little in terms of orders of magnitude. While variations may occasionally be important for control technology development (e.g., different sulfur loads on such removal systems as Rectisol, Stretford, and Claus units), the results

seem to indicate that a uniform approach to reactor parameter control can be taken for various coals. As mentioned, more work is intended in comparing pollutant results obtained thus far on the basis of test conditions such as average temperatures, combustion vs. nonautothermal testing, and steam/air and air/coal ratios. Most variations in the results are predictable and related to the major reactor parameters or coal characteristics such as reaction temperature, volatiles content, and sulfur content.

- The aqueous condensate is contaminated primarily by phenols, as is well known. If phenols and the other important byproduct in solution—ammonia—are removed, the condensate hazard factor is reduced to approximately 10. Further analysis of these species and cyanides is required to validate the conclusion.
- The small semibatch reactor works well in terms of simulating process variables and outputs and pollutant amounts. Ash, water, and carbon balances are satisfactory for this process, but improvements are required on sulfur balances and the nonair nitrogen balance. While slow heating rates may reduce tars and volatiles, the distribution of pollutants throughout the various streams is quite comparable to those reported in the literature and may simply point to one approach for controlling contaminants in full-scale reactors. The pyrolysis phase is by far the most important one for pollutant production and should be studied more extensively, including research on nonisothermal kinetics. Most pyrolysis research has been limited to studying total volatile production rather than examining individual pollutant species.
- Important pollutants requiring extensive examination can easily be limited to a number that can be quantitated on a per-test basis. While more than 420 compounds have been detected and more than 100 routinely quantitated, there is good evidence that control of a few priority pollutants beginning at the top of the pollutant ranking list in Table 10 should ensure environmentally safe coal gasification. The concentrations or micrograms produced per grams of carbon converted for various species from test to test are most notable for their consistency. Pol-

lutants routinely detected have been found in every type of coal analyzed, from peat to anthracite. The North Dakota lignite has shown some peculiar characteristics that have not yet been fully examined. These characteristics include the detection of both unique organic and mineral species in all streams. It is believed that baseline levels for pollutants from the U.S. coals tested are now better defined, allowing more confidence in studies dealing with variations in these levels.

Many of the results obtained thus far cannot be presented briefly or generally. Some must be evaluated on a test-by-test basis. The experimental model is being improved for evaluating the effects of reactor parameters on pollutant production or prevention. Such variables as pressure, coal mesh size, bed depth, temperature, heating rate, steam/air ratios, and rate of gas removal from the bed are being considered. If modeling problems can be overcome, fluidized bed operation will also be investigated. Fabrication of a continuous coal feeder and an improved pretreatment setup for eastern coals is nearly completed and will be included in further experimentation. More extensive evaluation of trace elements as pollutants utilizing neutron activation analysis is also intended.

ACKNOWLEDGMENTS

The Research Triangle Institute extends its greatest appreciation to the Fuel Process Branch, Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, for supporting this research.

REFERENCES

1. *Pollutants from Synthetic Fuels Production* (annual report). Research Triangle Institute. Research Triangle Park, N.C. EPA Grant Number R804979-02. February 1979.
2. *Pollutants from Synthetic Fuels Production* (quarterly report for the period May 1, 1978-July 31, 1978). Research Triangle Institute. Research Triangle Park, N.C. EPA Grant Number R804979-02. August 1978.
3. Cleland, J. G., F. O. Mixon, and D. G. Nichols. *Small Semi-Batch Gasifier Operation for Pollutant Determination and Control Evaluation*. (Presented at National AIChE Meeting. Philadelphia. June 4-8, 1978.)
4. Pellizzari, E. D. *Identification of Components of Energy-Related Wastes and Effluents* (final report). Research Triangle Institute. Research Triangle Park, N.C. EPA Contract Number 68-03-2368. 1978.
5. Personal Communication with Dr. Gordon Page, Radian Corp., Austin, Texas. 1978.
6. *Project H-Coal Report on Process Development* (final report). Hydrocarbon Research, Inc. PB-234 579, OCR/RDR 26/. 1978.
7. Personal Communication with W. J. McMichael, Pittsburgh Energy Research Center, on GLC Simulated Distillation for Synthane Tars Based on ASTM D288773 Method. 1978.
8. King, B., et al. *An Investigation of Aromatic Fractions from Coal Tar Produced by an Underground Coal Gasification Task*. Laramie Energy Research Center. CONS-77-0510-7. 1977.
9. Shults, W. D. (ed.). *Preliminary Results: Chemical and Biological Examination of Coal-Derived Materials*. ORNL/NSF/EATC-18. Oak Ridge National Laboratory. Oak Ridge, Tenn. 1976.
10. Lijinsky, W., G. Singer, and W. Taylor. Carcinogenesis by Environmental Pollutants Related to Energy Production. In: *Biomedical and Environmental Research for Support and Evaluation of Coal Conversion Technology*. Oak Ridge, Oak Ridge National Laboratory, 1975.
11. Jolley, R. L., W. W. Pitt, and J. E. Thompson. *Organics in Aqueous Process Streams of a Coal Conversion Bench-Scale Unit Using the Hydrocarbonization Process: HPLC and GC/MS Analysis*. (Presented at the Environmental Technology Annual Technical Meeting of the Institute of Environmental Sciences. Los Angeles. 1977.)
12. Sharkey, A. G., Jr., J. L. Shultz, C. E. Schmidt, and R. A. Friedel. Mass Spectrometric Analysis of Coal-Derived Liquids. In: *Proceedings of the Third Environmental Protection Conference*. Chicago, September 23-26, 1975.
13. Forney, A. J., W. P. Haynes, S. J. Gasior, G. E. Johnson, and J. P. Strakey. *Analysis of Tars, Chars, Gases, and Water in Effluents from the Synthane Process*. U.S. Pitts-

- burgh Energy Research Center. Pittsburgh, Pa. Bureau of Mines Technical Progress Report 76. 1974.
14. Glaser, F., A. Hershaft, and R. Shaw. *Emissions from Processes Producing Clean Fuels*. Booz-Allen Applied Research. Bethesda, Md. BA 9075-015. 1974.
 15. Kalfadelis, C. D., and E. M. Magee. *Evaluation of Pollution Control in Fossil Fuel Conversion Processes. Gasification. Sec. 1. Synthane Process*. EPA-650/2-74-009b. 1974.
 16. Forney, A. J., W. P. Haynes, S. J. Gasior, R. M. Kornosky, C. E. Schmidt, and A. G. Sharkey. *Trace Element and Major Component Balances Around the Synthane PDU Gasifier*. Pittsburgh Energy Research Center. Pittsburgh, Pa. PERC/TPR-75/1. 1975.
 17. Beychok, M. R. *Process and Environmental Technology for Producing SNG and Liquid Fuels*. EPA-660/2-75-011. 1975.
 18. Personal Communication on Lurgi Gasification with Gordon Page and Karl Bombaugh, Radian Corp., Austin, Texas. 1979.
 19. Cleland, J. G., and G. L. Kingsbury. *Multimedia Environmental Goals for Environmental Assessment*. Research Triangle Institute. Research Triangle Park, N.C. EPA Contract 68-02-2612, EPA-600/7-77-136a. November 1977.
 20. Greenwood, D. R., G. L. Kingsbury, and J. G. Cleland. *Draft—A Handbook of Key Federal Regulations and Criteria for Multimedia Environmental Control*. Research Triangle Institute. Research Triangle Park, N.C. EPA Contract Number 68-02-2612. January 1979.
 21. Shalit, L. M., and K. J. Wolfe. *SAM/IA: A Rapid Screening Method for Environmental Assessment of Fossil Energy Process Effluents*. Acurex Corp./Aerotherm Division. Mountain View, Calif. EPA Contract Number 68-02-2160, EPA-600/7-78-015. February 1978.
 22. Anthony, D. B., and J. B. Howard. Coal Devolatilization and Hydrogasification. *AIChE Journal*. 22(4):625-656. July 1976.
 23. Wiser, W. H., G. R. Hill, and N. J. Kerstamus. Kinetic Study of the Pyrolysis of a High-Volatile Bituminous Coal. *Ind Eng Chem Process Design Develop.* 6:183. 1967.
 24. *Pollutants from Synthetic Fuels Production*. Research Triangle Institute. Research Triangle Park, N.C. (Research Grant Application Submitted to Environmental Protection Agency.) July 1976.
 25. Howard, H. C. Pyrolytic Reactions of Coal. In: *Chemistry of Coal Utilization, Supplementary Volume*, Lowry, H. H. (ed.). New York, Wiley, 1963. p. 340-394.
 26. Koch, V., H. Juntgen, and W. Peters. Nicht-Isotherme Reaktionskinetik der Kohlenpyrolyse, Teil III: Zum Reaktionsablauf bei hohen Aufheizgeschwindigkeiten, Brennstoff. *Chem.* 50:369. 1969.
 27. Hughes, T. J., et al. *Mutagenicity of Coal Gasification Fractions* (Presented at Tenth Annual Meeting of the Environmental Mutagen Society. New Orleans. 1979.)

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ENVIRONMENTAL AND ENGINEERING EVALUATION OF THE KOSOVO COAL GASIFICATION PLANT—YUGOSLAVIA (PHASE I)

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INTRODUCTION

At the symposium on Environmental Aspects of Fuel Conversion Technology, III, held in September 1977 in Hollywood, Florida, we fully accounted for our investigations of this project. In addition, we stated why this research project was conducted in SFR Yugoslavia and identified local institutions engaged in the investigations.

Preliminary data from pilot operations indicate that a multiplicity of pollutants are emitted by the gasification reactor. Material in effluent and process streams includes major pollutants such as sulfur, nitrogen, NH_3 , particulate tars and oils, and minor pollutants such as trace elements and hydrocarbons. The purpose of investigating these pollutants was:

- To identify emissions and determine their concentrations in the existing gasification process;
- To determine the composition and amounts of pollutants originating to a greater or lesser extent from all process streams in various stream effluents or materials; (i.e., in air, water, and particulates);
- To identify the pollutants whose presence degrades the environment;
- To assess the capability of existing cleaning and purification systems; and
- To develop improved equipment and technology designed to reduce or eliminate environmental danger accompanying the operation of current technology.

In our investigations, priority was given to examining pollutants occurring in large amounts such as sulfur and nitrogen compounds, ammonium, coal, and tar and oil particulates. The investigations included pollutants

occurring in lower or trace amounts in the process and served to evaluate selected methods of sampling and sample analysis.

Investigations were carried out in Obilic, near Priština, Socialist Autonomous Province Kosovo, in a plant for the production of gas under pressure (clean gas net heating value 3,600 kcal/m³_N) from dried Kosovo lignite (Lurgi generators, Dia 3.6 m). Plant capacity is 480 million m³_N of clean gas per year.

Prior to sampling and analysis, the following tasks were completed:

- Detailed description of the lignite gasification plant was given, including required process flow sheets and description of individual operating stages of gas and byproducts production, various waste materials, and medium effluents;
- Presentation of fuel grade at the inlet and outlet, byproducts composition, and types of media;
- Detailed study of plant operating data; i.e., of the technological process and location of measurement points for pollutant sampling;
- Selection of the methodology for sampling and analysis of solid, liquid, and gaseous pollutants;
- Selection of the methodology for flow and particulates measurement; and
- Sampling test operating plan.

The obtained results are given below.

RESULTS

General

Investigations were completed during the course of three sampling campaigns carried out in periods with normal operating conditions. At each point of emission of solid, liquid, or gaseous

*Speaker.

media in the lignite gasification plant at Kosovo, preliminary quality investigations were performed. The amounts of the emissions were measured, estimated, or taken as designed by the project in order to evaluate the types and volumes of pollutants. This led to eliminating a number of measurement points because of their emissions volume and quality.

ASTM methods were used for sampling, analysis, preparation of measurement lines, volume measurements, etc. The content of fixed gases in gaseous streams was determined by an "Orsat" apparatus or gas chromatographic method. Chemical methods were used for H_2S , NH_3 , phenol, and HCN content determinations. Gas chromatography was used for determining the components occurring in lower amounts.

Generators

For investigations in the generator section, the following measurement points were selected:

- 2.0 Inlet dried lignite,
- 2.2 Dedusting cyclone discharge into the atmosphere,
- 3.1 Decompression of coal lock bucket,
- 3.2 Generator vent,
- 3.4 Vent of the collecting tank for tar condensate and other contaminated waters in generator section,
- 3.5 Vent from ash lock expander cyclone,
- 3.6 Coal lock expansion gases,
- 12.2 Slag (dry), and
- 12.3 Water.

Tables 1 through 10 present the data on amounts and quality of the most important generator section streams.

Rectisols

For investigations of gas streams in the Rectisol section, the following measurement points were selected:

- 7.3 Raw gas: feed for Rectisol section (it contains H_2S , cyanides, higher hydrocarbons, etc.);
- 7.2 Waste gas (CO_2) (it contains in addition to CO_2 , methanol, H_2S , and higher hydrocarbons);
- 7.1 H_2 waste gas (it contains H_2S , methane, and other hydrocarbons); and
- 7.4 Clean gas: final product.

Tables 11 through 16 present the data on amounts and quality of the most important Rectisol section streams.

Tar Separation

For investigations of gas streams in the tar separation section, the following measurement points were selected:

- 13.1 Tar tanks,
- 13.2 Unclean tar tank,
- 13.3 Medium oil tank,
- 13.4 Uncleaned oil tank,
- 13.5 Gas condenser tank,
- 13.6 Expansion gases to waste gases flare, and
- 13.7 Phenolic water tanks.

Tables 17 through 23 present the data on amounts and quality of the most important tar separation section gas streams.

Phenosolvan and Expansion Gases Large Flare

For investigating streams in the phenosolvan section and expansion gases large flare, the following measurement points were selected:

- 14.1 Cyclone vent;
- 14.2 Tank for gas water, tar, oil, and phenolic water separation;
- 14.3 Unclean oil tank;
- 14.4 Phenolic water tank;
- 14.5 Column vent;
- 14.6 Vent between pos. 25 and 16;
- 14.7 Column vent;
- 14.8 Phenosolvan section wastewater tank;
- 14.9 Crude phenol tank vent;
- 14.10 Diisopropylether tank;
- 20.1 Gases to large flare; and
- 14.11 Wastewaters to biological treatment.

Tables 24 through 28 present the data on amounts and quality of the most important gas streams from the phenosolvan section and from expansion gases large flare.

Storage

For investigating gas streams in the storage section, the following measurement points were considered:

- 15.1 Tar tank vent,
- 15.2 Medium oil tank vent,
- 15.3 Gasoline tank vent, and

• 15.4 Phenol tank vent.

Tables 29, 30, and 31 present the data on amounts and quality of the most important storage section gas emission (M.P. 15.3) into the atmosphere. Data on amounts and quality of gasoline, medium oil, and tar are included in Table 32.

SUMMARY AND RECOMMENDATIONS FOR CONTINUOUS ACTIVITY

Results presented in this report were obtained by testing the lignite gasification plant according to the Lurgi process. Prior to gasification, the run-of-mine Kosovo lignite was screened, classified, and dried by the "Fleissner" process. Investigations were completed through three sampling campaigns (i.e., during winter, summer, and autumn). Their objective was to evaluate the effect of the Lurgi process on environmental pollution. Composition and volume were determined for all major process waste streams. The volumes were calculated for pollutants that are discharged at a high rate into the plant, ambient, and broader surroundings in the form of waste gases, particulates, and wastewaters. ASTM methods were mainly used in the investigations.

Accurate sampling was difficult at some points (discontinuous, short-lasting discharges in some cases with high contents of water vapor, more than 90 percent). Despite modern equipment mainly provided by the U.S. Environmental Protection Agency (EPA) and Radian Corporation, the capabilities of the instruments, both for sampling and analysis, made the measurements time-consuming because of the number of components to be determined in a plant of this size. It was not possible to maintain constant operating conditions during a campaign (7 to 14 days).

Although the differences in results obtained chemically and chromatographically were observed and partially explained, it was considered necessary to repeat the check of various determination methods in heavily polluted streams.

Velocity measurements for flow determinations during short explosive discharges proved insufficient, and some flows were determined calculatively.

The EPA Method 5 for particulates determination proved inadequate for determinations

in streams with high-water vapor contents (more than 80 percent), so the method with "wet impingers" was used.

During our recordings, the percent of conveyed heat in the form of clean gas was 62.88 percent of the heat fed in the form of coal. The balance of carbon conveyed in the form of clean gas was 24.98 percent. The major amount of sulfur (about 91.1 percent) was combusted with the waste gases in the large flare. Approximately 4.13 percent of the sulfur remained in the liquid products.

The results of completed investigations indicate that during the production of gas by the Lurgi process, the following amounts of pollutants were emitted from 10 tons of dried lignite and by complete incineration of waste gases through the flare:

• Sulfur "S"	4.0 kg
(about 90 percent as H ₂ S)	
• Ammonium (NH ₃)	0.4 kg
• Phenols	4.7 kg
• Cyanides	0.06 kg
• Hydrocarbons (C _n H _m)	12.6 kg
• Hydrogen (H ₂)	2.6 kg
• Carbon monoxide (CO)	4.5 kg
• Carbon dioxide (CO ₂)	9,632.7 kg
• Methane (CH ₄)	10.0 kg
• Nitrogen oxide (NO ₂)	5.2 kg
• Sulfur dioxide (SO ₂)	180.0 kg
• Particulates	148.5 kg
Total	10,005.3 kg

With regard to the Lurgi flow sheet, particular care should be paid to generator operation. Experimental operation on a single generator with systematic variation of technological operating parameters could indicate the conditions affecting the variation of pollutants concentration and amount (pressure, steam-to-oxygen ratio, coal bed thickness, throughput capacity, charge size distribution, pour, etc.). Such investigations could lead to maximum gas production and gas quality in line with the reduction of pollutants volume production to a minimum. For the Lurgi plant in Kosovo, the presence of a large number of "minor" vents significantly increasing pollution is characteristic.

In Combine Kosovo, efforts are made to charge the optimum size distribution of dried lignite into the generators in order to achieve more efficient heat balance and higher produc-

tion of raw gas per generator in operation. A project was developed and is currently underway to combust the expansion gases in one of the boilers of the adjacent power generating plants. Hitherto, the gases were incinerated by the large flare, and combustion was unnecessary. Completion of this project will increase the gasification heat balance and reduce environmental pollution.

It is also necessary to investigate the effect of the stockpile of this type of coal on the environment; i.e., to examine the properties of coal dust particulates, the properties of groundwaters around the coal stockpiles, and the dissolution of various mineral matters and chemical compounds from the coal in atmospheric precipitations.

The lignite drying plant was not investigated. It is considered important to investigate the effect of the "Fleissner" process; i.e., coal-drying

process on the living environment. Of importance here are: composition and volume of waste gases, wastewaters properties, and properties and composition of dried coal dust particulates.

The impact of trace elements in generator slag on the environment and humans should also be investigated. It is important to determine the degree of mineral matters and individual element oxides dissolved in the water as well as the increase of their concentration in groundwater, and to examine the effect of the increase of concentration of different chemical element oxides in the water on agricultural products and other fauna and flora. In any case, the effect of slag dumps should be investigated, both those on the surface and underground.

Further investigations concentrate on the pollutants occurring in small amounts.

TABLE 1. VOLUMES OF GENERATOR SECTION EMISSIONS

Measurement point	A m o u n t s		
	Measured	from design	Calculated Estimated
	t	2(16 t/h)	3(10,3 t/h)
2.0. Inlet dried lignite		circa 16 t/h	10,3 t/h
2.2. Dedusting cyclone discharge into the atmosphere		5400 m ³ /h	3476 m ³ /h
3.1. Decompression of coal lock bucket		circa 9 m ³ /h	5,8 m ³ /h
3.2. Generator vent		circa 36 m ³ /h	23,2 m ³ /h
3.4. Vent of the collecting tank for tar gaseous water and other con- taminated waters in General Section		39 m ³ /h	25,1 m ³ /h
3.5. Vent from ash lock expander cyclone		9 m ³ /h	5,8 m ³ /h
3.6. Coal lock expansion gases		326 m ³ /h	209,9 m ³ /h
12.2 Slag (dry)		2,6 t/h	1,7 t/h
12.3 Wastewater		1,56 m ³ /h	1,0 m ³ /h

**TABLE 2. PROPERTIES OF DRIED LIGNITE KOSOVO, GRAIN SIZE: - 60 + 6 mm
(COMPOSITE SAMPLES OF LIGNITE) M.P. 2.0**

Proximate and ultimate analysis:

Moisture %	20,72	24,30
Ash %	10,33	17,74
Sulphur total, %	1,06	1,15
S bound %	0,90	1,01
S combust. %	0,16	0,14
Coke %	40,18	40,96
C fix %	29,85	23,22
Volatiles %	39,10	34,74
Combustibles %	68,95	57,96
Heating value		
Gross kcal/kg	4335	3470
Net kcal/kg	4035	3190
Carbon dioxide (CO ₂) %	1,44	3,32
Carbon %	46,30	37,80
Hydrogen %	3,79	2,96
Nitrogen %	1,13	1,03
Oxygen %	17,57	16,03
Bulk weight, t/m ³	0,50	0,55
Micum test		
(+6 mm) %	78	76
Tar %	3,3	2,1

Sulfur forms and ash chemical composition:

Sulfur forms

Sulfur total, %	6	1,34	1,15	1,52
Sulfur bound, %	0	1,13	1,01	1,34
Sulfur combust, %	6	0,21	0,14	0,18
Sulfur pyritic, %	1	0,90	0,78	1,04
Sulfur sulphate, %	5	0,06	0,08	0,11
Sulfur organic, %	0	0,38	0,28	0,37
Moisture %	2	-	24,30	-
Ash chemical composition				
SiO ₂ %	15,21		27,08	
Fe ₂ O ₃	6,78		7,18	
Al ₂ O ₃	4,74		7,27	
CaO	35,55		36,05	
MgO	11,35		5,49	
SO ₃	23,30		14,55	
P ₂ O ₅	0,30		0,22	
TiO ₂	0,50		0,70	
Na ₂ O	1,58		0,91	
K ₂ O	0,46		0,46	

Ratio: acid/Base

$$\frac{Al_2O_3 + SiO_2 + TiO_2}{(Fe_2O_3 + CaO + MgO + alkalis)} = 0,367 \quad 0,699$$

Ash fusibility:

(Oxidative atmosphere)

Initiation of sintering °C	925	1070
Softening temperature °C	1200	1250
Hemisphere temperature °C	1325	1275
Flow temperature °C	1335	1285

**TABLE 3. PARTICLE SIZE OF DRIED LIGNITE KOSOVO, GRAIN SIZE - 60 + 6 mm
(COMPOSITE SAMPLES OF LIGNITE)**

Particle size in mm	% share	$\Sigma\%$	% share	$\Sigma\%$
+ 60	15,79	15,79	3,33	3,33
- 60 + 50	15,79	31,58	4,45	7,78
- 50 + 40	7,37	38,95	7,78	15,56
- 40 + 30	16,84	55,79	24,44	40,00
- 30 + 25	6,32	62,11	6,67	46,67
- 25 + 20	7,37	69,48	13,33	60,00
- 20 + 15	8,42	77,90	23,33	83,33
- 15 + 10	7,37	85,27	12,22	95,55
- 10 + 5	2,10	87,37	1,11	96,66
- 6 + 3	7,37	94,74	1,11	97,77
- 3 + 2	1,58	96,32	0,56	98,33
- 2 + 1	1,05	97,37	0,56	98,89
- 1 + 0	2,64	100,00	1,11	100,00

TABLE 4. RESULTS OF THE WASTE GAS ANALYSIS FROM M.P. 2.2.

Gas Stream			
M.P. 2.2			
Section Generators			
Campaign	1	2	3
a) Gas Composition vol-%			
"Orsat" and G.C."	"Orsat"	G.C.	G.C.
- H ₂	0,8*	n.f*	n.f*
- CnHm	0,0	trace	n.f
- O ₂	20,4	19,81	20,8
- N ₂	78,7	78,99	78,2
- CH ₄	0,0	trace	n.f
- CO	0,0	trace	n.f
- CO ₂	0,1	n.f	n.f
b) Chem.meth. g/100 m _N ³ (dry)			
- H ₂ S	n.f	n.f	n.f
- NH ₃	-	0,8-2,3	n.f
- Phenols	-	0,059-0,149	-
- HCN	-	-	n.f
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S			n.f
- NO _x			-
- COS			n.f
- SO ₂			-
- methyl mercaptan			n.f
- ethyl mercaptan			n.f.
- unknown ppm			
d) Moisture %		2,47;	1,02
e) Particulates g/100 m _N ³ (dry)			
(method 5)		44	3,89
Dissolved solids			
Tar Components			
Total "e"		44	3,89
f) Flow: m _N ³ /h (dry)/Gener.in Operation			
- designed			
- calculated	5400		
- measured			5768

Note: For a) n.f = not found = < 0,01 vol.-%; trace = < 0,1 vol.-%

For b) n.f = < 5 ppmv

For c) n.f = <0,1 ppmv

* For other hydrocarbons n.f = < 0,0001 vol.-%

TABLE 5. RESULTS OF THE WASTE GAS ANALYSIS FROM M.P. 3.2

Gas Stream

M.P. 3.2

Section Generators

Campaign

	1	2	3
a) Gas Composition vol-% ("Orsat" and G.C)	"Orsat"	G.C.	G.C.
- H ₂	39,2	44,28	34,1
- CnHm	0,6*	1,32*	1,18*
- O ₂	0,0	1,52	0,70
- N ₂	5,0	2,17	2,54
- CH ₄	11,3	9,31	9,38
- CO	7,7	11,23	9,26
- CO ₂	36,2	28,49	42,0
b) Chem.meth. g/100 m _N ³ (dry)			
- H ₂ S	1371	945	576
- NH ₃	132	21,9	529
- Phenols	2,27	0,574	909
- HCN	-	-	5,77
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S		28,8	98,2
- NO _x		-	-
- COS		-	0,44
- SO ₂		-	-
- methyl mercaptan			54,9
- ethyl mercaptan			23,4
- unknown ppm			14,1
d) Moisture %			44,2; 8,4; 16,2
e) Particulates g/100 m _N ³ (dry) (method 5)			1,37** 2,37**
Dissolved solids			259,8 145,3**
Tar Components			913,0 1119,0**
Total "e"			1174,17**1266,67**
f) Flow: m _N ³ /h (dry)/Gen.in Operation			
- designed			
- calculated	36		
- measured			

Note: * Other hydrocarbons

** Wet impinger

TABLE 6. RESULTS OF THE WASTE GAS ANALYSIS FROM M.P. 3.5

Gas Stream
M.P. 3.5.
Section Generators

Campaign	1	2	3
a) Gas Composition vol-% (Orsat and G-C)	"Orsat"	G.C.	G.C.
- H ₂	0,0	n.f.	n.f.
- CnHm	0,0	trace	trace
- O ₂	0,0	0,0	73,43
- N ₂	78,5	84,46	0,00
- CH ₄	0,0	0,27	0,04
- CO	0,0	n.f.	n.f.
- CO ₂	21,5	18,17	26,53
b) Chem.meth. g/100 m _N ³ (dry)			
- H ₂ S	0,0	10,0	12,5
- NH ₃	0,57	22,6	261
- Phenols	0,020	4,62	0,217
- HCN	-	-	6,5
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S			n.f.
- NO _x			-
- COS			n.f.
- SO ₂			-
- methyl mercaptan			n.f.
- ethyl mercaptan			n.f.
- unknown ppm			
d) Moisture %		96,6;	90,6
e) Particulates g/100 m _N ³ (dry) (method 5)	210	130,9**	1,05**
Dissolved solids		97,3**	348,8**
Tar Components		89,3**	368,7**
Total "e"	210	317,5**	718,55**
f) Flow: m _N ³ /h (dry)/Gen.in Operation			
- designed			
- calculated	9		
- measured			

Note: * Other hydrocarbons; n.f. = < 0,0001 vol-%
 ** wet impingers
 For a) n.f. = < 0,01 vol.-%; trace = < 0,1 vol.-%
 For c) n.f. = < 0,1 ppmv

TABLE 7. RESULTS OF THE WASTE GAS ANALYSIS FROM M.P. 3.6

Gas Stream

M.P. 3.6

Section Generators

Campaign

	1	2	3
a) Gas Composition vol.-% ("Orsat" and G.C.)	"Orsat"	G.C.	G.C.
- H ₂	37,0-37,2	23,40	31,6
- CnHm	0,9-1,2	1,16*	0,95*
- O ₂	0,3-0,2	1,20	0,23
- N ₂	4,8-11,7	7,30	6,07
- CH ₄	9,6-2,9	9,95	11,0
- CO	8,0-12,0	13,20	12,7
- CO ₂	39,4-34,8	36,80	37,3
b) Chem. meth. g/100 m _N ³ (dry)			
- H ₂ S	421-363	235	364
- NH ₃	26	5,8	n.f
- Phenols	0,027	0,465	180
- HCN			10,2
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S		71,3	120,4; 101,8
- NO _x		-	-
- COS			76,9
- SO ₂			-
- methyl mercaptan		trace	86,1; 1,1
- ethyl mercaptan		trace	22,3
- unknown ppm			found
d) Moisture %			10,4; 10,3
e) Particulates g/100 m _N ³ (dry) (method 5)		23,1	1,2** 7,1**
Dissolved solids			33,8** 23,3**
Tar Components		161,9	81,1** 31,0**
Total "e"		185	116,1** 61,4**
f) Flow: m _N ³ /h (dry)/ Gen.in Operation			
- designed			
- calculated	326		
- measured			

Note: * Other hydrocarbons
 ** wet impingers
 For b) n.f. = < 5 ppmv
 For c) trace = < 1 ppmv

**TABLE 8. HYDROCARBON CONTENT IN SELECTED GENERATORS SECTION
GAS STREAMS**

Measurement points	Other hydro- carbons vol. - %	C ₂	C ₃	vol. - % C ₄	C ₅	C ₆ ⁺	Ben- zene
2.2.	trace	trace	trace	trace	trace	trace	
	trace	trace	trace	trace	trace	trace	
	not found	not found			not found		
3.2.	1,33	0,84	0,38	0,11	trace	trace	
	1,32	0,79	0,32	0,16	0,03	0,02	
	1,18	0,72	0,29	0,09	0,05	0,03	
3.5.	trace	trace	trace	trace	trace	trace	
	trace	trace	trace	trace	trace	trace	
	trace	trace	trace	trace	trace	trace	
3.6	1,16	0,63	0,17	0,19	0,12	0,05	
	9,30	2,68	6,25	0,08	0,20	0,09	
	1,02	0,71	0,21	0,02	0,02	0,01	0,05

N o t e: Trace for hydrocarbons = < 0,001 vol.-%
not found (n.f) = < 0,0001 vol.-%

**TABLE 9. SLAG PROPERTIES BECAUSE OF DRIED LIGNITE GASIFICATION; M.P. 12.2;
(COMPOSITE SLAG SAMPLES ANALYSIS)**

Proximate and ultimate analysis:

	36,46	-	30,87	-	34,86	-
Moisture %	58,06	91,38	62,27	90,07	57,83	88,78
Ash %	0,08	0,12	0,07	0,10	0,12	0,18
Sulfur total %	0,06	0,10	0,06	0,09	0,08	0,12
Sulfur bound %	0,02	0,02	0,01	0,01	0,04	0,06
Sulfur combust %	58,76	92,47	63,65	92,07	57,94	88,94
Coke %	0,70	1,09	1,38	2,00	0,11	0,16
C fix %	4,78	7,53	5,48	7,93	7,20	11,06
Volatiles mat. %	5,48	8,62	6,86	9,93	7,31	11,22
Combustibles mat. %	4,64	7,30	5,83	8,44	6,50	9,98
Carbon dioxide (CO ₂) %	1,35	2,12	1,72	2,49	2,46	3,78
Carbon %	0,36	0,57	0,39	0,57	0,40	0,61
Hydrogen %	3,75	5,91	4,74	6,86	4,01	6,77
(Nitrogen + Oxygen) %						

Slag chemical composition:

Slag spectrochemical
analysis "ppm"

SiO ₂	%	37,74	35,77	30,23	B	630
Fe ₂ O ₃	%	7,50	5,49	10,38	Ba	1670
Al ₂ O ₃	%	13,31	13,42	8,73	Be	below detection
CaO	%	31,60	35,80	41,05	Mn	2700
MgO	%	6,08	5,98	6,44	Se	2
SO ₃	%	0,29	0,27	0,36	Pb	29
P ₂ O ₅	%	0,24	0,24	0,27	Cr	240
TiO ₂	%	0,90	0,90	0,80	Ga	37
Na ₂ O	%	1,15	0,99	0,98	Ni	180
K ₂ O	%	0,81	0,73	0,47	Mo	30
Ratio Acid/Base:					V	137
Al ₂ O ₃ +SiO ₂ + TiO ₂					Cu	48
Fe ₂ O ₃ +CaO+MgO+alkalies =					Y	39
Ash fusibility:					Zn	56
(Oxidative atmosphere)					Zr	175
Initiation of sintering °C					Co	15
Softening temperature °C					Sr	4100
Hemisphere temperature °C					Sc	20
Flow temperature °C					Cd	1,2

TABLE 10. PROPERTIES OF WASTEWATER (SAMPLING POINT 12.3)

C o m p o n e n t s				
pH value	10,9	11,7	11,0	12,1
Suspended solides mg/l (105°C)	570	559	460	204
Total Residue of Evaporation mg/l (105°C)	1330	1991	2550	2314
Fixed Remainder of Total Eva- poration's residue mg/l (600°C)	130	1780	240	1778
Evaporation's residue of dissolved matter mg/l (105°C)	760	1432	2090	2110
Fixed remainder of Evaporation residue of dissolved matter, mg/l (600°C)	90	1275	215	1588
COD ($K_2Cr_2O_7$) mgO_2/l	18	-	49	154
Permanganate value, mg/l ($KMnO_4$)	33	-	94	139
BOD ₅ mgO_2/l	28	-	90	-
Volatile Phenols, mg/l	0,11	0,3	4,25	0,25
Ammonia free, mg/l	trace		trace	
Ammonia fixed, mg/l	1,6	1,5	2,3	2,2
Cyanide (CN^-), mg/l	0,01	< 0,01	trace	<0,01
Hydrogen sulfide mg/l	trace		trace	
Tar+Oil (ether extracts) mg/l	0,0	0,0	0,0	
Chloride (Cl^-) mg/l	20,5	25,5	36	36,5
Sulfates, mg/l	345	515	339	668
Rhodate (CNS^-), mg/l	0,025	0,03	0,03	0,02
Thiosulfates ($S_2O_3^-$), mg/l	trace		trace	
Fluorides (F^-), mg/l	0,90	0,65	1,0	1,19
Nitrites (NO_2^-), mg/l	0,60	0,29	0,30	0,82
Nitrates (NO_3^-), mg/l	5,5	4,0	4,3	5,61
Sulfites (SO_3^-), mg/l	trace		trace	

TABLE 11. VOLUMES OF RECTISOL SECTION STREAMS

Measurement Point	A m o u n t s		
	Measured	Estimated Calculated	From design
	1	2 (10,3 t/h)	3 (16 t/h)
7.3		10131 m ³ /h	17.220 m ³ /h
Raw gas (Feed for Rectisol Section)		10410 m ³ /h	
7.2	4870 m ³ /h	1753 m ³ /h	2174 - m ³ /h -5300
Waste gas CO ₂ and other components			
7.1.	3490 m ³ /h	2958 m ³ /h	2.546 m ³ /h
H ₂ S Waste gas and other components			
7.4.	7235 m ³ /h	5775 m ³ /h	12.500 m ³ /h
Glean gas (Final Product)		5934 m ³ /h	

TABLE 12. RESULTS OF THE RAW GAS ANALYSIS FROM M.P. 7.3

Gas Stream
M.P. 7.3
Section: Rectisol
Campaign

	1	2	3
a) Gas Composition vol.-% (Orsat and G.C. Methods)	"Orsat"	G.C.	G.C.
- H ₂	39,8-42,8	38,07-45,2	36,1
- CnHm	0,4-0,4	1,60-2,41*	1,21*
- O ₂	0,2-0,2	1,63-2,56	0,55
- N ₂	0,9-1,0	1,33-9,48	1,55
- CH ₄	9,9-8,8	11,9 -8,92	12,8
- CO	11,6-9,8	9,65-10,07	13,5
- CO ₂	37,2-37,0	35,82-21,37	33,4
b) Chem. meth. g/100 m _N ³ (dry)			
- H ₂ S	1097-1181		673-804
- NH ₃	130-138		0,25
- Phenols	0,352		0,129
- HCN	84-85		7,30
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S		150-425	681,5
- NO _x		-	-
- COS		-	19,8
- SO ₂		-	-
- methyl mercaptan		21-73	116,6
- ethyl mercaptan		-	27,2
- unknown ppm		-	-
d) Moisture %			
e) Particulates g/100 m _N ³ (dry) (method 5)			
Dissolved solids			
Tar Components			
Total "e"			
f) Flow: m _N ³ /h (dry)/ Gen. in operation			
- designed	17.220		
- calculated		10131; 10410	
- measured			

Note: * Other hydrocarbons

TABLE 13. RESULTS OF THE WASTE GAS ANALYSIS FROM M.P. 7.2

Gas Stream

M.P. 7.2

Section: Rectisol

Campaign

	1	2	3
a) Gas Composition vol.-% (Orsat and G.C. Methods)	"Orsat"	G.C.	G.C.
- H ₂	0,0	0,63-0,20	0,83
- CnHm	0,0	0,96-1,45*	0,49*
- O ₂	0,3	0,10-0,62	0,06
- N ₂	1,4	2,47-3,74	0,32
- CH ₄	9,4	1,41-1,81	0,94
- CO	1,2	-	-
- CO ₂	87,7	93,98-91,77	94,08
b) Chem.meth. g/100 m _N ³ (dry)			
- H ₂ S	0,0-21	13,7-00	10,0
- NH ₃	0,0	0,0	0,35
- Phenols	0,0-0,027	0,009-0,068	-
- HCN	-	-	1,53
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S	-	-	0,67
- NO _x			-
- COS			trace
- SO ₂			-
- methyl mercaptan			1,8
- ethyl mercaptan			0,9
- unknown ppm			4,0
d) Moisture %			
e) Particulates g/100 m _N ³ (dry) (method 5)			
Dissolved solids			
Tar Components			
Total "e"			
f) Flow: m _N ³ /h (dry)/Gen.in operation			
- designed	2174-5300		
- calculated	4870		
- measured			

Note: * Other hydrocarbons
For c) trace = < 1 ppmv

TABLE 14. RESULTS OF THE WASTE GAS ANALYSIS FROM M.P. 7.1

	1	2	3
a) Gas Composition vol-% (Orsat and G.C. Methods)	"Orsat"	G.C.	G.C.
- H ₂	1,6	0,02-0,07	NF
- C _n H _m	0,2	1,46-1,54*	0,77*
- O ₂	0,0	0,41-0,23	0,51
- N ₂	0,2	0,81-0,59	1,39
- CH ₄	8,6	4,44-1,65	4,15
- CO	1,8	2,93-1,65	2,64
- CO ₂	87,0	87,94-91,45	86,94
b) Chem.meth. g/100 m _N ³ (dry)			
- H ₂ S	1519	4138 - 4224	3541
- NH ₃	0,86	0,0 - 1,7	167
- Phenols	0,028	0,007-0,011	0,27
- HCN	-	-	10,1
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S		3293	4083
- NO _x		-	-
- COS		trace	133,9
- SO ₂		-	-
- methyl mercaptan		210	786,4
- ethyl mercaptan		-	201,5
- unknown ppm		-	-
d) Moisture %			
e) Particulates g/100 m _N ³ (dry) (method 5) Dissolved solids Tar Components Total "e"			
f) Flow: m _N ³ /h (dry)/Gen.in operation			
- designed	2546		
- calculated			
- measured		3490**	
g) Heating value***			
Gross kcal/m _N ³	965	840-555	650
Net kcal/m _N ³	870	785-525	600

N o t e : *Other hydrocarbons; **at M. P. 20, 1 (1.7.1978); For c)
trace = < ppmv; ***Calculated without Sulfur Compounds
Combustion (Prof. G. Wagener)

TABLE 15. RESULTS OF CLEAN GAS ANALYSIS FROM M.P. 7.4

Gas Stream

M.P. 7.4

Section: Rectisol

Campaign

	1	2	2	3	
a) Gas Composition vol.-% (Orsat and G.C. Meth.)	"Orsat"	"Orsat"	G.C.	"Orsat"	G.C.
- H ₂	66,1	62,4-65,0	64,78-62,09	62,2	63,9
- CnHm	0,3	0,4-0,4	0,42-0,54*	0,3	0,27
- O ₂	0,1	0,1-0,1	1,50-1,76	0,1	1,23
- N ₂	1,5	0,8-1,0	2,71-2,46	2,0	5,87
- CH ₄	13,5	16,1-14,2	16,25-15,22	17,6	11,93
- CO	16,5	17,3-16,5	11,06-15,34	17,1	14,33
- CO ₂	2,0	2,6-2,6	2,65-2,22	0,7	n.f.
b) Chem.meth. g/100 m _N ³ (dry)					
- H ₂ S	0,0	0,0		-	
- NH ₃	0,0	0,24-0,20		-	
- Phenols	-	0,016-0,014		-	
- HCN	-	-		-	
c) G.C. meth. g/100 m _N ³ (dry)					
- H ₂ S				0,20	
- NO _x				-	
- COS				n.f.	
- SO ₂				n.f.	
- methyl mercaptan				0,2	
- ethyl mercaptan				trace	
- unknown ppm					
d) Moisture %					
e) Particulates g/100 m _N ³ (dry) (method 5)					
Dissolved solids					
Tar Components					
Total "e"					
f) Flow: m _N ³ /h (dry)/Gen. in operation					
- designed 12.500					
- calculated	5775;	5934			
- measured		7235			
g) Heating value**					
Gross kcal/m _N ³	3870	4050	3925	3950 3930	4155 3580
Net kcal/m _N ³	3415	3590	3470	3480 3480	3685 3155

Note: * Other hydrocarbons; n.f = not found.

For a) n.f = 0,01 vol.-%; For c) n.f. = < 0,1 ppmv; trace = < 1 ppm;

** Calculated (Prof. G. Wagener)

TABLE 16. HYDROCARBON CONTENT IN SELECTED RECTISOL SECTION GAS STREAMS

Measurement Points	Other hydro- carbons	vol. - %					Ben- zene
		C ₂	C ₃	C ₄	C ₅	C ₆ ⁺	
7.3	1,60	1,04	0,35	0,20	0,01	trace	
	2,41	1,11	0,40	0,24	0,37	0,29	
	1,21	0,65	0,35	0,15	0,04	0,02	
7.2	0,96	0,37	0,27	0,21	0,09	0,02	
	1,45	0,59	0,37	0,23	0,17	0,09	
	0,49	0,29	0,20	trace	trace	n.f	
7.1	1,46	0,63	0,32	0,27	0,21	0,03	
	1,54	0,73	0,39	0,19	0,11	0,12	
	0,77	0,34	0,22	0,14	0,06	0,01	
7.4	0,42	0,35	0,07	n.f	n.f	n.f	
	0,54	0,45	0,09	n.f	n.f	n.f	
	0,27	0,25	0,004	n.f	n.f	n,02	

N o t e: n.f = not found = < 0,0001 vol.-%

Trace for hydrocarbons = < 0,001 vol.-%

TABLE 17. VOLUMES OF TAR SEPARATION SECTION EMISSIONS

Measurement Point	A m o u n t s		
	Measured	From design	Evaluated and calculated
	1	2 (16 t/h)	3 (10,3 t/h)
13.1. Tar Tanks		0,5 m _N ³ /h	0,32 m _N ³ /h
13.3. Medium Oil Tank		94 m _N ³ /h	60,5 m _N ³ /h
13.5. Gas Condenser Tank		9 m _N ³ /h	5,8 m _N ³ /h
13.6. Expansion gases to waste gases flare		30-360 m _N ³ /h	210,3 m _N ³ /h
13.7. Phenolic water tanks		13 m _N ³ /h	8,4 m _N ³ /h

TABLE 18. RESULTS OF WASTE GAS ANALYSIS FROM M.P. 13.1

Gas Stream

M.P. 13.1

Section: Tar Separation

Campaign

	1	2	3
a) Gas Composition vol.-% (Orsat and G.C)	"Orsat"	G.C	G.C
- H ₂	1,1	n.f	trace
- C _n H _m	0,0-0,6	0,01*	0,01*
- O ₂	15,6	19,20	19,60
- N ₂	80,4	78,90	72,12
- CH ₄	0,6	0,08	0,10
- CO	0,3	n.f	n.f
- CO ₂	2,0	1,11	3,09
b) Chem meth. g/100 m _N ³ (dry)			
- H ₂ S	297	52,3-1140	1920 (1920)
- NH ₃	2,81	151	198 (198)
- Phenols	0,0185	2,046	22,06
- HCN	-	-	15,37
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S		59,2-75,9	273
- NO _x			-
- COS			n.f
- SO ₂			-
- methyl mercaptan		trace - 26	130,1
- ethyl mercaptan			66,7
- unknown ppm			-
d) Moisture %			26,8
e) Particulates g/100 m _N ³ /dry/ (method 5)			
- dissolved solids			
- Tar Components			
Total "e"			
f) Flow: m _N ³ /h (dry)/ Gener. in Operation			
-designed			
-calculated 0,5			
-measured			

Note: Other hydrocarbons x; Trace for hydrocarbons = < 0,001%
n.f = not found

TABLE 19. RESULTS OF WASTE GAS ANALYSIS FROM M.P. 13.3

Gas Stream			
M.P. 13.3			
Section Tar Separation			
Campaign	1	2	3
a) Gas Composition vol.-% (Orsat and G.C)	"Orsat"	G.C	G.C
- H ₂	20,4	22,48	n.f
- CnHm	0,9	2,75*	0,96*
- O ₂	0,6	0,84	0,89
- N ₂	1,1	3,02	3,36
- CH ₄	9,7	2,74	7,64
- CO	5,3	3,06	n.f
- CO ₂	62,0	50,67	86,36
b) Chem. meth. g/100 m _N ³ (dry)			
- H ₂ S	5639-3647	6275	940
- NH ₃	3,49	1,3	408
- Phenols	0,0177	0,114	45,2
- HCN	-	-	6,31
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S		952	1882
- NO _x			-
- COS			-
- SO ₂			-
- methyl mercaptan		135	216,4
- ethyl mercaptan			126,5
- unknown ppm			-
d) Moisture %			11,4
e) Particulates g/100 m _N ³ (dry) (method 5)			
- Dissolved solids			
Tar Components			
Total "e"			
f) Flow: m _N ³ /h (dry)/ Gener.in			
Operation			
- designed			
- calculated	94		
- measured			

Note: * Other hydrocarbons
n.f = not found

TABLE 20. RESULTS OF WASTE GAS ANALYSIS FROM M.P. 13.5

Gas Stream

M.P. 13.5

Section Tar Separation

Campaign	1	2	3
a) Gas Composition vol. - % (Orsat and G.C.)	"Orsat"	G.C	G.C
- H ₂	16,2	13,78	14,63
- CnHm	0,8	0,13* - 2,63*	0,22*
- O ₂	12,8	15,14	16,60
- N ₂	49,8	58,01	60,99
- CH ₄	4,6	2,10	1,19
- CO	3,6	n.f	n.f
- CO ₂	12,2	9,06	6,15
b) Chem. meth. g/100 m _N ³ (dry)			
- H ₂ S	788	1055	938,4
- NH ₃	3,72	62	n.f.
- Phenols	0,0177	4,79	0,456
- HCN	-	-	20,34
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S			125,8
- NO _x			-
- COS			-
- SO ₂			-
- methyl mercaptan			45,2
- ethyl mercaptan			19,76
- unknown ppm			-
d) Moisture %			1,0
e) Particulates g/100 m _N ³ (dry) (method 5) Dissolved solids Tar Components Total "e"			
f) Flow: m _N ³ /h (dry)/Gen.in Operation			
- designed			
- calculated 9			
- measured			

N o t e: *Other hydrocarbons
Not found = n.f

TABLE 21. RESULTS OF WASTE GAS ANALYSIS FROM M.P. 13.6

Gas Stream			
M.P. 13.6			
Section Tar Separation			
Campaign	1	2	3
a) Gas Composition vol.- % (Orsat and G.C.)	"Orsat"	G.C	G.C
- H ₂	25,4	9,87	11,1
- C _n H _m	0,8	2,69*	1,23*
- O ₂	0,6	1,10	0,47
- N ₂	3,5	1,78	0,56
- CH ₄	9,3	5,91	6,07
- CO	7,8	6,75	7,17
- CO ₂	52,6	71,73	72,1
b) Chem. meth. g/100 m _N ³ (dry)			
- H ₂ S	1594	2936	2081
- NH ₃	4,0	32,0	1484**
- Phenols	0,056	4,454	4,157
- HCN	-	-	8,22
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S			1745
- NO _x			-
- COS			n.f
- SO ₂			-
- methyl mercaptan			195,2
- ethyl mercaptan			76,7
- unknown ppm			-
d) Moisture %			
e) Particulates g/100 m _N ³ (dry) (method 5)			
Dissolved solids			
Tar Components			
Total "e"			
f) Flow: m _N ³ /h (dry)/Gener. in Operation			
- designed 30-360			
- calculated			
- measured			

Note: * Other hydrocarbons; Trace for hydrocarbons = < 0,001%
 Condensate had 1436 g/100 m_N³ phenols in Campaign 2
 ** with condensate
 n.f = not found

TABLE 22. RESULTS OF WASTE GAS ANALYSIS FROM M.P. 13.7

Gas Stream
M.P. 13.7
Section Tar Separation

Campaign	1	2	3
a) Gas Composition vol.-% (Orsat and G.C.)			
	"Orsat"	G.C.	G.C.
- H ₂	0,0	0,02	Trace
- C _n H _m	0,0-2,2	0,14*	0,25*
- O ₂	13,0	10,78	12,60
- N ₂	53,4	48,65	52,65
- CH ₄	0,4	0,20	0,18
- CO	0,0	n.f.	n.f.
- CO ₂	33,0	39,32	28,9
b) Chem. meth. g/100 m _N ³ (dry)			
- H ₂ S	1054	2518	981
- NH ₃	3,75	618	895
- Phenols	0,021	7,12	0,366
- HCN	-	-	4,64
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S		74,4	274,7
- NO _x			-
- COS			n.f.
- SO ₂			-
- methyl mercaptan		trace	131,9
- ethyl mercaptan			110,4
- unknown ppm			-
d) Moisture %			41,0
e) Particulates g/100 m _N ³ (dry) (method 5)			
Dissolved solids			
Tar Components			
Total "e"			
f) Flow: m _N ³ /h (dry)/Gen.in Operation			
- designed			
- calculated 13			
- measured			

Note: * Other hydrocarbons; trace for hydrocarbons = < 0,001%;
Condensate in Campaign 2 had 14,36 g/100 m_N³ phenols;
not found = n.f

**TABLE 23. HYDROCARBONS CONTENT IN SELECTED TAR SEPARATION SECTION
GAS STREAMS**

Measurement Points	Other hydrocarbons vol. - %	C ₂	C ₃	vol. - % C ₄	C ₅	C ₆ ⁺	Ben- zene
13.1	0,01	0,01	trace	trace	n.f	n.f	
	0,31	0,04	0,03	0,24	trace	n.f	
	0,01	trace	0,004	0,005	trace	0,001	
13.3	1,56	0,39	0,24	0,39	0,21	0,33	
	2,76	0,42	0,32	1,66	0,20	0,16	
	0,956	0,62	0,16	0,006	0,08	0,09	
13.5	1,07	0,40	0,21	0,27	0,13	0,06	
	0,13	0,09	0,02	0,02	trace	trace	
	0,22	0,07	0,05	0,03	0,04	0,03	
13.6	1,49	0,91	0,37	0,21	trace	trace	
	1,19	0,72	0,29	0,11	0,05	0,02	
	2,69	1,05	0,62	0,72	0,15	0,15	
	0,85	0,53	0,21	0,09	0,02	trace	
	1,23	0,4	0,33	0,27	0,15	0,08	
13.7	0,28	0,11	0,06	0,02	0,07	0,02	
	0,14	0,01	0,08	0,05	trace	n.f	
	0,25	0,02	0,01	0,05	0,09	0,08	

N o t e: Trace for hydrocarbons = < 0,001 Vol. - %
not found (n.f) = < 0,0001 vol. - %

TABLE 24. VOLUMES OF PHENOSOLVAN SECTION STREAM EMISSIONS AND OF EXPANSION GASES LARGE FLARE

Measurement Points	A m o u n t s		
	Measured	From design	Evaluated and calculated
	1	2 (16 t/h)	3 (10,3 t/h)
14.5 Column 1 vent		144 m ³ _N /h	92,7 m ³ _N /h
14.9 Grude phenol tank vent		0,1 m ³ /h	0,06 m ³ /h
20.1 Gases to Large Flare		2990-3320 m ³ _N /h	3448,4 m ³ _N /h
14.11 Waste waters		13 m ³ /h	8,4 m ³ /h

N o t e: During sampling the Phenosolván Section was not in normal production conditions; wastewater had a high content of phenols. For that reason the quality data of wastewaters are not given.

TABLE 25. RESULTS OF WASTE GASES ANALYSIS FROM M.P. 14.5

Gas Stream
M.P. 14.5
Section Phenosolvan
Campaign

	1	2	3
a) Gas Composition vol.-% (Orsat and G.C. methods)	"Orsat"	G.C.	G.C.
- H ₂	-	n.f	n.f
- C ₂ H ₆	0,4	0,07*	trace*
- O ₂	-	2,30	16,07
- N ₂	-	1,99	59,20
- CH ₄	-	trace	trace
- CO	-	n.f	n.f
- CO ₂	99,0-17,6	91,42	24,50
b) Chem. meth. g/100 m _N ³ (dry)			
- H ₂ S	0,0	534	6510-7058
- NH ₃	2611	16,6	16931-43563
- Phenols	0,0925	614,3	15758-15529
- HCN	-	-	29,97
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S		trace	1093
- NO _x			-
- COS			n.f.
- SO ₂			n.f.
- methyl mercaptan		trace	30,85
- ethyl mercaptan			8,8
- unknown ppm			
d) Moisture %			82,1; 88,3
e) Particulates g/100 m _N ³ (dry) (method 5)			
Dissolved solids			
Tar Components			
Total "e"			
f) Flow: m _N ³ /h (dry)/Gen. in Operation			
- designed			
- calculated 144			
- measured			

Note: * Other hydrocarbons; trace = < 0,001 vol.-%
n.f = not found; For a) n.f = < 0,01 vol.-% For c) n.f.=< 0,1
ppmv; Content of H₂S in condensate = 548-615 g/100 m_N³
Content of NH₃ in condensate = 26632 g/100 m_N³ (Campaign 3)

TABLE 26. RESULTS OF WASTE GASES ANALYSIS FROM M.P. 14.9

Gas Stream

M.P. 14.9

Section Phenosolvan

Campaign

	1	2	3
a) Gas Composition vol.-% (Orsat and G.C. Methods)	"Orsat"	G.C	G.C
- H ₂	0,0	n.f	n.f
- C _n H _m	0,0	trace*	trace*
- O ₂	18,6	18,79	20,45
- N ₂	80,8	79,89	76,26
- CH ₄	0,6	trace	trace
- CO	0,0	n.f	n.f
- CO ₂	0,0	n.f	n.f
b) Chem.meth. g/100 m _N ³ (dry)			
- H ₂ S	0,0	456-1070	27,3
- NH ₃	0,0	19,8	0,92
- Phenols	0,0174	28,7	8,62
- HCN	-	-	4,07
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S		-	n.f
- NO _x			
- COS			
- SO ₂			
- methyl mercaptan		-	n.f
- ethyl mercaptan		-	n.f
- unknown ppm			
d) Moisture %			
e) Particulates g/100 m _N ³ (dry) (method 5)			
Dissolved solids			
Tar Components			
Total "e"			
f) Flow: m _N ³ /h (dry)/Gen. in Operation			
- Designed			
- Calculated 0,1			
- Measured			

Note: n.f = not found; * Other hydrocarbons
 For a) trace = < 0,1 vol.-%
 For c) n.f. = < 0,1 ppmv

TABLE 27. RESULTS OF EXPANSION-WASTE GASES ANALYSIS FROM M.P. 20.1

Gas Stream

M.P. 20.1

Section Expansion
gases Large Flare

Campaign	1	2	3
a) Gas Composition vol.- % (Orsat and G.C. Methods)	"Orsat"	G.C	G.C
- H ₂	-	n.f	trace
- C _n H _m	-	0,79*	2,84*
- O ₂	-	0,37	0,06
- N ₂	-	1,86	0,5
- CH ₄	-	4,83	10,41
- CO	-	n.f	n.f
- CO ₂	-	91,55	88,10
b) Chem. meth. g/100 m _N ³ (dry)			
- H ₂ S	0,4 vol.-%	2900	1295-1625
- NH ₃			n.f
- Phenols			0,424-0,467
- HCN			12,5
c) G.C. meth. g/100 m _N ³ (dry)			
- H ₂ S		167	2747
- NO _x			-
- COS			75,5
- SO ₂			-
- methyl mercaptan		trace	317
- ethyl mercaptan			165
- unknown ppm			-
d) Moisture %			
e) Particulates g/100 m _N ³ (dry) (method 5)			
Dissolved solids			
Tar Components			
Total "e"			
f) Flow: m _N ³ /h (dry)/Gener. in Operation			
- designed			
- calculated 2990-3320			
- measured		3490	

Note: * Other hydrocarbons; Not found = n.f.

for a) trace = < 0,1 vol.- % n.f. = < 0,01 vol.-%

For b) n.f. = < 5 ppmv

For c) trace = < 1 ppmv

TABLE 28. HYDROCARBONS CONTENT IN SELECTED PHENOSOLVAN SECTION GAS STREAMS AND IN EXPANSION GASES LARGE FLARE

Measurement Points	Other Hydrocarbons vol.- %	C ₂	C ₃	C ₄	C ₅	C ₆ ⁺	Ben- zene
14.5	0,07	0,02	0,01	0,04	n.f	n.f	
	trace	trace	trace	trace	trace	trace	
	trace	trace	trace	trace	n.f	n.f	
14.9	trace	trace	trace	trace	trace	n.f	
	trace	trace	trace	trace	n.f	n.f	
20.1	0,79	0,38	0,27	0,09	0,04	0,01	
	0,52	0,19	0,11	0,12	0,08	0,02	
	2,84	1,01	1,03	0,59	0,14	0,07	

N o t e: Trace for hydrocarbons = < 0,001 vol.- %
Not found = n.f = < 0,0001 vol.- %

TABLE 29. VOLUMES OF THE MOST IMPORTANT STORAGE SECTION GAS EMISSION INTO THE ATMOSPHERE

Measurement Point	A m o u n t s		
	Measured	From design	Evaluated and calculated
	1	2 (16 t/h)	3 (10,3 t/h)
15.3 Gasoline Tank Vent		0,14 m ³ _N /h	0,09 m ³ _N /h

TABLE 30. RESULTS OF THE WASTE GAS ANALYSIS FROM M.P. 15.3

Gas Stream			
M.P. 15.3			
Section Storage			
Campaign	1	2	3
a) Gas Composition vol.-%			
(Orsat and G.C. Methods)	"Orsat"	G.C	G.C
- H ₂	0,0	n.f	n.f
- CnH _m	0,2	0,223*	0,69*
- O ₂	9,0	4,12	3,89
- N ₂	90,6	95,29	95,32
- CH ₄	0,0	trace	n.f
- CO	0,0	n.f	n.f
- CO ₂	0,4	n.f	n.f
b) Chem.meth. g/100 m _N ³ (dry)			
- H ₂ S	28,56	126-329	237
- NH ₃	1,77	0,9	n.f
- Phenols	0,034	0,268	0,0562
- HCN	-	-	129,45
d) G.C. Meth. g/100 m _N ³ (dry)			
- H ₂ S		n.f	10,5**
- NO _x			-
- COS			n.f.
- SO ₂			-
- methyl mercaptan		n.f	872,1
- ethyl mercaptan		n.f	1857
- unknown ppm			18
d) Moisture %			
e) Particulates g/100 m _N ³ (dry)			
(method 5)			
Dissolved solids			
Tar Components			
Total "e"			
f) Flow: m _N ³ /h (dry)/Gen. in Operation			
- designed			
- calculated 0,14			
- measured			

Note: * Other hydrocarbons; ** unsure identification

For a) trace = < 0,1 vol.-%; Not found = n.f = < 0,01 vol.-%

For b) not found = n.f. = < 5 ppmv

For c) not found = < 0,1 ppmv

TABLE 31. HYDROCARBON CONTENT IN SELECTED STORAGE SECTION GAS EMISSION INTO THE ATMOSPHERE

Measurement Point	Other hydrocarbons vol. - %	vol. - %					Ben- zene
		C ₂	C ₃	C ₄	C ₅	C ₆ ⁺	
15.3	0,223	0,007	0,004	0,030	0,095	0,087	
	0,69	0,009	0,007	0,10	0,39	0,18	

TABLE 32. DATA ON LIQUID PRODUCTS

Products	Gasoline	Medium Oil	Tar	Phenol
Measurement Point	15.3	15.2	15.1	15.4
Amounts, calculated from design	0,65 t/h	1,55 t/h	2,2 t/h	0,38 t/h
Water, %		0,80	1,08	
Ash, %	0,0	-	0,92	
Total Sulfur %	1,45	0,95	0,75	
Heating value				
Gross kcal/kg	9395	9880	8710	
Net kcal/kg	8925	9395	8275	7790
Carbon %	78,07	82,43	72,51	
Hydrogen %	8,72	8,96	8,06	
Phenols %	-	2,1	0,7	
Other Phenols % cca (o,m,p,cresol; ethyl phenol; dimethylphenol; trimethyl phenol)	0,2	12,0	3,8	
Pyridines % cca	10	-	-	
Spec.gravity, g/cm ³	0,845	0,972	1,059	
Residue after extraction with toluene and benzene %	-	-	6,9	

TABLE 33. HEAT BALANCE

Feed	Amount	Heating value kcal/kg	Amount of heat (kcal/kg of lignite)	% share
Coal	1 kg	3.470 Kcal/kg	3.470,0	76,68
Steam	0,8 kg/kg of coal	743 kcal/kg	594,4	13,14
Electric curr.	0.1535 KW/kg of coal	3,000 kcal/KW	460,5	10,18
			4.524,9	100,00
Output	Amount	Heating value kcal/m ³ ; kcal/kg	Amount of heat kcal/kg of coal	% share
Clean gas	0,6062 m ³ _N per kg coal	3600 kcal/m ³ _N	2.183,3	48,22
Liquid prod. (gasoline, med.oil,tar, phenol)	0,0594 kg/kg of coal	8042 kcal/kg	477,7	10,56
Waste gases flare	0,3348 m ³ _N per kg coal	766 kcal/m ³ _N	256,5	5,67
Heavy tar	0,00625 kg per kg coal	7000 kcal/kg	43,8	0,97
CO ₂ vent	0,1702 m ³ _N per kg coal	190 kcal/m ³ _N	32,4	0,72
Other vents	0,3615 m ³ _N	19,95 kcal/m ³ _N	7,2	0,16
Heat consump- tion for re- quired power generation	460,5 kcal per kg coal	70%	322	7,11
Heat consump- tion for re- quired steam generation	594,4 kcal per kg coal	10%	69,4	1,32
Conveyed heat (Steam-raw gas)	0,7 kg/kg of coal	660 kcal/kg	462	10,21
Conveyed heat (hot dry raw gas)	1,0636 m ³ _N per kg coal	101 kcal/m ³ _N	107,6	2,38
Slag losses	0,1625 kg per kg coal	120 kcal/kg	19,5	0,43
Other not sta- ted heat losses and balancing error			554,5	12,25
			4.524,9	100,00

TABLE 34. CARBON BALANCE

F e e d	1 kg of coal	Carbon con- tent "C" 42.72%	Amount kg C/kg of coal 0,4272	% share 100,00
<u>Output:</u>				
Clean gas	0,6062 m ³ /kg coal	0,176 kg/m ³ _N	0,1067	24,98
Waste gases flare	0,3348 m ³ /kg coal	0,490 kg/m ³ _N	0,1640	38,39
CO ₂ vent	0,1702 m ³ /kg coal	0,512 kg/m ³ _N	0,0871	20,39
Other vents	0,3615 m ³ /kg coal	0,0326 kg/m ³ _N	0,0118	2,76
Liquid prod- ucts (gaso- line, medium oil, tar, phe- nol)	0,0594 kg/kg coal	78,15%	0,0464	10,86
Heavy tar	0,00625 kg/kg coal	72%	0,0045	1,05
Slag-ash	0,1625 kg/kg coal	2,83%	0,0046	1,08
Losses (waste- water, etc.) and balancing error			0,0021	0,49
			0,4272	100,00

TABLE 35. SULFUR BALANCE

Coal feed	1 kg	S content 1.15%	Amount (gS/kg of coal) 11.5	% share 100
<u>Output:</u>				
Slag	0,1625 kg/kg coal	0,1375%	0,223	1,94
Waste gases flare	0,3348/m ³ /kg coal	31,29 gS/m ³ _N	10,477	91,11
CO ₂ flare	0,1702 m ³ /kg coal	0,0258 gS/m ³ _N	0,0038	0,033
Clean gas	0,6062 m ³ /kg coal	2,14.10 ⁻⁶ gS/m ³ _N	1,30.10 ⁻⁶	0,000
Liquid pro- ducts	0,0594 kg/kg coal	0,8%	0,475	4,13
Heavy tar	0,00625 kg/kg coal	0,71%	0,044	0,38
Other vents	0,3615 m ³ /kg coal	1,06 g/m ³ _N	0,383	3,33
Total			11,61	100,923
Balancing error			+ 0.11	+ 0.923%

TABLE 36. EMISSIONS OF OTHER MAJOR POLLUTANTS

(During gasification of 10 t/h of dried lignite)

As determined by measurements, the following is emitted during gas production according to Lurgi process at a rate of 10 t of dried Kosovo lignite per hour:

- a) From various vents in sections: Generators, Phenosolvan, Tar Separation and Storage (Measurement Points: 2.2; 3.2; 3.5; 13.1; 13.3; 13.5; 13.7; 14.5; 14.9; 15.3)

Pollutants	Flow rate (m_N^3/h)	Concentration (g/ m_N^3)	Amount g
Sulfur (H_2S ; COS, CH_3SH , $\text{CH}_3\text{CH}_2\text{SH}$) As "S"	3615	1,06	3 832
<u>Ammonium</u> (NH_3)	3615	0,11	398
<u>Phenols</u>	3615	1,28	4 627
<u>Hydrocyanic acid</u> (HCN)	3615	0,0099	35,8
<u>Hydrocarbons</u> (C_nH_m)	3615	0,4	1 446
<u>Hydrogen</u> (H)	3615	0,3773	1 364
<u>Carbon monoxide</u> (CO)	3615	1,239	4 478
<u>Carbon dioxide</u> (CO_2)	3615	86,59	313 032
<u>Methane</u> (CH_4)	3615	0,0627	227
<u>Particulates</u>	3615	41,08	148 498

TABLE 36. (continued)

b) From CO₂ Vent; Section Rectisol; Measurement Point 7.2.

Pollutants	Flow rate (m _N ³ /h)	Concentration (g/m _N ³)	Amount g
<u>Sulphur</u> (H ₂ S, COS, CH ₃ SH) (CH ₃ CH ₂ SH)			
As "S"	1702	0,0258	43,9
<u>Ammonium</u> (NH ₃)	1702	0,01	17,0
<u>Phenols</u>	1702	0,068	115,7
<u>Hydrocyanic acid</u> (HCN)	1702	0,0153	26,0
<u>Hydrocarbons</u> (C _n H _m)	1702	6,557	11169
<u>Hydrogen</u> (H)	1702	0,719	1 224
<u>Carbon monoxide</u> (CO)	1702	0,0	0,0
<u>Carbon dioxide</u> (CO ₂)	1702	1860	3 165700
<u>Methane</u> (CH ₄)	1702	5,713	9726

TABLE 36. (continued)

c) From Plant waste gases Large Flare, Measurement
Point 20.1. (Waste gases from MP 3.6; 13.6; 7.1)

Pollutants	Flow rate (m_N^3/h)	Concentra- tion (g/m_N^3)	Amount g	After inci- neration, g
<u>Sulphur</u> (H_2S ; COS , CH_3SH , $\text{CH}_3\text{CH}_2\text{SH}$) As "S"	3348	26,88	89 994	
<u>Ammonium</u> (NH_3)	3348	0,52	1 741	
<u>Phenols</u>	3348	0,04	134	
<u>Hydrocyanic acid</u> (HCN)	3348	0,1	335	
<u>Hydrocarbons</u> (C_nH_m)	3348	13,4	44 863	
<u>Hydrogen</u> (H)	3348	2,534	8 485	
<u>Carbon monoxide</u> (CO)	3348	45,2	151 247	
<u>Carbon dioxide</u> (CO_2)	3348	1635,6	5 475 896	6 154 000
<u>Methane</u> (CH_4)	3348	3,344	11 196	
<u>Nitrogen oxides</u> (NO_2)	3348			5 164
<u>Sulphur dioxide</u> (SO_2)	3348			179 988

TABLE 36. (continued)

d) In the slag (Measurement point 12.2)

Pollutants	Flow rate (t/h)	Concentration (g/t)	Amount g
Sulfur as "S"	1,625	1,33	2,161

e) In Wastewater (Measurement Point 12.3)

Pollutants	Flow rate m^3/h	Concentration g/m^3	Amount g
<u>Sulphur "S"</u> (Sulphites, thiosulphates, sulphates, rhodanides, hydrogen sulphide)	1,0	155	155
<u>Ammonium</u>	1,0	1,9	1,9
<u>Phenols</u>	1,0	1,227	1,227

Blank

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KOSOVO GASIFICATION TEST PROGRAM RESULTS—PART II DATA ANALYSIS AND INTERPRETATION

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Abstract

This presentation is a progress report on an EPA-sponsored program to characterize environmental problems associated with the gasification of lignite in a commercial-scale plant using Lurgi gasifiers. The data acquisition activities associated with this program are being conducted at a gasification complex in the Kosovo region of Yugoslavia as an international, cooperative effort between the United States and Yugoslavia.

The Kosovo test program is being implemented in two phases. Phase I, now completed, addressed major and minor pollutant emissions. Phase II, to begin in the summer of 1979, will focus on significant trace pollutant emissions, such as trace elements and hazardous trace organics.

Because this presentation is based on the data that was gathered during the first test phase, it addresses primarily the bulk properties of the plant's major emission and effluent streams. It will be presented in two parts. The first part, by M. Mitrović, addresses test procedures and results. The second part, by Radian Corporation, considers the implications of those results in relation to control requirements for U.S. gasification plants.

INTRODUCTION

The overall objective of the Kosovo test program is to characterize the environmental problems associated with an operating, state-of-the-art, commercial-scale, Lurgi gasification system. Because the Lurgi process has been prominently mentioned in several companies' plans for pressurized gasification systems in the United States, the U.S. Environmental Protection Agency (EPA) is anxious to develop a sound basis for ensuring the environmental acceptabil-

ity of those facilities. Through its participation in the Kosovo test program, the EPA hopes to gather critical data needed to specify control priorities and support reasonable performance standards for future U.S. gasification facilities based on Lurgi technology.

The Kosovo test program is divided into two phases of effort. In Phase I, a broad screening study of the Kosovo Plant and its emission streams was conducted. Approximately 50 key process and emission streams were sampled, and analyses were performed to determine the concentrations of the major components present in those streams. Phase I testing was completed in November 1979.

In Phase II of the Kosovo test program, a more select group of process and emission streams (approximately 30) will be characterized in greater detail. A major portion of this test phase will involve measuring the concentrations of trace and minor components in the plant's "high priority" emission streams. Work on this test phase is scheduled to be initiated in early summer of 1979.

The first part of this paper summarizes the processes and emission streams studied, the procedures used, and the results obtained during the Phase I test period. This writeup includes an interpretive analysis of the Phase I test results. The topics to be addressed include:

- Lurgi process environmental problems and control priorities, and applicability of the Kosovo data to the U.S. gasification industry;
- Key data gaps, additional questions raised, and problems unresolved by the Phase I test results; and
- Phase II test plans.

As a result of the Phase I test program, the emission streams specifically associated with the Kosovo gasification facility and generally associated with Lurgi technology have been defined. In subsequent sections of this paper, the data gathered to characterize the air emis-

*Speaker.

sions, liquid effluents, and solid wastes generated in the Kosovo plant are discussed, and plans for future testing are summarized.

In order to provide a consistent basis for the discussions that follow, the reader's attention is directed toward Table 1 and Figures 1 through 8. These materials indicate the sources for all of the plant's major emission streams.

Air Emission Streams

The major sources of air emissions in the Kosovo plant are summarized in Table 2. As indicated in that table, there are nine major classes of air emission sources in the plant.

One of the most significant air emission sources at Kosovo is the plant's Rectisol unit. Because the Kosovo Rectisol unit is a selective (Rectisol II) acid-gas removal process, a CO_2 -rich stream that normally contains minor amounts of H_2S and other sulfur species is generated along with an H_2S -rich stream that should contain most of the other acid gases and sulfur species. The CO_2 -rich stream is vented directly to the atmosphere at Kosovo. The same approach has been proposed in several conceptual U.S. plants. Phase I data do not indicate that this would be a serious problem, except perhaps during upset conditions. Components other than CO_2 that were found in the CO_2 -rich vent gas include methane and other light hydrocarbons (which may present hydrocarbon emission problems in some areas of the United States because of the relatively large flow rate of this stream). Minor amounts of H_2S , HCN , and mercaptans were also found in this stream.

The H_2S -rich gas stream generated in the Rectisol unit is a significant waste stream. At Kosovo, this stream is flared. In the United States, a treatment process (e.g., Claus, Stretford) that produces elemental sulfur is the preferred approach. However, potential problems with this approach are indicated by the Phase I data. The CO_2 content of this stream may be too great to permit the economical use of a Claus system. Also, the presence of mercaptans and hydrocarbons in this stream could result in residual sulfur or hydrocarbon emissions.

As shown in Figure 3, several potential air emission sources are associated with the Kosovo plant lignite drying system. This section of the plant is not addressed in this paper because it will not be studied until Phase II.

The coal-feeding system at Kosovo is another significant air emission source. The high-pressure gas stream from the coal lock system is flared, while the low-pressure vent stream is released directly to the atmosphere. Venting this stream would not be an environmentally acceptable option in the United States.

The generator startup vent gas stream was not studied in Phase I. Variations in the flow and composition of this stream will be studied in Phase II.

In the tar separation section, the condensation of tars, oils, and phenolic water (at about 25 atm pressure) and the subsequent depressurization and release of those liquids into a series of surge tanks results in generation of:

- A low-pressure flash gas stream that is routed to the flare; and
- Flash gases from the tar, medium oil, and phenolic water surge tanks that are vented directly to the atmosphere.

The vent gas streams leaving the medium oil and phenolic water surge tanks at Kosovo are particularly significant because of their high flow rates and relatively high concentrations of problem pollutants.

The only remaining waste stream that is particularly significant at Kosovo is the phenosolvan unit condensate stripper vent. This stream results from the steam stripping of process condensate upstream of the phenol plant ether extraction section. As anticipated, this stream was found to contain NH_3 , acid gases, and a variety of other volatile components that leave the tar separation section with the process gas liquor.

All of the streams mentioned above would require considerable attention in U.S. gasification plants. With the exception of the two Rectisol section acid-gas vent streams (which require special attention), all of these streams should be collected and either incinerated or recycled.

Other air emission streams that are not as significant as those mentioned above but that will require attention in a U.S. gasification facility are the following:

- Coal bunker and ash lock vent gases: these streams mainly represent potential sources of particulate emission; and
- Storage tank vent gases: these sources should be controlled in a U.S. Lurgi plant, but their collective impact is considerably less than the impact caused by the surge tank vents in the tar separation section.

TABLE 1. SIGNIFICANT KOSOVO PLANT PROCESS AND EMISSION STREAMS

Stream Number	Stream Description	Stream Type	Estimated Flow Rate ^a	Comments on Components of Environmental Concern
Fleissner Drying - See Figure 3				
1.0	"Wet" coal from mine	S	24 MT/hr	Detailed characterization desired
1.1	Coal bunker vent	G	? }	Coal dust plus volatile organics and possibly inorganics
1.2	Autoclave vent	G		
1.3	Fleissner Condensate	L	?	Detailed characterization desired
1.4	Condensate tank vent	G	?	Volatile organics/inorganics
Gasification - See Figure 4				
2.0	Dried sized coal	S	16.0 MT/hr	Detailed characterization desired
2.1	Coal bunker area - ambient sample	G	-	Mostly air with traces of coal dust and possibly raw gas components
2.2	Coal bunker vent	G	4000 Nm ³ /hr	
3.1	Coal bucket vent	G	26 Nm ³ /hr ^b	Coal dust plus raw gas components
3.2	Low pressure coal lock vent	G	36 Nm ³ /hr	
3.3	Start-up vent (to flare)	G	?	
3.4	Liquor tank vent	G	40 Nm ³ /hr	Raw gas components
3.5	Ash lock vent	G	28 Nm ³ /hr ^b	Steam plus ash dust
3.6	High pressure coal lock vent (to main flare)	G	350 Nm ³ /hr	Coal dust plus raw gas components
12.1	Gasifier ash (dry)	S	2.7 MT/hr	Leachable species
12.2	Gasifier ash (wet)	S	>2.7 MT/hr	Leachable species
12.3	Gasification section wastewater	L	3 m ³ /hr	Coal and ash dust plus soluble contaminants leached from ash

Continued - Next page

TABLE 1 (continued)

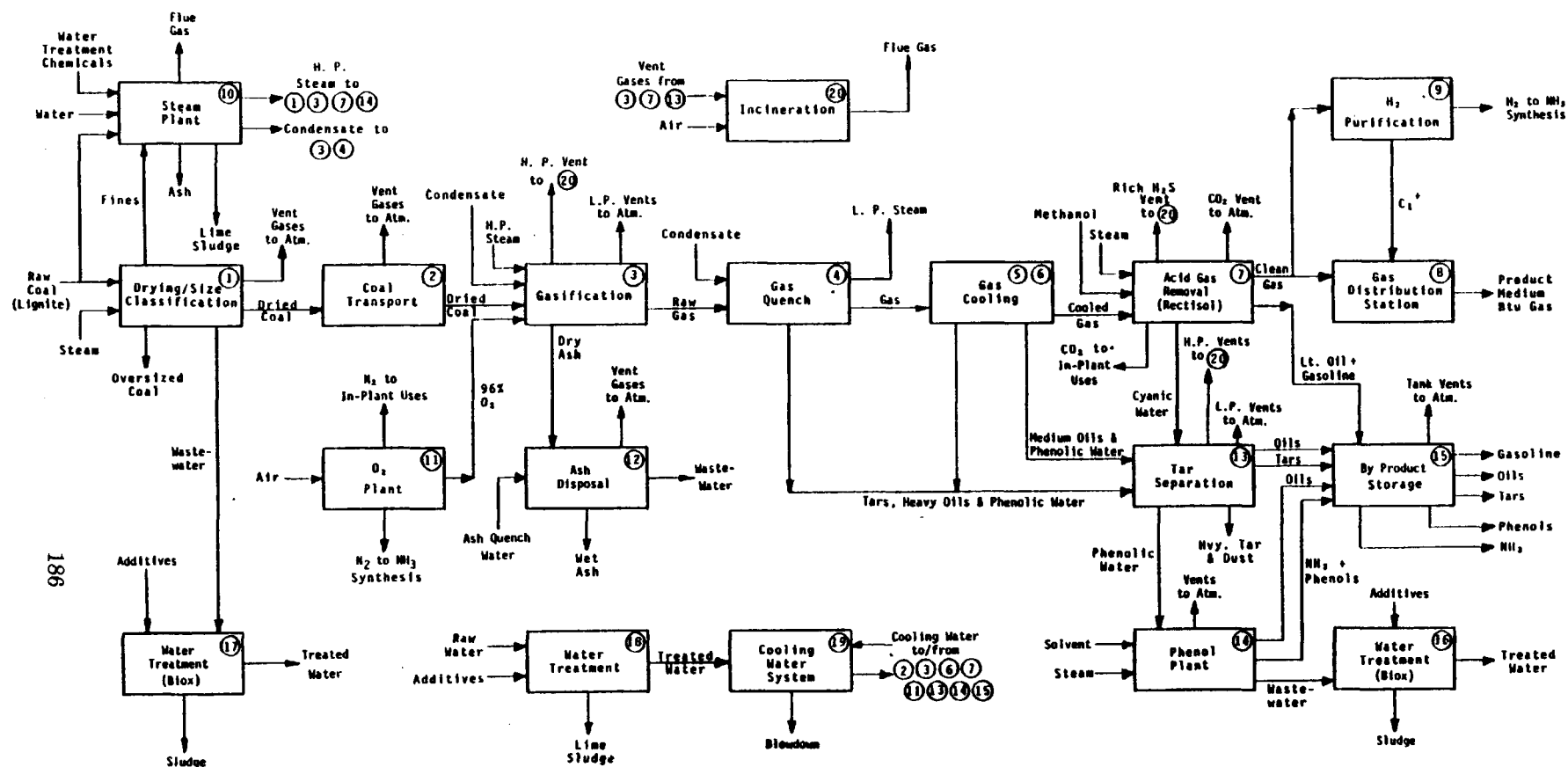
Stream Number	Stream Description	Stream Type	Estimated Flow Rate ^a	Comments on Components of Environmental Concern
Tar Separation - See Figure 5				
13.1	Tar tank vent	G	.4 Nm ³ /hr ^c	Volatile organics/inorganics
13.2	Impure tar tank vent	G	?	Volatile organics/inorganics
13.3	Medium oil tank vent	G	.25 Nm ³ /hr ^c	Volatile organics/inorganics
13.4	Impure medium oil tank vent	G	?	Volatile organics/inorganics
13.5	Condensate tank vent	G	?	Volatile organics/inorganics
13.6	Expansion gases (to main flare)	G	26 Nm ³ /hr	Volatile organics/inorganics
13.7	Phenolic water tank vent	G	13 Nm ³ /hr ^c	Volatile organics/inorganics
13.8	Heavy tar and dust	L/S	.1 MT/hr	Volatile organics/inorganics
13.9	Heavy tar	L	.4 MT/hr	Volatile organics/inorganics
13.10	Light tar	L		Volatile organics/inorganics
13.11	Medium oil	L	.25 MT/hr	Volatile organics/inorganics
13.12	Phenolic water to phenosolvan	L	13 m ³ /hr	Detailed characterization desired
Rectisol - See Figure 6				
7.1	H ₂ S rich gas (to main flare)	G	2,500 Nm ³ /hr	Acid gases, sulfur species, hydrocarbons
7.2	CO ₂ vent gas	G	2,200 Nm ³ /hr	Acid gases, sulfur species, hydrocarbons
7.3	Rectisol inlet gas	G	17,200 Nm ³ /hr	Acid gases, sulfur species, hydrocarbons
7.4	Rectisol outlet gas	G	12,000 Nm ³ /hr	Acid gases, sulfur species, hydrocarbons
7.5	Cyanic water	L	.8 m ³ /hr	Acid gases, sulfur species, hydrocarbons
7.6	Product gasoline to storage	L	.13 MT/hr	Volatile components which can escape with storage tank vent gases
7.7	Raw gas to CO ₂ absorber	G	14,500 Nm ³ /hr	Acid gases, sulfur species, hydrocarbons
7.8	Regenerated methanol	L	200 m ³ /hr	Acid gases, sulfur species, hydrocarbons

Continued - Next page

TABLE 1 (continued)

Stream Number	Stream Description	Stream Type	Estimated Flow Rate ^a	Comments on Components of Environmental Concern
Phenosolvan - See Figure 7				
14.0	Phenosolvan inlet water	L	13.1 m ³ /hr	Comprehensive characterization desired
14.1	Cyclone (C1) vent	G	2 Nm ³ /hr	
14.2	Phenolic water tank (T2) vent	G	?	Volatile organics/inorganics; particularly acid gases, sulfur species, hydrocarbons
14.3	Unclean oil tank (T3) vent	G	?	
14.4	Filtered water tank (T5) vent	G	?	
14.5	Degasing column (C7) vent	G	9 Nm ³ /hr	
14.6	NH ₃ stripper cooler (E25) vent	G	4 Nm ³ /hr	
14.7	2nd degasing column (C9) vent	G	.4 Nm ³ /hr	
14.8	Slop tank (T10) vent	G	?	
14.9	Phenol storage tank (T24) vent	G	.08 Nm ³ /hr ^c	Ether vapors, other volatile organics
14.10	DIPE tank (T22) vent	G	.5 Nm ³ /hr	
14.11	Treated wastewater	L	13 m ³ /hr	Comprehensive characterization desired
14.12	NH ₃ absorber (C26) vent	G	?	Volatile organics/inorganics, acid gases, NH ₃
14.13	NH ₃ storage tank (T27) vent	G	?	
14.14	NH ₄ OH product to storage	L	.2 MT/hr	NH ₃ + other volatile species (acid gases, organics)
14.15	Unclean oil to storage	L	.03 MT/hr	Volatile organics
14.16	Raw phenols to storage	L	.09 MT/hr	Comprehensive characterization desired
By-Product Storage - See Figure 8				
15.1 A/B/C ^d	Tar tank vent	G/L/S	.5 Nm ³ /hr ^c	Volatile species present in all by-product streams
15.2 A/B/C ^d	Medium oil tank vent	G/L/S	.25 Nm ³ /hr ^c	
15.3 A/B/C ^d	Gasoline tank vent	G/L/S	.13 Nm ³ /hr ^c	
15.4 A/B/C ^d	Raw phenol tank vent	G/L/S	.08 Nm ³ /hr ^c	
15.5 A/B/C ^d	Unclean oil tank vent	G/L/S	.03 Nm ³ /hr ^c	
15.6 A/B/C ^d	NH ₄ OH tank vent	G/L/S	.2 Nm ³ /hr ^c	
19.1	Cooling tower vent gases	G	?	Volatile species resulting from process leaks into the circulating cooling water system
20.1	Waste gases to flare (3.6 + 7.1 + 13.6)	G	2,900 Nm ³ /hr	Behavior of hazardous species in flare

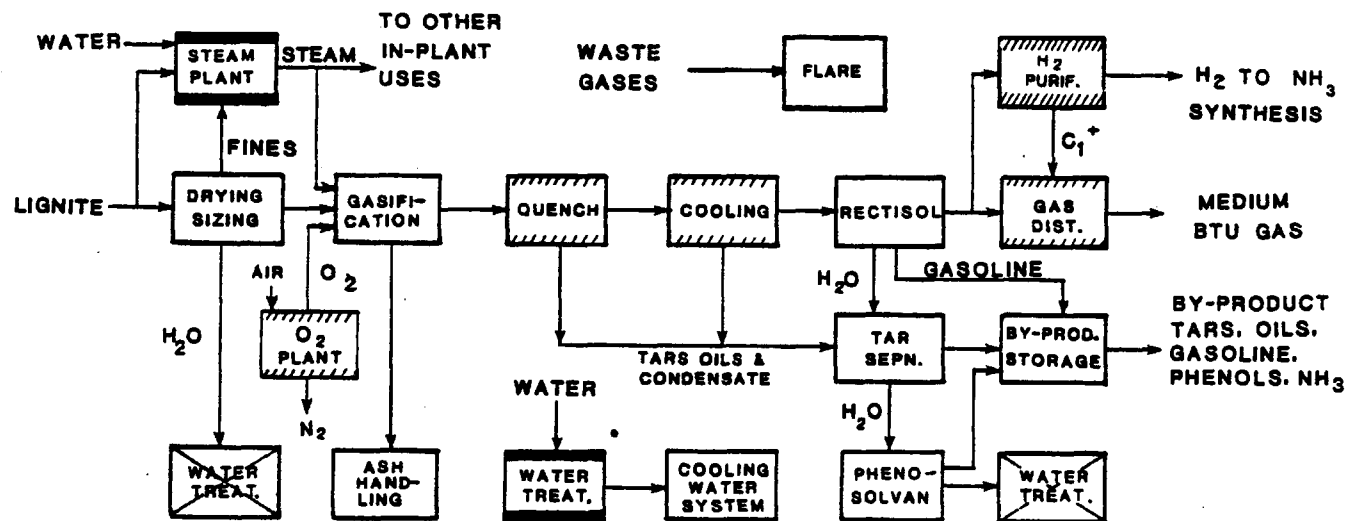
^aFlow data normalized to a one-gasifier-in-service basis.^bProcess gas flow only; does not consider the steam which is present.^cTank vent flows assumed equal to the volume displaced by normal process stream flow.^dA - vent gas; B - liquid in tank; C - sludge in bottom of tank.



NOTES:
 H. P.-High Pressure
 L. P.-Low Pressure
 ○ -Number Codes Used to Identify Specific Plant Sections are Keyed to the Sample Points listed in Table 1.

RADIAN CORPORATION P.O. BOX 9948/AUSTIN, TEXAS/78768		
FIGURE 1 OVERALL PLANT FLOW SCHEME KOSOVO LURGI GASIFICATION PLANT		
SIZE	CODE IDENT NO.	DRAWING NO.
C	200-143	70-1276-3
SCALE N/S		SHEET 1 OF 1

Figure 1. Overall plant flow scheme for Kosovo Lurgi gasification plant.



PLANT SECTIONS WHICH ARE
BEING STUDIED IN THE
KOSOVO TEST PROGRAM



PLANT SECTIONS NOT BEING STUDIED



PLANT SECTION NOT IN SERVICE



PLANT SECTION IS NOT A DIRECT SOURCE OF
MAJOR PROCESS. WASTE OR BY-PRODUCT
STREAMS REQUIRING CHARACTERIZATION
(EXCLUDES CONSIDERATION OF FUGITIVE EMISSIONS)



PLANT SECTION IS A SIGNIFICANT WASTE STREAM
SOURCE: HOWEVER, ADEQUATE CHARACTERIZATION
DATA ALREADY EXISTS FOR THIS TYPE OF SOURCE

Figure 2. Simplified flow schematic: Kosovo gasification complex.

Figure 4. Process flow diagram showing sampling points in Kosovo plant generator section.

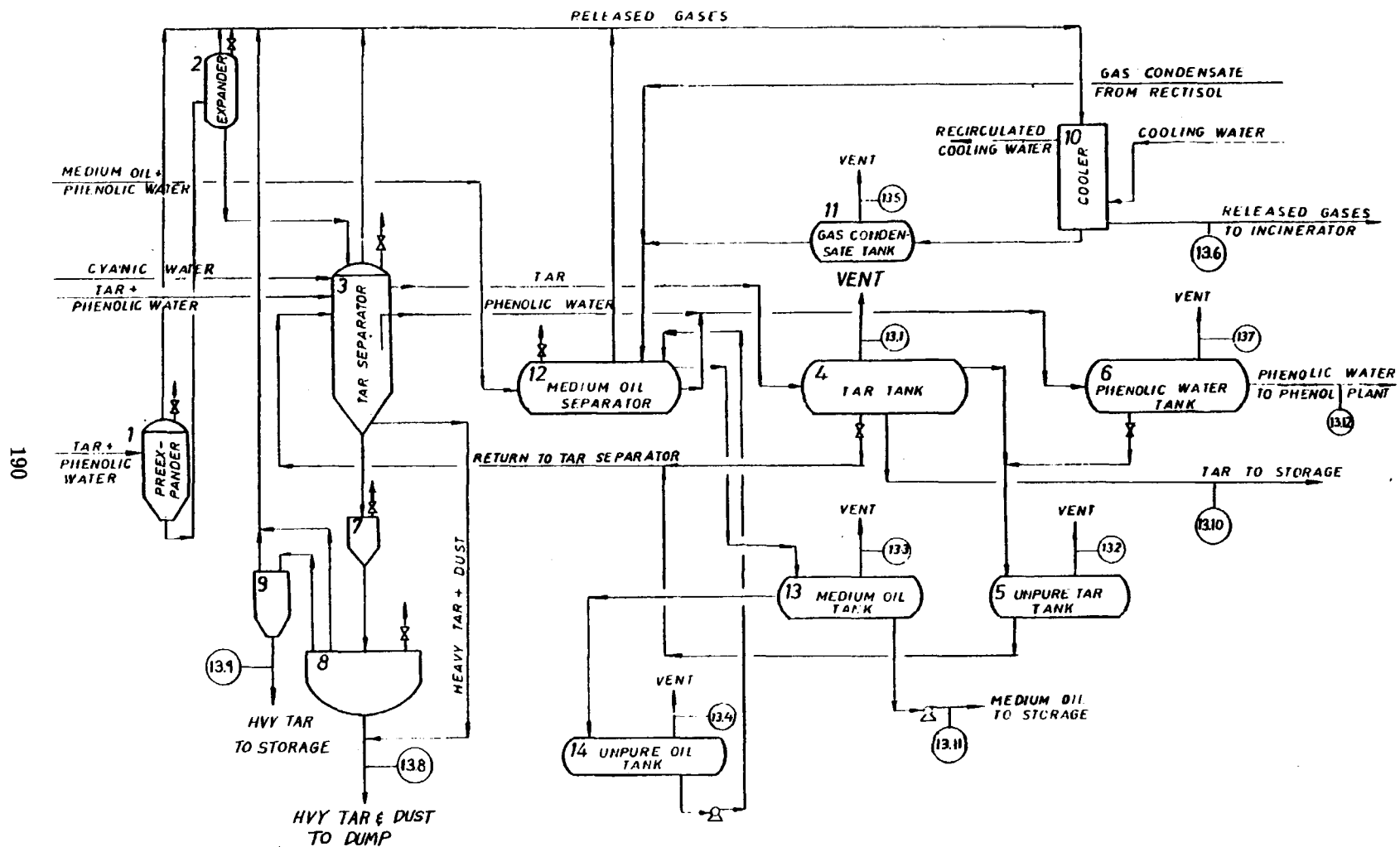


Figure 5. Process flow diagram showing sampling points in Kosovo plant tar separation section.

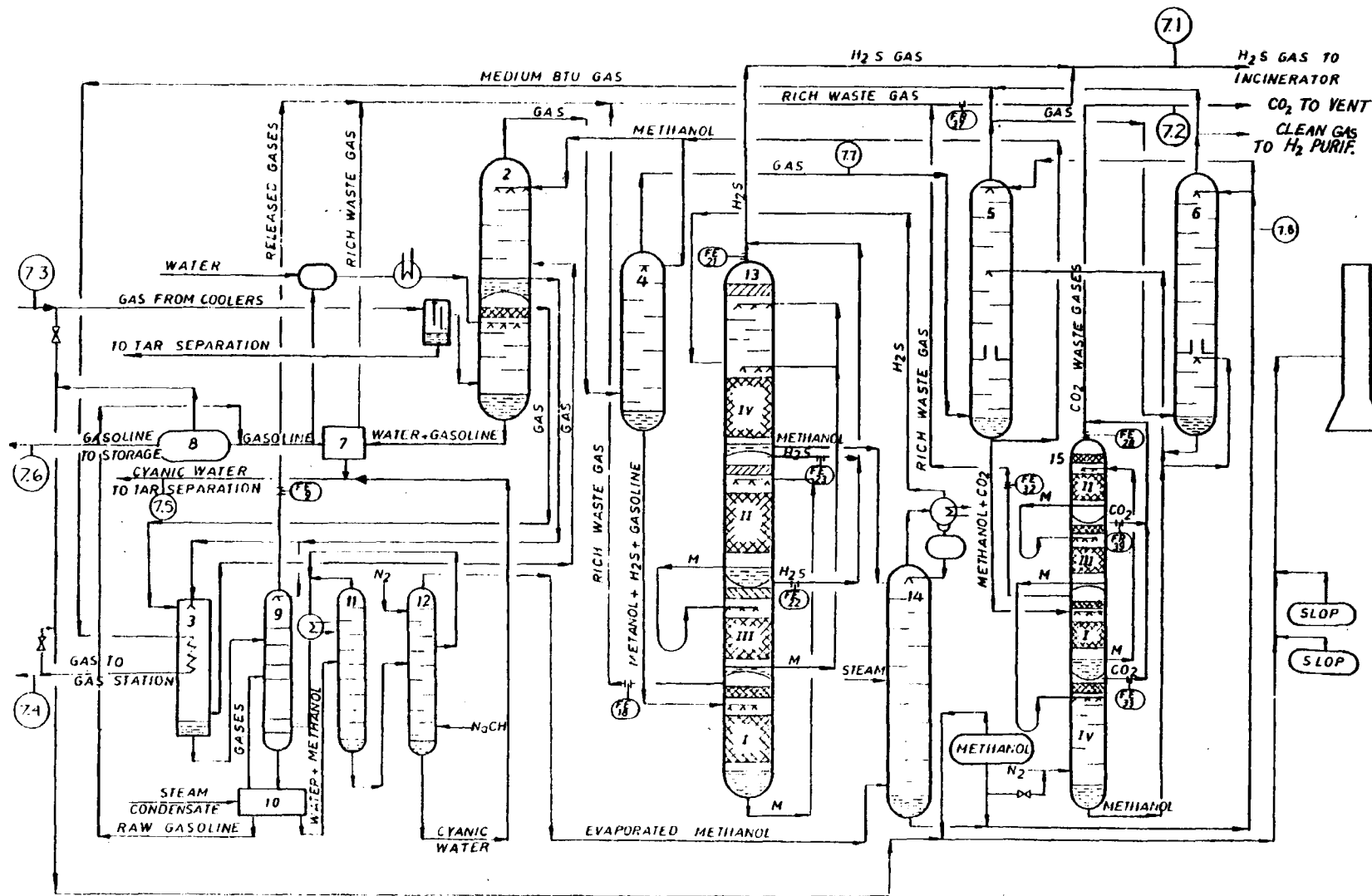


Figure 6. Process flow diagram showing sampling points in Kosovo plant Rectisol section.

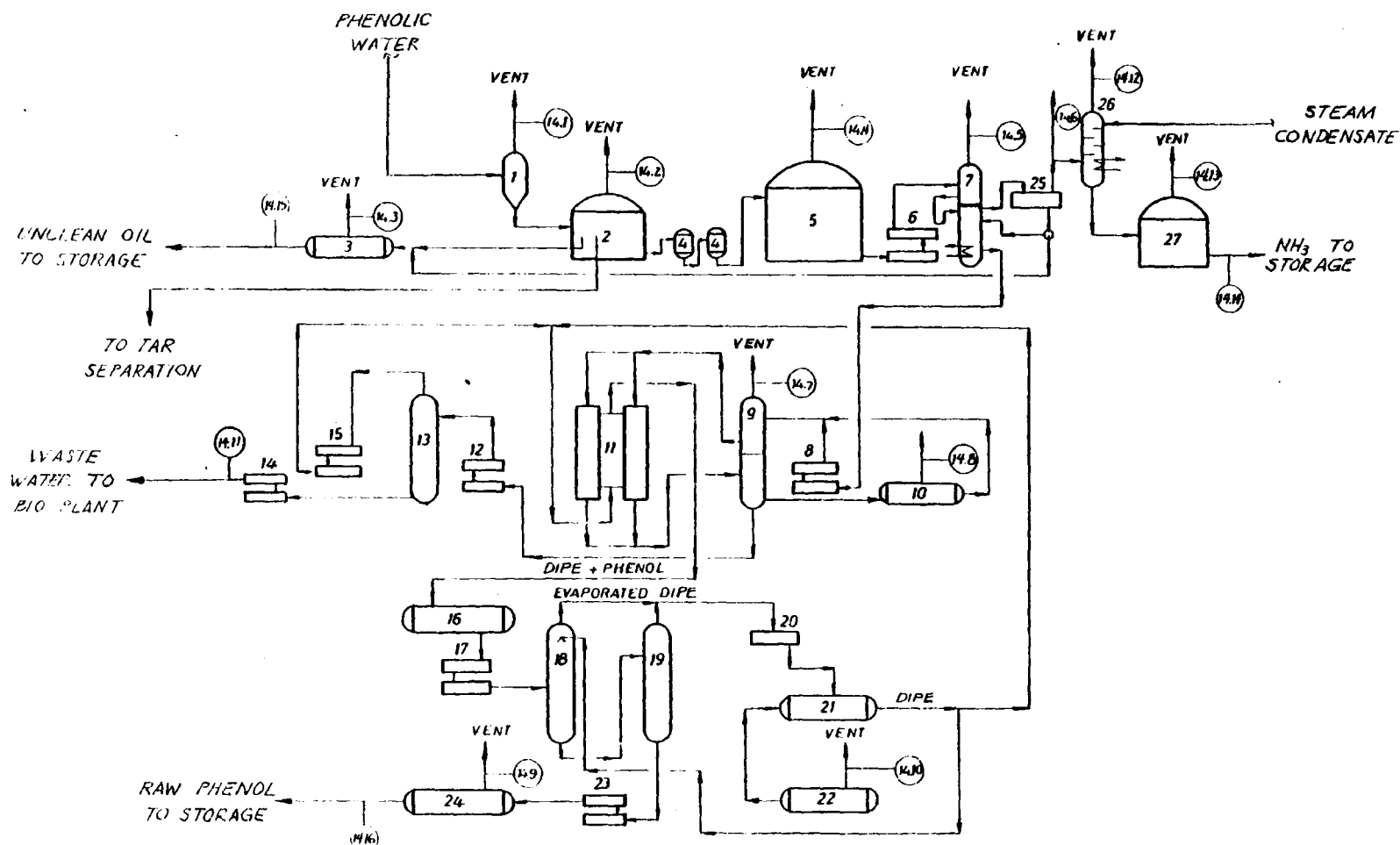
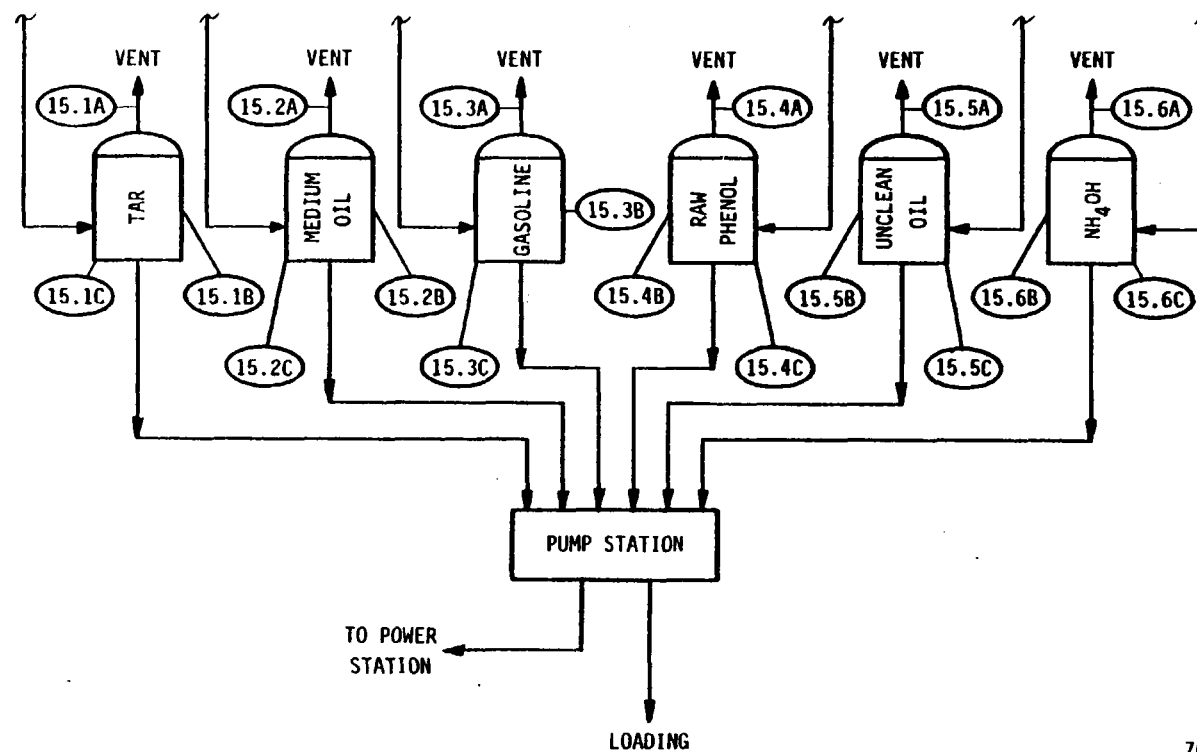


Figure 7. Process flow diagram showing sampling points in Kosovo plant phenosolvan section.



70-1466-1

LEGEND

A - VENT GAS

B - LIQUID IN TANK

C - SLUDGE

Figure 8. Process flow diagram showing sampling points in Kosovo plant byproducts storage area.

TABLE 2. KOSOVO PLANT: MAJOR AIR EMISSION SOURCES

	Approximate Flow Per Gasifier* (Nm ³ /hr)	Disposition	Studied in Phase I	To Be Studied in Phase II
1. Rectisol Process				
H ₂ S Rich Gas (7.1)	[2500]	Flare	x	x
CO ₂ Rich Gas (7.2)	5000	Vent	x	x
2. Fleissner Lignite Drying Process				
Autoclave Vent (1.2)	Unknown	Vent		x
Condensate Tank Vent (1.4)	Unknown	Vent		
3. Coal Feeding System (Lock Hopper) Vents				
High Pressure (3.6)	400	Flare	x	x
Low Pressure (3.2)	40	Vent	x	x
4. Generator Startup Gases (3.3)	?	Vent		x
5. Gas Cooling/Tar Separation Section Flash Gases				
High Pressure Expansion Gases (13.6)	[30]	Flare	x	x
Tar/Medium Oil Surge Tank Vents (13.1-13.4)	50	Vent	x	x
Condensate Surge Tank Vents (3.4; 13.5; 13.7)	40	Vent	x	x
6. Incinerator (20.1)	[2900]	Flare	x	x
7. Phenosolvan Condensate Strippers (Primarily 14.5)	400	Vent	x	x
8. By-Product Storage Tank Vents (15.1-15.6)	1	Vent	x	x
9. Air/Oxygen-Rich Vents				
Ash Lock Vent (3.5)	30	Vent	x	x
Coal Bunker Vents - Fleissner (1.1)	Unknown	Vent		x
- Gasification (2.2)	4000	Vent	x	x

*Note: Data points in brackets are derived from plant design data. Other data points are measured values.

A reasonable basis for establishing priorities not only for the air emission streams studied in the Phase I program but also for the individual components present in those streams is provided by EPA's source analysis model (SAM). This analysis tool, which was developed under EPA contract by Acurex Corporation,¹ provides a convenient format for assessing the potential environmental problems associated with particular emission streams. The SAM analysis approach relies heavily on health-effect related multiple acute toxicity effluent (MATE) values that are listed for a variety of organic and inorganic compounds in Reference 2.

The health-effect related MATE values for

the specific gaseous species measured in the Phase I test program are listed in Table 3. An inspection of Table 3 shows that the most toxic ambient pollutants addressed in the Phase I test program were benzene and methyl and ethyl mercaptans. MATE values can be used to establish priorities for emission stream control by making the following calculations:

$PDOH_i$ = Potential degree of hazard for component i

$$= \frac{\text{Measured concentration of pollutant } i}{\text{MATE value for pollutant } i}$$

PTUDR = Potential toxic unit discharge rate

$$\text{PTUDR} = F \times \sum_{i=1}^{\text{All components}} \text{PDOH}_i$$

where F = stream flow rate.

Because of the nature of these calculations, PDOHs are useful in establishing priorities for

the components present within specific streams, and PTUDRs are useful in comparing one stream to another.

Potential degree of hazard calculations for the high-priority emission streams that were discussed above are shown in Table 4. The gas stream analytical data used to support these calculations are provided in Table 5.

By examining the data presented in Table 4, the following conclusions can be drawn:

- With respect to the fixed gases analyzed, CO appears to be the most significant pollutant.

TABLE 3. KOSOVO GASES AND THEIR RESPECTIVE MATE VALUES (AIR-HEALTH)

	Component	($\mu\text{g}/\text{m}^3$)
<u>Fixed Gases</u>	H ₂	NA
	O ₂	NA
	CH ₄	3.3×10^5
	CO	4.0×10^4
	CO ₂	9.0×10^6
<u>Hydrocarbons</u>	C ₂ 's	6.1×10^6
	C ₃ 's	9.0×10^6
	C ₄ 's	1.4×10^6
	C ₅ 's	1.8×10^6
	C ₆ 's	3.6×10^5
	Benzene	3.0×10^3
	Toluene	3.8×10^5
<u>Sulfur Species and Other</u>	H ₂ S	1.5×10^4
	COS	4.4×10^5
	CH ₃ SH	1.0×10^3
	C ₂ H ₅ SH	1.0×10^3
	NH ₃	1.8×10^4
	HCN	1.1×10^4
	Phenol	1.9×10^4

TABLE 4. CALCULATED PDOH AND PTUDR VALUES FOR "HIGH-PRIORITY" AIR EMISSION STREAMS SAMPLED AT KOSOVO DURING THE PHASE I TEST PROGRAM

	3.2 Lock Hopper Vent Low Pressure	3.6 Vent Gases High Pressure	13.1 Tar Tank Vent	13.3 Medium Oil Tank Vent	13.6 Tar Separation Expn. Gases	13.7 Phen. H ₂ O Tank Vent	14.5 Stripper Vent	7.1 H ₂ S Vent	7.2 CO ₂ Vent	7.3 Rectisol Inlet Gas
<u>Fixed Gases</u>										
H ₂	-	-	-	-	-	-	-	-	-	-
O ₂	-	-	-	-	-	-	-	-	-	-
N ₂	-	-	-	-	-	-	-	-	-	-
CH ₄	200	240	2.2	170	130	4.3	TR	91	20	280
CO	2900	4100	NF	NF	2300	NF	NF	810	NF	4100
CO ₂	91	80	7.0	190	160	63	72	190	200	72
<u>Hydrocarbons</u>										
C ₂	1.6	1.6	TR	1.3	0.9	TR	TR	0.7	0.7	1.5
C ₃	0.7	0.4	TR	0.4	0.7	TR	TR	0.4	0.7	0.9
C ₄	1.9	0.4	TR	3.7	5.6	TR	TR	1.9	TR	3.7
C ₅	0.9	0.4	TR	1.8	3.6	TR	TR	1.8	TR	0.7
C ₆	3.2	1.1	TR	11.0	11.0	TR	NF	1.1	NF	2.1
Benzene	2300	-	4700	5800	12,000	19,000	NF	-	-	700
Toluene	-	-	1.1	22	43	65	NF	-	-	-
<u>Sulfur Species</u>										
H ₂ S	71	110	190	1300	1200	190	760	2300	0.5	470
COS	1.1	1.9	NF	<2.5	-	NF	NF	3.5	NF	0.5
CH ₃ SH	590	910	1400	2200	2100	1500	330	9300	18	1200
C ₂ H ₅ SH	250	750	690	1300	810	1200	83	2100	9.7	280
<u>Other</u>										
NH ₃	290	NF	110	-	830	510	2900	94	0.2	0.2
HCN	5.3	19	14	-	7.5	4.2	130	9.1	1.4	6.6
PDOH (Stream)*	6700	6200	7100	11,000	20,000	23,000	4300	15,000	250	7100
Stream Flow Rate (Nm ³ /hr)	40	400	2	50	26	40	400	2500	5000	-
PTUDR (Nm ³ /hr)	2.7E5	2.5E6	1.4E4	5.5E5	5.1E5	9.0E5	1.7E6	3.7E7	1.3E6	

All
Components

$$* \text{PDOH (Stream)} = \sum_{i=1} (\text{PDOH})_i$$

TABLE 5. GAS STREAM ANALYTICAL DATA FOR "HIGH-PRIORITY" PHASE I EMISSION STREAMS

Compound	3.2 Lock Hopper Vent Low Pressure	3.6 Vent Gases High Pressure	13.1 Tar Tank Vent	13.3 Medium Oil Tank Vent	13.6 Tar Separation Expn. Gases	13.7 Phen. H ₂ O Tank Vent	14.5 Stripper Vent	7.1 H ₂ S Vent	7.2 CO ₂ Vent	7.3 Rectisol Inlet Gas
<u>Fixed Gases (Vol. %)</u>										
H ₂	34.0	32.0	TR	NF	11.0	TR	NF	-	0.8	36.1
O ₂	0.7	0.2	21.0	0.9	0.5	13.0	9.0	0.5	0.1	0.6
N ₂	2.5	6.1	76.0	3.4	0.6	53.0	58.0	1.4	0.3	1.6
CH ₄	9.4	11.0	0.1	7.6	6.1	0.2	TR	4.2	0.9	13.0
CO	9.3	13.0	NF	NF	7.2	NF	NF	2.6	NF	13.0
CO ₂	42.0	37.0	3.2	86.0	72.0	29.0	32.0	86.0	94.0	33.0
<u>Hydrocarbons (Vol. %)</u>										
C ₂	0.7	0.7	TR	0.6	0.4	TR	TR	0.3	0.3	0.7
C ₃	0.3	0.2	TR	0.2	0.3	TR	TR	0.2	0.3	0.4
C ₄	0.1	0.02	TR	0.2	0.3	TR	TR	0.1	TR	0.2
C ₅	0.05	0.02	TR	0.1	0.2	TR	TR	0.1	TR	0.04
C ₆	0.03	0.01	TR	0.1	0.1	TR	NF	0.01	NF	0.02
Benzene	0.2	-	0.4	0.5	1.0	1.6	NF	-	-	0.06
Toluene	-	-	0.01	0.2	0.4	0.6	NF	-	-	-
<u>Sulfur Species (ppm)</u>										
H ₂ S	700	1100	1900	13,000	12,000	1900	7500	23,000	4.6	4700
COS	170	300	NF	<400	-	NF	NF	<560	0.5	80
CH ₃ SH	270	420	630	1000	950	680	150	4300	8.5	570
C ₂ H ₅ SH	90	270	250	480	290	420	30	740	3.5	100
<u>Others (g/100 Nm³)</u>										
NH ₃	530	NF	198	-	1500	920	5300	170	0.4	0.3
HCN	5.8	21	15.3	-	8.2	4.6	140	10	1.5	7.3

Data from Campaign Three Test; November 1978

- Negligible CO levels exist in several flash gas streams, apparently because of the low solubility of CO in both condensed organic and aqueous liquids.
- With respect to the light hydrocarbons analyzed, benzene appears to be by far the most significant source of environmental concern.
- With respect to the sulfur species analyzed, mercaptan levels appear to be at least as great a source of concern as H₂S.
- Between the two nitrogen species analyzed, NH₃ appears to be more of a problem than HCN.

While the data presented in Table 4 show some interesting trends, several factors limit the extent to which these data can be used to draw firm conclusions about the Phase I test results. Some of these factors are:

- The data presented in Table 5 are single-point measurements, not necessarily representative of either normal plant operation or the range of operating conditions likely to be encountered.
- Some degree of judgment is involved in selecting specific levels for most MATE values.
- Inherent inaccuracies exist in the sampling/analytical procedures used to gather Phase I test data.
- Other components (those not measured in Phase I) may have more of an impact on final PDOH and PTUDR values than any of the components measured thus far.

Generally, the Kosovo Phase I test data provide a reasonable definition of the scope and magnitude of the air emission problems that will have to be addressed in a U.S. Lurgi plant. These results also justify continued testing at Kosovo.

Some of the data needs indicated from Phase I test results are outlined below. Most of these needs will be addressed in subsequent phases of work at Kosovo.

- Levels of other hazardous components such as trace elements and trace organics encountered in key emission streams.
- Rectisol process performance information (this unit is the source of two key streams):
 - Further characterization of the H₂S-rich gas stream is desired to assess its suitability for feed to an elemental sulfur recovery unit. More specifically, levels of problem components such as mercaptans,

COS, hydrocarbons, and CO₂ (effectively a diluent) should be monitored as functions of time.

- Further characterization of the CO₂-rich vent gas stream is necessary to confirm that this stream can be safely vented to the atmosphere (as proposed in several U.S. designs). Possible sources of problems with this approach should be identified.
- Generator startup gases: Significance relative to the other key emission streams needs to be addressed. Although not addressed in the Phase I program, this effort will be initiated as part of the Phase II program.
- Fates of hazardous gas stream components in a combustion process: In a U.S. gasification facility, most of the emission streams identified in this paper would be collected and either recycled back into the process gas stream (unlikely because of the compression requirements involved) or incinerated (for example, in the firebox of onsite stream generators). If an incineration approach is used, the fates of hazardous species present in those streams needs to be assessed. Currently, no plans for making this type of measurement are incorporated into the Phase II test program.
- Fugitive emissions: A program to characterize the fugitive emissions from the Kosovo plant is now being discussed with the Yugoslavs.

Liquid Effluents, Liquid Byproducts, and Solid Wastes

Generally, the liquid and solid wastes produced in the Kosovo facility did not receive the same level of attention that the air emissions did in the Phase I test program. Considerable useful data concerning these streams was gathered, however.

The major Kosovo plant liquid effluent, liquid byproduct, and solid waste streams are summarized in Table 6. This table also indicates which streams are being studied in the Phase I and Phase II test programs.

The major aqueous waste stream at Kosovo is the phenosolvan effluent water stream. According to the plant design, this stream was to be treated in a biological oxidation process, but currently this system is not in operation.

TABLE 6. KOSOVO LURGI GASIFICATION PLANT—MAJOR SOURCES OF LIQUID EFFLUENTS,
LIQUID BYPRODUCTS, AND SOLID WASTES

	Approximate Flow*	Studied in Phase I	To Be Studied in Phase II
<u>Aqueous Wastes</u>			
Phenosolvan Effluent	13 MT/hr	x	x
Fleissner Condensate	Unknown		x
Generator Section Wastewater	3 MT/hr	x	x
<u>Liquid By-Products</u>			
Tars, Oils, Gasoline	.8 MT/hr	x	x
Phenols	.1 MT/hr		
NH ₄ OH	.2 MT/hr		
<u>Solid Wastes</u>			
Gasifier Ash		x	x
Heavy Tar & Dust		x	x
Other Process Residues			x (By-Product Storage Residues)

* Design values; normalized to a one gasifier in service basis.

Preliminary data obtained from a series of source screening samples indicate that the Kosovo plant's phenosolvan unit is effective in recovering the phenols present in the raw process gas liquor. However, as the data in Table 7 indicate, the organic loading in the effluent water from the phenosolvan unit is still substantial. The indicated phenol concentration is not sufficient to account for the COD figures that were obtained for that stream. As a result, it can be anticipated that the organic characterization work to be done in Phase II will shed considerable light upon the nature of the environmental hazards and control needs associated with that particular stream.

As shown in Figure 3, the generator section wastewater stream is a composite stream. It consists primarily of ash quench water. However, small quantities of coal bunker and ash lock vent gas scrubber blowdown liquid are also discharged via this stream. This stream has a relatively high pH because of the highly alkaline nature of the Kosovo ash.

Very little characterization data on the nature of the Kosovo plant liquid byproduct streams were gathered during the Phase I test period. What little data were gathered are pre-

sented in Table 8. One of the major points to be noted here is that the sulfur contents of the liquid byproducts become progressively higher with a move from "heavies" to "lights." These data indicate that heavy hydrocarbon byproducts similar to those generated at Kosovo could be used to satisfy onsite fuel needs in the United States without causing serious SO₂ emission control problems.

As mentioned previously, the bulk of the work to characterize the liquid and solid wastes associated with the Kosovo plant will be performed as part of the Phase II program. Some of the concerns in this area include:

- Trace and minor components present in all significant liquid and solid waste streams will be quantified. Of particular concern are the leachable species present in the solid waste streams and the soluble components found in the aqueous wastes.
- One of the most practical disposal options for the liquid hydrocarbon byproducts is to use these materials to satisfy onsite fuel needs. The fates of hazardous species present in those streams in a combustion process could cause concern, although no specific plans to study this problem have been made.

TABLE 7. KOSOVO WASTEWATER PROPERTIES (PHASE I DATA)

	Phenosolvan Effluent Water	Generator Section Wastewater	Units
pH	9.2-9.4	11.4-12.1	mg/l
Susp. Solids	150-190	180-590	mg/l
Diss. Solids	880-1300	1100-2100	mg/l
COD (K ₂ Cr ₂ O ₇)	3100-3300	.8-150	mg O ₂ /l
Phenols	170-270	-	mg/l
CN ⁻	.02	.01 Max.	mg/l
Cl ⁻	16-120	20-70	mg/l
SO ₄ ⁼	100-110	320-670	mg/l
CNS ⁻	3	.01-.03	mg/l
F ⁻	Trace	.6-1.2	mg/l
NO ₃ ⁻	11-12	4-6	mg/l

**TABLE 8. KOSOVO LURGI GASIFICATION PLANT
LIQUID BYPRODUCT DATA**

	Feed Coal (Dry)	Heavy Tar + Dust	Tar	Medium Oil	Gasoline
C		56.0	81.9	81.2	85.7
H		7.6	8.4	8.9	9.8
N		0.87	1.3	1.0	0.2
S	1.1	0.33	0.49	0.71	2.2
Ash		6.6	0.22	0.03	-
O ₂		28.6	7.8	8.2	2.1
HV ($\frac{\text{KJ}}{\text{g}}$)	21.6	26.5	37.3	38.3	41.6
$\frac{\text{ng SO}_2}{\text{J}}$ *	510	120	130	190	530

SO₂ Emission Limitations

Solid Fuels 86-516 ng/J (0.2-1.2 lb/10⁶ Btu)

Liquid Fuels 344 (0.8 lb/10⁶ Btu)

* Assuming 100% conversion of S to SO₂

REFERENCES

1. Schalit, L. M., and K. J. Wolfe. SAM/IA: A Rapid Screening Method for Environmental Assessment of Fossil Energy Process Effluents. Acurex Corp./Energy and Environmental Division. Mountain View, Calif. EPA Contract Number 600/7-78-015 (NTIS Number PB 277-088). February 1978.
2. Cleland, J. G., and G. L. Kingsbury. *Multimedia Environmental Goals for Environmental Assessment, Volumes I and II* (final report). Research Triangle Institute. Research Triangle Park, N.C. Report Number EPA-600-7-77-136a, b, NTIS Number PB 276-919 (Volume I), PB 276-920 (Volume II). EPA Contract Number 68-02-2612. November 1977.

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ENVIRONMENTAL ASSESSMENT REPORT: HIGH-Btu GASIFICATION TECHNOLOGY

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Abstract

As part of a comprehensive program for the environmental assessment of high-Btu gasification technology, the available data on high-Btu gasification and associated operations and processes have been analyzed, and gaps in the existing data base have been identified. This paper describes the data analysis methodology and identifies limitations of the available data. The program was sponsored by the Fuel Process Branch of the U.S. Environmental Protection Agency's Industrial Environmental Research Laboratory (EPA IERL), Research Triangle Park, N.C.

BACKGROUND

As part of its 3-yr program sponsored by the U.S. Environmental Protection Agency (EPA) for environmental assessment of high-Btu coal gasification, TRW has recently completed a three-volume document entitled *Environmental Assessment Data Base for High-Btu Gasification* (report number EPA-600/7-78-186a, b, and c). The document represents the summary and analysis of the existing data base and includes identification of data gaps.

The preparation of the data base document drew information from several sources, including published and unpublished EPA documents, open literature, process developers and EPA/DOE contractors, and authorities in industry and academic institutions. Gasification and related processes judged to have the greatest likelihood of being employed in commercial SNG facilities are discussed in the data base document.

DATA BASE METHODOLOGY

To facilitate systematic analysis, the technologies for high-Btu coal gasification were

divided into four "operations" (Figure 1). They include coal preparation, gasification, gas purification, and gas upgrading. In addition, the auxiliary processes to be used in commercial SNG facilities for pollution control were grouped into air pollution control processes, water pollution control processes, and solid waste management processes.

For analysis, the operations and auxiliary processes were further subdivided into modules, each module comprised of nearly interchangeable processes or processes applicable to different operating conditions and input requirements.

For each process within a module, a data sheet was prepared with key information items, thereby imparting high visibility to engineering facts and figures, allowing ready comparison between alternate processes in a given module, and underlining specific areas where significant gaps existed in the available data. Representative data sheets for the dry-ash Lurgi gasification process and the Rectisol acid-gas removal process (single-adsorption mode) are contained in Appendixes A and B, respectively. Data sheets were prepared for 11 gasification processes, 22 gas purification processes, 4 gas upgrading processes, 18 air pollution control processes, 17 water pollution control processes, and 3 solid waste disposal processes.

TECHNICAL DISCUSSION

The 11 gasification processes that were investigated are presented in Table 1. These processes use five different types of gasifier designs, as shown in the table. Data contained in the gasification data sheets are summarized in Table 2. Typical data include: developmental status, coal feed and pretreatment, coal feeding method, gasifier design, gasifier temperature and pressure, quench and dust removal, ash/char removal, typical product gas composition, tar/oil production, and gas yield. As can be seen in Table 2, there is a wide range of gas composi-

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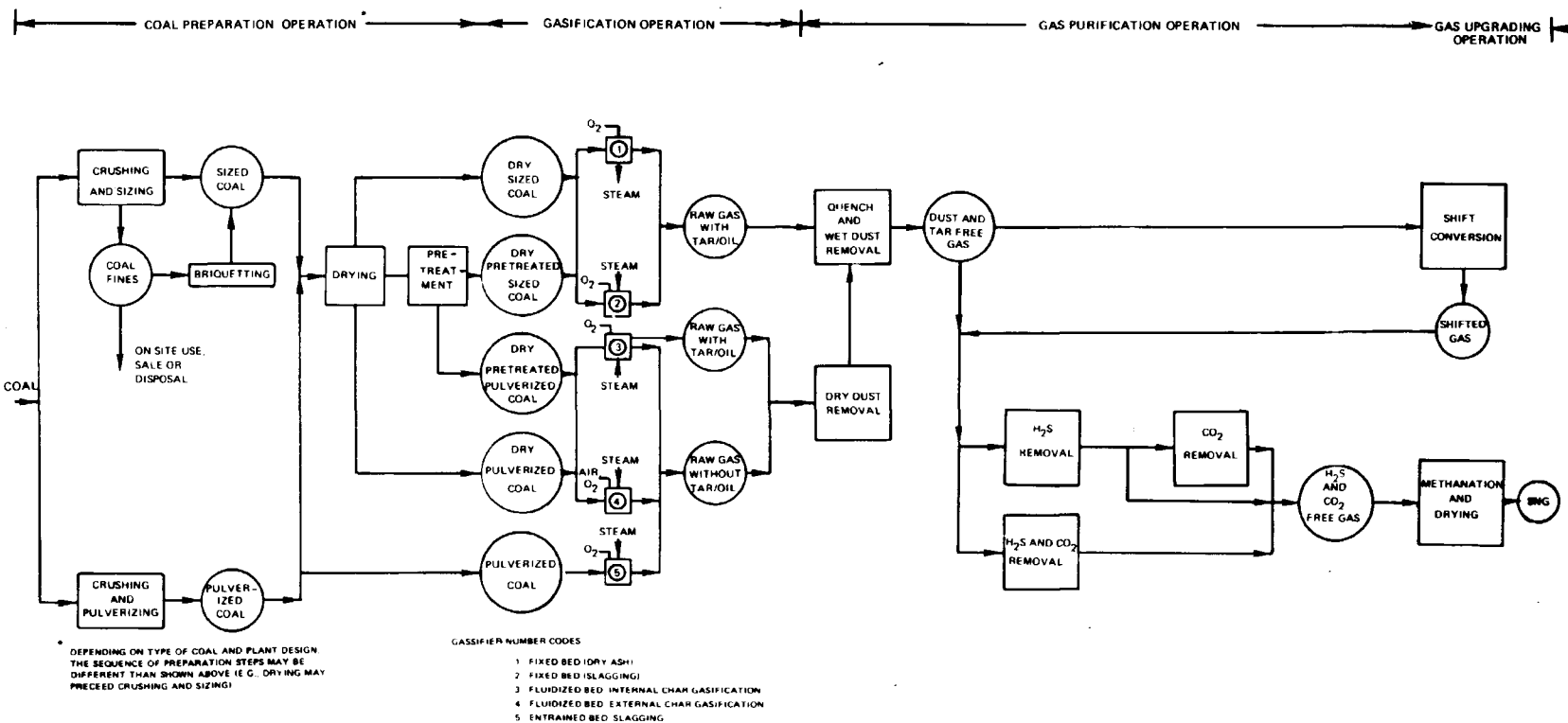


Figure 1. High-Btu gasification operations and process modules.

TABLE 1. GASIFICATION PROCESSES EVALUATED

Lurgi (dry ash)	Fixed bed (dry ash)		
Lurgi Slagging Gasifier	Fixed bed (slagging)		
Hygas (steam-oxygen)	Fluidized bed (internal char gasification)		
Cogas	Fluidized bed (external char gasification)		
CO ₂ -Acceptor	"	"	"
Hydrane (Hydrogasification)	"	"	"
Synthane	"	"	"
Self-Agglomerating Ash	"	"	"
Bigas	Entrained bed (slagging)		
Koppers-Totzek	"	"	"
Texaco	"	"	"

tions and yields from the gasifiers investigated. The Hydrane gasifier, for instance, produces 57 to 79 percent (volume) methane, while the Lurgi (dry ash) only produces 8 to 11 percent methane.

Table 3 presents a matrix of the advantages and disadvantages of the 11 gasifiers. These characteristics are based on operational characteristics, waste streams, and utility requirements.

Gas purification processes are employed to remove acid gases from the raw product gas to prevent methanation catalyst poisoning and to produce a product with a heating value equivalent to that of natural gas. Processes were investigated that remove H₂S and CO₂ simultaneously or selectively. Three types of acid-gas removal processes were included in the investigation: hot gas H₂S removal, solvent processes for acid-gas removal, and methanation guards. The solvent processes are most common, being extensively employed by petroleum refineries. Table 4 presents key features of the solvent processes included in the data base document. Listed in the table are the solvents em-

ployed by each process, operating pressure, selectivity, component distribution, solvent losses, and utility requirements.

The gas upgrading operation generally includes a shift conversion step, an acid-gas removal step, and a methanation and drying step. The data base for both shift conversion and methanation steps is limited by the lack of commercial-scale facilities or operating experience with these processes.

The air pollution control section reviews the sources and characteristics of gaseous waste streams associated with:

- The gasification, gas purification, and gas upgrading operations;
- Water pollution control and solid waste management; and
- Other auxiliary processes unique to the operation of commercial high-Btu gasification facilities.

Processes that have been used for or that may apply to the control of gaseous emissions in gasification facilities are reviewed. Alternative control strategies for integrated facilities are

TABLE 2. KEY FEATURES OF HIGH-Btu GASIFICATION PROCESSES

Process	Development Status	Coal Feed and Pretreatment	Coal Feeding Method	Gasifier Design	Gasifier Temperature °K(°F)	Gasifier Pressure MPa(psia)
Lurgi (dry ash)	Commercial for fuel and synthesis gas production	Limited to non-caking coals. Fine coal sizes must be briquetted	Pressurized lock-hopper	Fixed bed, counter-current gas/solids flow, temperature increases downward to effect pyrolysis and gasification	Max. bed temp. 1255-1644 (1800-2500)	2.1 - 3.2 (300-465)
Lurgi (Slagging Gasifier)	Pilot scale; demonstration plant under design	Limited to non-caking coals. Fine coal sizes may be utilized by injection into center of gasifier bed	Pressurized lock-hopper	Same as dry ash Lurgi	Max. bed temp. 1255-1644 (1800-2500)	0.7 - 3 (95 - 415)
Hygas (steam-oxygen)	Pilot scale; demonstration plant under design	Can use all domestic coals. Caking coals are pretreated with air and steam in fluidized bed at 315-400°K	Coal is slurried with light aromatic oil and charged to gasifier by high pressure slurry pump	Two stage, fluidized bed hydrogasification. Fluidized steam-oxygen gasification stage provides heat and gas for hydrogasification	Hydrogasification 750-1000 (900-1350) Steam-oxygen gasification: 1100 (1600)	6.2 - 7.1 (911-1040)
Cogas.	Pilot scale; demonstration plant under design	Can use all domestic coals. Pretreatment for caking coals is accomplished in first stage pyrolyzer	Pneumatic feeding with recycle product gas	Coal is pyrolyzed in four fluidized stages with progressively higher temperatures. Char produced from pyrolysis of coal is sent to gasifier. Crude gas is produced from the reaction of char and steam, obtaining heat indirectly from the combustion of char with air. Gasifier gas flow counter-current to coal and char	Pyrolyzers 500-1000 (450-1500) Gasifier: 1200 (1700)	0.13 (20) 0.20 (29)
CO ₂ -Acceptor	Pilot scale; no demonstration or commercial project planned	Limited to more reactive coals (e.g., lignite and sub-bituminous coal)	Pressurized lock-hopper	In the gasifier, calcined dolomite supplies heat for steam gasification of coal. Carbonated dolomite is recalcined in a regenerator by burning char with air. Both vessels fluidized	Gasifier: 1090 (1500) Regenerator: 1230 (1860)	1.0 (150) 1.0 (150)
Synthane	Pilot scale	Can use all domestic coals. Caking coals are pretreated with O ₂ and steam within the gasifier in a free fall fluidized bed zone	Pressurized lock-hopper	Steam and oxygen used to gasify coal in fluidized bed gasifier	960-1090 (1280-1500)	4.2 - 6.8 (600-1000)
Bigas	Pilot scale	Can use all domestic coals. No pretreatment is required	Coal is slurried with water and injected into pressurized drier before entering gasifier	Coal is gasified in an entrained bed with a steam/synthesis gas mixture. Char is gasified in an entrained bed using O ₂ and steam to generate synthesis gas	Upper stage: 1200 (170) Lower stage: 1755 (2700)	8 (1175)
Hydrane	Bench scale	Caking coal permitted without pretreatment.	Injection nozzle	Direct hydrogasification of coal with hydrogen in a fluidized bed. Hydrogen would be produced by char gasification with subsequent purification	-6300 (-1500)	7.0 (1015)

(continued)

TABLE 2 (continued)

Process	Quench and Dust Removal	Ash/Char Removal	Typical Product Gas Composition* (vol %)				Tar/Oil Production	Gas Yield* Nm ³ /kg (scf/lb) of Dry Feed Coal
			CH ₄	H ₂	CO	CO ₂		
Lurgi (dry ash)	Water spray cooler to condense tars/oils and remove bulk particulates	Lockhopper water quench, water slurry transport	8-11	40	15-20	28-31	Yes	0.9-1.7 (16-30)
Lurgi (Slagging Gasifier)	Same as dry ash Lurgi	Lockhopper, followed by water quench of slag	5-8	28-30	57-61	3-7	Yes	2.0-2.1 (34-36)
Hygas (steam-oxygen)	Cyclone followed by water quench for oil and particulate removal	Water quench at gasifier pressure, water slurry transport	13-28	26-37	8-10	28-35	Yes	1.0-1.2 (17-20)
Cogas	Cyclone followed by venturi scrubber for removal of char fines and for recovery of oil	Slag quenched, transport not known	8-15	5-40	4-19	22-29	Yes	Gas: 0.12-.60 (2-12) Oil: 0.04--0.2 l/kg (0.005-0.025 gal/lb) coal
CO ₂ -Acceptor	Internal gasifier cyclone, external water spray tower for particulate removal	Coal ash leaves regenerator with flue gas and is collected by cyclone and scrubbing systems	14	56-59	15	9-11	No	1.35 (23)
Synthane	Internal gasifier cyclone, venturi scrubber	Lockhopper, water quench, steam transport	7-13	23-35	3-12	37-64 [‡]	Yes [§]	1.2-1.5 (20-25)
Bigas	Cyclone, water spray tower for particulate removal	Slag quenched followed by lockhopper	5-8	32-38	15-19	21-23	No	2.0-4.0 (32-68) [‡]
Hydrane	No information	No information, char utilization has not been determined	57-79	21-28	1-6	1	?	0.6-1.0 (10-17)

*Based upon data for actual operation for the most advanced stage of development

[†]N₂ free basis[‡]Includes CO₂ used to pressurize the lockhopper[§]With "free-fall" mode of coal injection; recent pilot plant runs involving "deep-bed" injection of coals have indicated little tar production

**TABLE 3. ADVANTAGES AND DISADVANTAGES OF HIGH-Btu
GASIFICATION PROCESSES**

Process	Commercially Developed	Developed Through Pilot Plant Scale	Can Use All Coals	Requires Pretreatment of Caking Coals	Can Utilize All Size Fractions	Produces Condensable Organics (tars/oils)	High Throughput Rate	Methane Formation in Gasifier	Ratio of Hydrogen to Carbon Monoxide in Product Gas	Steam/Electricity Consumption	Operating Pressure	Complete Char Utilization	Turndown Ability	CO ₂ Removal Required	Oxygen Plant Needed	Comments
Lurgi (dry ash)	Yes	Yes	No	Yes	No	Yes	No	Moderate	Moderate	Moderate	Moderate	Yes	High	Yes	Yes	Commercial operations not for high Btu gas production at present. Basis for several proposed commercial SNG projects
Lurgi (Slagging Gasifier)	No	Yes	No	Yes	No	Yes	Yes	Low	Low	Low	Moderate	Yes	High	Yes	Yes	Extensive tests at a modified dry ash Lurgi plant. Basis for a DOE-sponsored demonstration plant.
Hygas (steam-oxygen)	No	Yes	Yes	Yes	Yes	Yes	No	High	High	Moderate	High	Yes	Low	Yes	Yes	Pilot plant has demonstrated operations with several coals. High carbon utilization has not been attained to date. Basis for DOE-sponsored demonstration program.
Cogas	No	Yes	Yes	No	Yes	Yes	No	Moderate	High	Moderate	Low	Yes	Low	Yes	No	Integrated pyrolysis and gasification/combustion operations not demonstrated. Basis for DOE-sponsored demonstration program.
CO ₂ -Acceptor	No	Yes	No	Yes	Yes	No	No	High	Very High	Low	Moderate	Yes	Low	No	No	Successful demonstration at pilot plant stage. High cost of acceptor is a major obstacle to further demonstration of process.
Synthane	No	No	Yes	Yes	Yes	Yes*	No	High	High	High	High	No	Low	Yes	Yes	High pressure lockhopper feeding not demonstrated. Pilot plant has limited steady state operating time.
Bigas	No	No	Yes	No	Yes	No	Yes	Low	Moderate	Moderate	High	Yes	Moderate	Yes	Yes	Ability to control slag flow at a pilot plant has not been demonstrated.
Hydrane	No	No	Yes	Yes	Yes	Yes	Yes	Very High	Very High	High	High	No	Low	Yes	?	Small scale test only. Char utilization and hydrogen production not tested.

*With "free-fall" mode of coal injection; recent pilot plant runs involving "deep-bed" injection of coal have indicated little tar production.

TABLE 4. KEY FEATURES OF SOLVENT PROCESSES FOR ACID-GAS REMOVAL

Process Name	Solvent/Reagent	Operating Pressure (acid gas partial pressure)	Selectivity		Component Distribution*							Solvent Losses (Replacement Requirement)	Utility Requirements
			H ₂ S/CO ₂	CO ₂ /HC	CO ₂	CS ₂	RSH	NH ₃	HCN	Higher Organics	Water Vapor		
PHYSICAL SOLVENTS													
Rectisol	Methanol	High	Good	Poor	a,b	a,b	a,c,d	c,d	a,c,d	a,b,c,d	d	High	Moderate/low
Selexol	Dimethyl ether of polyethylene glycol	High	Good	Moderate	a,b	a,b	a,c,d	c,d	a,c,d	a,b,c,d	d	Low	Low
Purisol	N-methyl 2-pyrrolidone	High	Good	Moderate	a,b	a,b	a,d	a,d	a,c,d	a,b,c,d	d	Low	Low
Fluor solvent	Propylene carbonate	High	Moderate	Moderate	a,b	a,b	a,d	a,d	a,c,d	a,b,d	d	Low	Low
Estasolvan	Tri-n-butyl phosphate	High	Moderate	Moderate	a,b	a,b	a,d	a,d	a,c,d	a,b,d	d	Low	Low
CHEMICAL SOLVENTS													
Amine Solvents													
Sulfiban	Monoethanolamine (MEA)	Low	Poor	Good	e	e	a,b,d	a,d	e	a,d	d,g	High	Very high
MDEA	Methyl-diethanol- amine	Low	Moderate	Good	a,b	a,b	a,b,d	a,d	e	a,d	d,g	Moderate	High
DEA	Diethanolamine	Low	Poor	Good	a,b	a,b	a,b,d	a,d	e	a,d	d,g	High	Very high
ADIP	Diisopropanolamine	Low	Poor	Good	a,b	a,b	a,b,d	a,d	e	a,d	d,g	Moderate	High
Fluor Econamine	Diglycolamine (DGA)	Low	Poor	Good	a,b	a,b	a,b,d	a,d	e	a,d	d,g	Low	High
Alkazid	Dimethyl or diethyl glycine	Low	Moderate	Good	f,g	f,g	d,g	a,d	e	a,d	d,g	Low	High
Carbonate Solvents													
Benfield	Potassium carbonate and diethanolamine	Moderate	Moderate	Excellent	f,g	f,g	f,g	a,d	f,a,d	g	g	Low	Moderate
Catacarb	Potassium carbonate and amine borates	Moderate	Moderate	Excellent	f,g	f,g	f,g	a,d	f,a,d	g	g	Low	Moderate
MIXED SOLVENTS													
Sulfinol	Cyclotetramethylene sulfone and diisopro- panolamine	Moderate	Poor	Moderate	a,b	a,b	a,d	a,d	a,d	a,b,d	d,g	Low	Moderate
Amisol	Methanol and mono- or diethanolamine	Moderate	Poor	Moderate	a,b	a,b	a,d	a,d	a,d	a,b,d	d,g	High	Moderate
REDOX PROCESSES													
Glamarco- Vetrocoke	Potassium carbonate and arsenate/arsenite	Moderate	Good	Excellent	f,g	f,g	f,g	a,d	f,a,d	g	g	Low	Moderate
Stretford	Alkaline metavanadate and anthraquinone di- sulfonic acid	Moderate	Good *	Excellent	g	g	g	g	e	g	g	Low	Moderate

- * a) with acid gas stream after simultaneous CO₂ and H₂S removal
b) with CO₂ stream after separate CO₂ and H₂S removal
c) with H₂S stream after separate CO₂ and H₂S removal
d) with aqueous or organic liquid phase prior to or integral with process
e) degrades solvent
f) hydrolyzes
g) remains with treated gas

[†]Depends on acid gas partial pressure, selective vs. non-selective design, and residual sulfur allowed; rating is for moderate to high pressure application with <10 ppm residual H₂S in treated gas.

[‡]Selectivity good, but high CO₂ lowers H₂S absorption rate and requires large systems for efficient H₂S removal.

discussed. Table 5 shows the air pollution processes reviewed according to applicability to high-Btu gasification and the purpose of each type of control process. Key features of each process are compared in the data base document. Options for the management of sulfur-bearing waste gases in integrated facilities are shown in Table 6. It can be seen that a variety of acid-gas streams are expected to be present in an integrated facility and that several options are available for their handling. An integrated approach to the handling of acid gases, as well as of other wastes, will be required when environmentally acceptable SNG plants are designed.

Several process and air and water pollution control modules in an integrated facility would generate aqueous wastes requiring treatment. Only those aqueous wastes that are specific to high-Btu gasification and related facilities were considered. Table 7 lists aqueous waste streams associated with the different gasification processes. Each stream—with possible control methods—is characterized in the data base.

The sources of solid waste in a gasification plant include: chars and ashes from gasification and air pollution control, spent catalysts from shift conversion and methanation, inorganic solids and sludges from acid-gas removal and air and water pollution control, tar and oil sludges, and biosludges from water pollution control. Of these, only ash, spent catalysts, and inorganic solids and sludges would be generated in all gasification facilities. The other types of waste may or may not be generated, depending on specific processes chosen. Solid waste management options included in the data base were: resource recovery, incineration, soil application, and land burial/landfilling. In comparison with aqueous and gaseous wastes (for which some composition and treatability data are available for certain streams), the composition of solid wastes and disposal hazards of such wastes are essentially unknown.

DATA GAPS AND LIMITATIONS

A primary goal of the first phase of the en-

TABLE 5. AIR POLLUTION PROCESSES REVIEWED

Sulfur Recovery	Claus, Stretford, Giammarco-Vetrocoke
Tail Gas Treatment	SCOT, Beavon, IFP-1, IFP-2, Sulfreen, Cleanair
SO ₂ Control and/or Recovery	Wellman-Lord, Chiyoda Thoroughbred 101, Shell copper oxide, lime/limestone slurry scrubbing, double alkali, and magnesium oxide scrubbing
Incineration	Thermal oxidation, catalytic oxidation,
CO, Hydrocarbon and Odor Control	Thermal oxidation, catalytic oxidation, activated carbon adsorption
Particulate Control	Fabric filter, electrostatic precipitation, venturi scrubbing, cyclones
Compression and Recycling	Compression and recycling
NO _x Control	Combustion modification and dry and wet processes

TABLE 6. OPTIONS FOR THE MANAGEMENT OF SULFUR-BEARING WASTE GASES

Waste Gas	Control Options*	Comments
Concentrated Acid Gases	1. Claus plant sulfur recovery 2. Claus plant sulfur recovery and tail gas incineration 3. Claus plant sulfur recovery and tail gas treatment 4. Same as 1 plus SO₂ control and/or recovery 5. Stretford or G-V sulfur recovery 6. Same as 5 plus tail gas treatment 7. Same as 6 plus incineration 8. Incineration 9. Same as 8 plus SO₂ control and/or recovery 10. Incineration, treatment for control and/or recovery in combination with flue gases from utility boilers or char combustion	1. Probably unacceptable because of high concentration of total sulfur in the tail gas; only applicable to streams containing more than 15% H₂S. 2. Probably unacceptable because of high levels of SO₂ in the tail gas; only applicable to streams containing more than 15% H₂S. 3. Tail gas treatment not highly effective when feed gases contain high levels of CO₂; only applicable to streams containing more than 15% H₂S. 4. Reasonable option when feed gases contain more than 15% H₂S; total sulfur removal efficiency may be less than option 5. 5. Inapplicable to waste gases containing high levels of H₂S; may not be economical for gases containing high CO₂ levels; discharge may contain high COS and HC levels. 6. Same as for Option 5. 7. Same as for Option 5 except for oxidation of CO and HC compounds 8. Unacceptable because of high SO₂ emissions. 9. Many SO₂ recovery processes generate sludges requiring disposal; no by-product sulfur is recovered; regenerable SO₂ removal processes must be operated in conjunction with sulfur recovery units. 10. Same as for Option 9; some economy of scale may be realized if flue gas desulfurization is required on utility boilers.
Depressurization and Stripping Gases	1. Combining with concentrated acid gas streams and use of any of the treatment options listed above 2. Compression and addition to product gas stream 3. Use as fuel 4. Incineration 5. Same as 4 plus SO₂ control and/or recovery	1. See individual options above; may have considerable dilution effect on the concentrated acid gas streams. 2. Permits material recovery; some energy input required for compression. 3. Stripping gases may have limited fuel value; may have high SO₂ emissions. 4. High levels of SO₂ emissions. 5. See comments for Options 9 and 10 for Concentrated Acid Gases.
Pretreatment Off-Gases	1. Combining with product gas 2. Injection into gasifier 3. Use as fuel 4. Incineration 5. Same as 4 plus SO₂ control and/or recovery	1. Product gas dilution and energy requirement for compression; permits material and energy recovery. 2. Permits material and energy recovery; will require gasifier design modification and energy input for compression. 3. May have high SO₂ emissions. 4. See comment for Option 4, Depressurization and Stripping Gases. 5. See comment for Option 5, Depressurization and Stripping Gases.
Lockhopper Vent Gases	1. Compression and recycling 2. Incineration 3. Same as 2 plus SO₂ control and/or recovery 4. Use as fuel	1. See comment for Option 2, Pretreatment Off-Gases. 2. See comment for Option 4, Depressurization and Stripping Gases 3. See comments for Options 9 and 10, Concentrated Acid Gases. 4. See comment for Option 3, Depressurization and Stripping Gases.
Catalyst Regeneration/Decommissioning Off-Gases	1. Incineration 2. Same as 1 plus SO₂ control and/or recovery	1. See comment for Option 4, Depressurization and Stripping Gases. 2. See comments for Options 9 and 10, Concentrated Acid Gases.
Char Combustion, Incineration and Treatment Gases	1. Incineration (for transient gases) 2. Same as 1 plus SO₂ control and/or recovery	1. See comment for Option 4, Depressurization and Stripping Gases. 2. See comments for Options 9 and 10, Concentrated Acid Gases.

*Except where gas compression and recycling is used, all options culminate in discharge of the treated gas to the atmosphere

**TABLE 7. AQUEOUS WASTE STREAMS ASSOCIATED WITH DIFFERENT HIGH-Btu
GASIFICATION PROCESSES**

Wastewater Category	Gasification Process							
	Lurgi (dry ash)	Lurgi (slagging)	Hygas (steam-oxygen)	Cogas	CO ₂ -Acceptro	Synthane	Bigas	Hydrane
Particulate scrubber waters from treatment of:								
Pretreater Flue Gas	Yes	Yes	Yes	No	Yes	No	No	*
Lockhopper Vent Gas	Yes	Yes	No	No	Yes	Yes	No	*
Char Combustion Flue Gas	No	No	No	Yes	Yes	Yes	No	No
Raw Gas Quench Waters								
Cyclone Slurry	No	No	Yes	*	No	No	No	*
Quench Blowdown	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Ash Quench Water	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Shift Condensate	Yes	Yes	Yes [†]	Yes [†]	No	Yes	Yes	No
Methanation Condensate	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Waste Sorbents & Reagents	‡	‡	‡	‡	‡	‡	‡	‡
Miscellaneous Wastewaters	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

*Not known at this time; process not sufficiently developed or information not publicly available

†Depending on feed coal and operating conditions, shift may or may not be required

‡Depends upon specific acid gas treatment and pollution control processes employed.

vironmental assessment was to identify the data gaps and limitations for study in the next phase of the program. The limitations and gaps fall into two categories: data that are nonexistent or unavailable, and data that are available but either incomplete or obtained under conditions significantly different than those anticipated in an integrated commercial SNG plant in the United States.

Examples of the gaps in the first category are the lack of detailed data on: emissions associated with decommissioning spent methanation catalyst, combined effluent in an SNG plant, and sludges resulting from the treatment of such effluent or from the treatment of tar and oily condensates. Because no integrated SNG facility currently exists, this type of information is not available from actual operation. Even though environmental characteristics of SNG plant wastes can be estimated through engineering studies, to date only a limited number of such studies have been conducted. In the case of emissions from catalyst decommissioning, even though some data might exist, such data are not publicly available because of proprietary considerations.

Examples of the second category of data gaps and limitations are the lack of trace element, organic, toxicological, and ecological characteristics data for various waste streams in a gasification plant, and data on the performance of various control systems in SNG service. In comparison with the limited data available on most gasification processes, considerable data are available on the characteristics of aqueous wastes from the Hygas and dry-ash Lurgi processes. These data, however, do not cover organic and trace element constituents, bioassay information, waste treatability, and hazardous characteristics such as biodegradability, health effects, and potential bioaccumulation and environmental persistence. For the Stretford process, which has been used in refinery and byproduct coke applications for H_2S removal from acid gases containing relatively low levels of CO_2 , limited commercial experience exists with acid gases containing high levels of CO_2 that would be encountered in an SNG plant. With the exception of a few pollution control processes (e.g., flaring for hydrocarbon and H_2S control, venturi scrubbing for particulate removal, Phenosolvan for recovery of phenols from wastewaters, sour water strip-

ping for NH_3/H_2S removal, and trickling filters for biological treatment), the various air, water, and solid waste control processes that would be potentially employed at commercial facilities have not been used in coal gasification applications. Even for the few processes that have been used for coal gasification, very little data are available on the characteristics of the treated streams and on the performance and costs of these applications.

The first category of data gaps can only be partially filled (e.g., through engineering analysis) at the present time because SNG facilities do not exist and the existing pilot plants do not incorporate all the units or design features of a large-scale facility. Many gaps in the second category, however, can be and should be filled through multimedia environmental sampling and analysis of the process/discharge streams at pilot plants and foreign gasification facilities, through bench-scale studies and engineering analysis. Even though some of the unit operations and conditions in the gasification pilot plants are not scalable to or representative of commercial facilities, in the absence of such commercial facilities, sampling at the pilot plants represents the best and only means of acquiring meaningful data on process and waste stream characteristics and on the performance of various processes. Such sampling and analysis programs, coupled with related engineering studies and bench-scale testing, can provide valuable and timely input to the evolution of the SNG industry that would ensure:

- Inclusion of environmental considerations in selection of processes, equipment, and waste management options for commercial SNG plants; and
- Drafting of new source performance standards for SNG facilities based on sound technical and engineering data.

Several programs are currently underway or planned that involve testing/sampling at pilot plants, bench-scale units, or foreign commercial facilities.

Major programs that are expected to generate some of the data needed for high-Btu gasification environmental assessment fall into three categories: EPA-sponsored programs, DOE-sponsored programs, and miscellaneous programs. Limited data are available on the programs in the miscellaneous category that are primarily carried out under private funding.

Of the EPA programs, the one most directly related to the high-Btu gasification is the TRW environmental assessment effort for which the data base development effort has been the first step. DOE synthetic fuel pilot and demonstration programs include sampling and analysis at various facilities, bench-scale studies for process and environmental data acquisition, and

related environmental engineering studies.

Preparation of the data base document represents completion of the first phase of the TRW program. The second phase of the program includes data acquisition through sampling and analysis of process/waste streams at selected gasification facilities.

APPENDIX A

DRY-ASH LURGI GASIFICATION PROCESS

GENERAL INFORMATION

1. Operating Principles: high-pressure coal gasification in a gravitating bed by injection of steam plus oxygen with countercurrent gas/solid flow; ash is maintained below the fusion temperature.
2. Development Status: commercially available since 1940.
3. Licensor/Developer: Lurgi Mineralöstechnik GmbH.
American Lurgi Corporation
377 Rt. 17 South
Hasbrouch Heights, N.J.
4. Commercial applications: See Table A-1.

PROCESS INFORMATION

1. Commercial Scale: see Figure A-1 for flow sheet.
- A. Gasifier: see Figures A-2 and A-3.*
 - (1) Equipment^{1 2}
 - Construction: vertical, cylindrical steel pressure vessel.
 - Gasifier dimensions:
 - 2.5 to 3.8 m (8.5 to 12.3 ft) in diameter,
 - 2.1 to 3.0 m (7 to 10 ft) coal bed depth, and
 - 5.8 m (19 ft) approximate overall height of gasifier.
 - Bed type and gas flow: gravitating bed; continuous countercurrent gas flow; lateral gas outlet near the top of the gasifier.
 - Heat transfer and cooling mechanism: direct gas/solid heat transfer; water jacket provides gasifier cooling.
 - Coal feeding: intermittent; pressurized lock hopper at the top of the gasifier dumps the coal onto a rotating, water-cooled coal distributor.
 - Gasification media introduction: continuous injection of steam plus oxygen at the bottom of the coal bed through a slotted ash extraction grate.
 - Ash removal: rotating, slotted grate at the bottom of the coal bed; refractory-lined, pressurized lock hopper collects the ash and dumps it intermittently.
 - Special features:
 - Direct quench gas scrubber and cooler that knocks out the majority of particulates, tars, oils, phenols, and ammonia; is attached to the gasifier at the gas outlet.
 - Gasifier water jacket supplies approximately 10 percent of the required gasification steam.
 - Rotating coal distributor provides uniform coal bed depth.

*Figure A-2 shows the evolution of Lurgi gasifiers with corresponding increases in capacity. Figure A-3 presents the commercial model that is the basis for further discussion.

TABLE A-1. LURGI, DRY-ASH, COMMERCIAL INSTALLATIONS¹

Plant No.	Location	Year	Type of Coal	Gasifier I.D.	Capacity (MMSCFD)	No. of Gasifiers
1	Bohlen, Central Germany	1940	Lignite	8'6"	9.0	5
2	Bohlen, Central Germany	1943	Lignite	8'6"	10.0	5
3	Most, CSSR	1944	Lignite	8'6"	7.5	3
4	Zaluzi-Most, CSSR	1949	Lignite	8'6"	9.0	3
5	Sasolburg, South Africa	1954	Sub-Bitum. with 30% ash and more	12'1"	150.0	9
6	Dorsten, West Germany	1955	Caking Sub-Bitum. with high chlorine content	8'9"	55.0	6
7	Morwell, Australia	1956	Lignite	8'9"	22.0	6
8	Daud Khel, Pakistan	1957	High Volatile coal with high sulfur content	8'9"	5.0	2
9	Sasolburg, South Africa	1958	Sub-Bitum. with 30% ash and more	12'1"	19.0	1
10	Westfield, Great Britain	1960	Weakly Caking Sub-Bitum.	8'9"	28.0	3
11	Jealgora, India	1961	Different grades	N/A	0.9	1
12	Westfield, Great Britain	1962	Weakly Caking Sub-Bitum.	8'9"	9.0	1
13	Coleshill, Great Britain	1963	Caking Sub-Bitum. with high chlorine content	8'9"	46.0	5
14	Naju, Korea	1963	Graphitic anthracite with high ash content	10'5"	75.0	3
15	Sasolburg, South Africa	1966	Sub-Bitum. with 30% ash and more	12'1"	75.0	3
16	Luenen, GFR	1970	Sub-Bitum.	11'4"	1400 MM Btu/hr	5
17	Sasolburg, South Africa	1973	Sub-Bitum. with 30% ash and more	12'4"	190.0	3

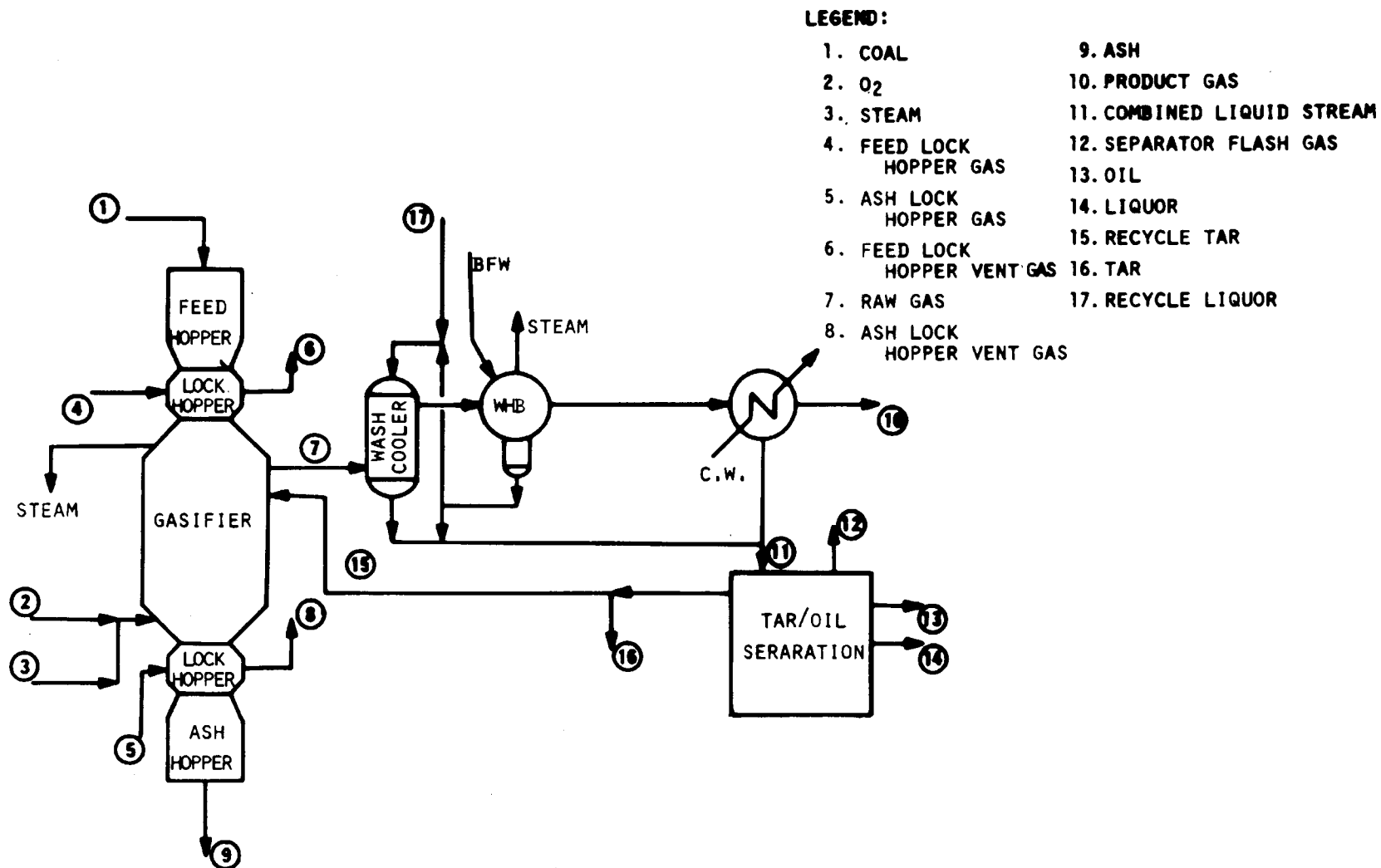


Figure A-1. Lurgi gasifier (Based on Westfield Lurgi Installation).

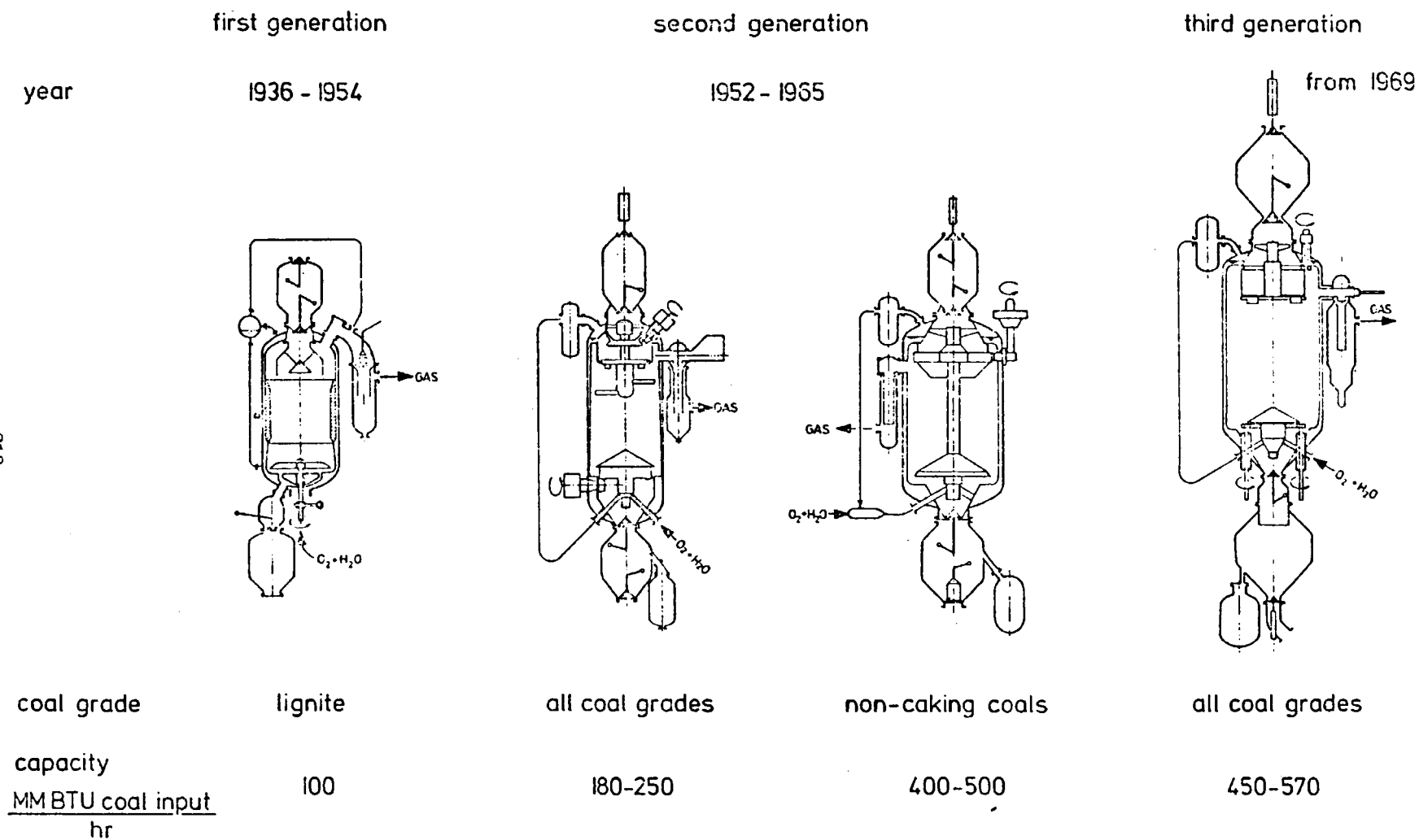


Figure A-2. Stages of Lurgi gasifier development.

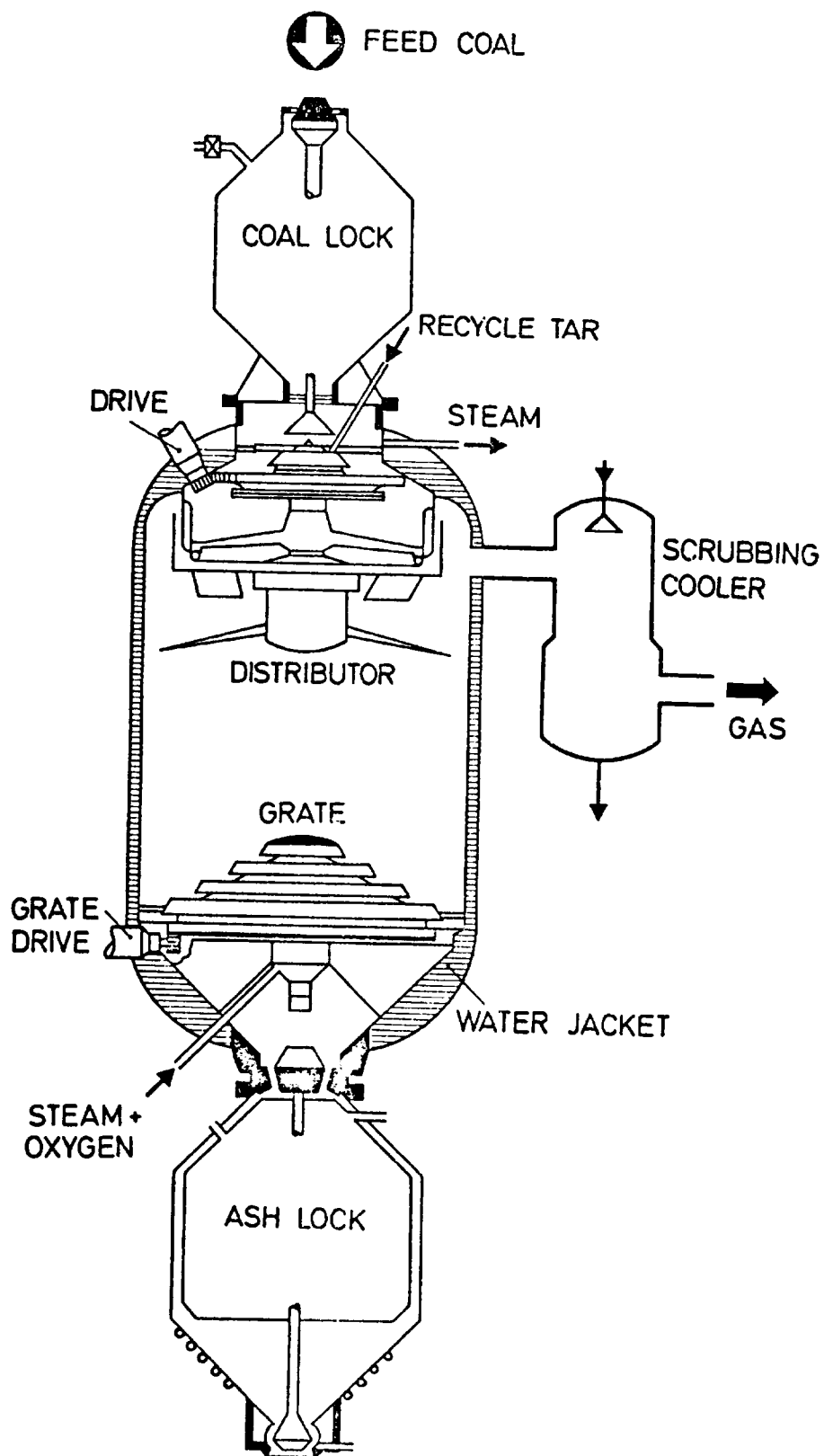


Figure A-3. Lurgi pressure gasifier.

- Tar injection nozzle at the top of the gasifier permits recycle of byproduct tar (separated external to the gasification module), which also helps to reduce coal fines carryover in the product gas (optional features).
- Rotating, water-cooled coal bed agitator aids gasification of strongly caking coals (optional feature).

(2) Operating Parameters^{1 2}

- Gas outlet temperature:
Range: 644 K to 866 K (700° F to 1,100° F).
Normal: 727 K (850° F).
- Coal bed temperatures:
1,255 K to 1,644 K (1,800° F to 2,500° F).
- Gasifier pressure:
Range: 2.1 to 3.2 MPa (300 to 465 psia).
Normal: 2.1 MPa (300 psia).
- Coal residence time in gasifier:
Approximately 1 hr.

(3) Raw Material Requirements^{1 2}

- Coal feedstock:

Type: All types; strongly caking coals require agitator-reduced throughput and increased steam rate.

Size: 3.2 to 38.1 mm (0.125 to 1.5 in):
Coal is usually fed in two size ranges; coal with up to 10 percent minus 3.2 mm (0.125 in) can be accepted.

Rate:† 136 to 544 g/sec-m² (100 to 400 lb/hr-ft²).
- Coal pretreatment: crushing and sizing, drying to less than 35 percent moisture; partial oxidation is required for use of strongly caking coals in gasifiers without agitators.
- Steam: 1.11 to 2.59 kg/kg coal.³
- Oxygen: 0.26 to 0.62 kg/kg coal.³
- Quench water: 3.3×10^{-4} m³/kg coal.²

(4) Utility Requirements¹

- Water:
Boiler: 2.42×10^{-3} m³/kg coal (580 gal/ton coal).
Cooling: ?
- Electricity: 25 kwh/metric ton (23 kwh/ton).

(5) Process Efficiency

- Cold gas:³ 63 to 60 percent
[=] $\frac{[\text{Product gas energy output}]}{[\text{Coal energy input}]} \times 100$
- Overall thermal:¹ 76 percent.
[=] $\frac{[\text{Total energy output (Product gas + HC by products + steam)}]}{[\text{Total energy input (coal + electric power)}]} \times 100.$

†Rate varies with gasifier design and coal type.

(6) Expected Turndown Ratio¹ = 100/25.

$$[=] \frac{[\text{Full capacity output}]}{[\text{Minimum sustainable output}]}$$

(7) Gas Production Rate/Yield:³

0.37 to 0.68 m³/sec-m² (4875 to 900 scf/hr-ft²)
0.93 to 1.70 Nm³/kg coal (16 to 30 scf/lb-coal).

2. Coal Feed Pretreatment: coal feed is from pressurized lock hoppers; no pretreatment is required in third-generation gasifiers.
3. Quench and Dust Removal: crude gas leaves the top of the gasifier and flows through a scrubber cooler, where it is washed by recirculating quench liquor from the tar-oil separation section. The gases then pass through a waste heat boiler and a final cooler. Dust, tars, and condensables are collected from these units.

PROCESS ECONOMICS

Because of advanced development of the Lurgi gasifier, numerous studies related to costs have been completed.^{4 5 6 7} However, most of these studies address themselves only to integrated facilities rather than to the gasification module. The one exception, in which equipment lists are presented and detailed cost estimates made, is the Bureau of Mines Study.⁴ For a 250-MMSCFD SNG facility costing \$737,538,000 in 1974 dollars, 27.1 percent is estimated to be attributable to the gasification section. Lurgi⁷ estimates total plant costs of \$440,000,000 also in 1974 dollars. No gasification section cost estimates are made.

PROCESS ADVANTAGES

- Present gasifiers can accept caking and noncaking coals.
- Pressurized operation favors formation of methane in the gasifier and reduces upgrading costs. The high pressure of the product gas would also reduce the cost of gas transmission via pipeline. High pressure may be advantageous for combined-cycle synthesis gas utilization.
- Gasifier has been operated commercially for many years.
- Small reactor size may be advantageous for small-scale industrial applications.

PROCESS LIMITATIONS

- Caking coals reduce throughput rate and increase steam consumption, which also increases the amount of liquid waste to be treated.
- Maintaining the coal-bed temperature below the ash fusion temperature limits the maximum process efficiency.
- Process condensate and byproducts require additional processing for environmental acceptability.
- Maintaining a low coal-bed temperature results in low steam conversion in the gasifier.
- Limited reactor size may necessitate use of multiple units in parallel for large installations.

INPUT STREAMS^{3 8}

1. Coal (Stream No. 1): see Table A-2.

2. Oxygen (Stream No. 2)

Coal No.	1	2	3	4	5
Rate: kg/kg (Includes 6 percent inerts)	0.26	0.48	0.49	0.62	--
Pressure: MPa (psia)	3.6(370)	3.5(360)	3.5(360)	3.5(360)	--

3. Steam (Stream No. 3)

Coal No.	1	2	3	4	5
Rate: kg/kg	1.11	1.97	1.84	2.59	--
Pressure: (psia)	(370)	(362)	(360)	(360)	--
Temperature: K (°F)					

4. Feed Lock Hopper Gas (Stream No. 4): no data reported.

5. Ash Lock Hopper Gas (Stream No. 5): no data reported.

INTERMEDIATE STREAMS

1. Gaseous Streams

A. Feed Lock Hopper Vent Gas (Stream No. 6): no operational data reported.

B. Raw Gas (Stream No. 7): no operational data reported.

C. Ash Lock Hopper Vent Gas (Stream No. 8): no operational data reported.

2. Liquid Streams

A. Combined Liquid Stream (Stream No. 11): no data reported.

B. Recycle Liquid (Stream No. 17): no data reported.

C. Recycle Tar (Stream No. 15)³

Coal No.	1	2	3	4	5
Toluene (wt percent)	32.3	8.6	8.0	3.2	--
Insoluble ash (dust)	29.2	10.8	11.1	12.2	--
Composition	(See Tars--Stream No. 16)				

DISCHARGE STREAMS

1. Gaseous

- Product gas (Stream No. 10): see Table A-3.
- Separator flash gas (Stream No. 12): see Table A-4.

2. Liquid Streams

- Tars (Stream No. 16): see Tables A-5 and A-9.
- Oils (Stream No. 13): see Tables A-6 and A-9.
- Liquors (Stream No. 14): see Tables A-7 and A-9.

3. Solids Streams

- Ash (Stream No. 9): see Tables A-8 and A-9.

TABLE A-2. PROPERTIES OF COAL FEED TO LURGI GASIFICATION (STREAM NO. 1)

Coal No. Type/Origin	1 Montana Rosebud* Subbituminous A	2 Illinois #6* High Volatile	3 Illinois #5* Bituminous	4 Pittsburgh #8	5 South African† Subbituminous
Size: mm (in)	6.4-31.8 (1/4-1 1/4)	6.4-31.8 (1/4-1 1/4)	6.4-31.8 (1/4-1 1/4)	6.4-31.8 (1/4-1 1/4)	
HHV (dry): Kcal/kg (Btu/lb)	6553 (11,436)	7094 (12,770)	7228 (13,010)	7826 (14,087)	4989 (8,980)
Swelling No.	0	3	2.2-5	7.5	--
Caking Index	0	15	15	30	--
Composition:					
Moisture: %	24.70	10.23	11.94	4.58	8.0
Volatile matter: %	29.20	34.70	35.21	37.37	--
Ash: %	9.73	9.10	8.13	7.74	31.6
C: %	67.15	71.47	72.80	77.71	52.4
H: %	4.22	4.83	4.95	5.28	2.6
O: %	13.02	9.02	7.99	4.74	11.7
S: %	1.45	3.13	3.56	2.64	0.43
N: %	1.20	1.35	1.39	1.42	1.2
Trace Elements‡(ppm)					
Be	--	1.6	2.0	--	--
Hg	--	1.1	0.2	--	--
Ca	--	< .03	< .03	--	--
Sb	--	0.1	.2	--	--
Se	--	--	9	--	--
Mo	--	7	7	--	--
Co	--	4	4	--	--
Ni	--	14	32	--	--
Pb	--	10	28	--	--
As	--	1	2	--	--
Cr	--	20	15	--	--

(continued)

TABLE A-2 (continued)

Coal No. Type/Origin	1 Montana Rosebud* Subbituminous A	2 Illinois #6* High Volatile	3 Illinois #5* Bituminous	4 Pittsburgh #8	5 South African [†] Subbituminous
Trace Elements [‡] (cont) (ppm)					
224 Cu	--	12	10	--	--
B	--	132	307	--	--
Zn	--	43	200	--	--
V	--	29	21	--	--
Mn	--	20	22	--	--
F	--	79	57	--	--
Cl	400	600	800	1000	--

*From trials of American coals at Westfield⁽³⁾.

†Data from SASOL unit in South Africa⁽⁸⁾.

‡Data from trials of American coals at Westfield⁽¹⁰⁾.

**TABLE A-3. PRODUCTION RATE AND COMPOSITION OF LURGI
PRODUCT GAS-STREAM NO. 10³ 8**

Coal No.	1	2	3	4	5
Production Rate:					
Nm ³ /kg coal (CO ₂ , N ₂ , and O ₂ free basis)	0.98 m ³ /kg	1.36	1.79	1.32	1.36
Gas Analysis:					
H ₂	41.1%	39.1	38.8	39.4	40.05
O ₂ (includes N ₂ +Argon)	1.2	1.2 (N ₂ -0.6)	1.5 (N ₂ -0.7)	1.6 (N ₂ -0.8)	--
CO	15.1	17.3	17.5	16.9	20.20
CH ₄	11.2	9.4	9.2	9.0	8.84
CO ₂	30.4	31.2	31.0	31.5	28.78
C ₂ H ₆	0.5%	0.7	0.5 (C ₂ H ₄ -0.3)	0.7 (C ₂ H ₆ -0.1)	0.54
H ₂ S	666g/100Nm ³	1510	1420	1010	422
Total Organic					
Sulfur	12-40	23	30	15	--
NH ₃	0.09	0.18	not detectable	0.18	--
HCN	0.27g/100Nm ³	2.8	8.7	0.50	--
Naphthalene	0.24	0.68	1.1	1.2	--
St. ClairdeVille Condensable	389	460	531	277	--

TABLE A-4. COMPOSITION OF LURGI SEPARATOR FLASH GAS-STREAM NO. 12
(VOLUME PERCENT)³

Coal No.	1		2		3		4		5
	Tar Sep.	Oil Sep.	Tar Sep.	Oil Sep.	Tar Sep.	Oil Sep.	Tar Sep.	Oil Sep.	--
H ₂ S	3.8	8.6	5.7	5.5	6.2	6.8	4.4	5.5	--
NH ₃	6.3	12.0	1.0	1.8	4.6	2.7	2.9	3.5	--
CO ₂	64.7	59.3	84.9	85.5	62.9	67.0	71.3	73.9	--
CO	5.9	4.7	1.5	0.8	4.5	4.2	4.7	3.8	--
H ₂	2.9	2.3	3.5	3.6	11.7	13.3	12.0	9.6	--
O ₂ +Argon	3.1	2.5	0.4	0.6	1.3	1.4	0.3	0.2	--
N ₂	8.0	6.4	1.2	1.0	5.9	2.3	1.0	0.8	--
CH ₄	5.3	4.2	1.8	1.2	2.9	2.3	3.4	2.7	--

TABLE A-5. PROPERTIES OF LURGI TAR—STREAM NO. 10

Coal No.	1	2	3	4	5
Production Rate: kg/kg coal	0.02	0.03	0.04	0.03	0.02*
Water: wt. %	30.0	26.7	10.4	11.9	--
Toluene insoluble wt. %	22.0	4.5	7.1	8.5	--
Density: grams/cc	1.025	1.145	1.148	1.175	--
Phenols: (wet) wt. %	5.3	2	4.7	1	--
Calorific Value					
Gross: Kcal/kg (Btu/lb)	8794 (15,830)	8829 (15,893)	8837 (15,906)	8956 (16,120)	--
Ultimate Analysis (dry, dust-free basis)					
C wt. %	83.06	85.48	85.85	88.51	--
H wt. %	7.69	6.44	6.40	5.93	--
N wt. %	0.65	1.18	1.19	0.87	--
S wt. %	0.28	1.70	2.39	1.52	0.3
Cl wt. %	0.04	N.D.	N.D.	N.D.	--
Ash wt. %	0.05	0.03	0.01	0.01	--
O (by difference) wt. %	8.23	5.17	4.16	3.16	--

TABLE A-6. PROPERTIES OF LURGI OIL—STREAM NO. 13³

Coal No.	1	2	3	4	5
Production rate kg/kg	0.02	0.003	0.007	0.01	0.004
Water: wt. %	22.3	4.3	5.4	15.4	--
Dust: wt. %	0.4	0.8	0.1	0.02	--
Density: grams/cc	0.937	1.015	1.011	0.991	--
Phenols: (dry, dust-free) wt. %	19.1	20.1	19.2	10.0	--
Calorific Value					
Kcal/kg (Btu/lb)	(16,960)	(16,482)	(16,578)	(17,134)	--
Ultimate Analysis:					
C: wt. %	81.34	84.82	8.488	87.33	--
H: wt. %	9.17	7.77	7.65	7.61	--
N: wt. %	0.46	0.70	0.49	0.45	--
S: wt. %	0.50	2.40	2.27	1.50	0.25
Cl: wt. %	0.04	N.D.	N.D.	N.D.	--
Ash: wt. %	0.03	0.01	0.01	0.01	--
Oxygen: (by difference) wt. %	8.46	4.30	4.70	3.10	--

TABLE A-7. PROPERTIES OF LURGI LIQUORS—STREAM NO. 14³

Coal No.	1		2		3		4		5
Prod. Rate kg/kg	0.93		2.11		1.77		2.60		1.06
Tar: ppm	350	650	1130	2150	2150	2200	300	1100	5000 (tar & oil)
Analysis on tar free basis	Inlet tar sep.	Inlet oil sep.	Inlet tar sep.	Inlet oil sep.	Inlet tar sep.	Inlet oil sep.	Inlet tar sep.	Inlet oil sep.	
Tar free basis									
pH	9.6	8.3	9.8	8.5	9.5	8.3	9.3	8.2	--
S.G. at 60°F	1.003	1.025	1.003	1.032	1.002	1.027	1.000	1.026	--
T.D.S.: ppm	4030	1765	2770	1570	3180	1120	1550	1240	--
T.D.S. after ignition ppm	45	35	110	35	85	25	105	120	--
Sulfide H ₂ S, ppm	130	115	25	440	15	490	65	520	--
Total S; ppm	150	265	180	730	160	930	155	720	--
Fatty acids: ppm	1250	1670	490	280	400	260	275	610	0.03%
Ammonia:									
Free: ppm	3990	14015	1700	17650	1520	13970	1600	14000	10,600
Fixed ppm	395	525	280	210	410	330	320	250	150-200
Carbonate: ppm	4070	19460	1280	6550	680	9210	1360	10740	--

(continued)

TABLE A-7 (continued)

Coal No.	1		2		3		4		5
Total phenols: ppm	4200	4406	2200	1900	2900	3750	1400	2150	3250-4000
Cyanide: ppm	2	4	3	11	7	14	1	12	6
Thiocyanate: ppm	6	15	65	160	79	158	70	185	--
Cl: ppm	45	40	135	75	290	170	240	210	--
BOD: ppm	9900	13400	3800	4700	6000	6200	4100	5400	--
COD: ppm	22700	20800	10100	12000	9300	10600	650	7500	--

TABLE A-8. PROPERTIES OF LURGI ASH—STREAM NO. 9³ 10

Coal No.	1	2	3	4	5
Production Rate: kg/kg	0.097	0.090	0.087	0.077	0.313
Angle of repose	24 ⁰	33 ⁰	41 ⁰	43 ⁰	--
Bulk Density Poured:					
kg/Nm ³ (lb/ft ³)	918 (57.4)	762 (47.6)	990 (61.9)	(42.1)	--
Tapped:					
kg/Nm ³ (lb/ft ³)	1078 (67.4)	894 (55.9)	1106 (69.1)	(48.9)	--
Ash Fusion Temp. Oxidizing:					
I.F.: °C	1240	1350	1280	1340	--
H.P.: °C	1260	1365	1300	1360	--
F.P.: °C	1290	1390	1330	1380	--
Reducing:					
I.F.: °C	1165	1090	1030	1145	--
H.P.: °C	1175	1150	1060	1170	--
F.P.: °C	1210	1225	1070	1180	--
Partial analysis					
Carbon: wt. %	6.5	3.2	2.0	7.6	--
SiO ₂ : wt. %	46.8	49.6	46.1	43.6	52
Al ₂ O ₃ : wt. %	17.7	20.5	18.1	20.7	28
Fe ₂ O ₃ : wt. %	11.2	17.2	19.7	15.0	5
CaO: wt. %	8.3	2.1	3.9	3.0	7
MgO: wt. %	3.9	1.0	0.7	0.7	1.7
Sulfur (as SO ₃): wt. %	1.7	1.3	0.6	0.8	0.2
Cl: wt. %	0.01	0.01	0.01	0.01	--

(continued)

TABLE A-8 (continued)

Coal No.	1	2	3	4	5*
Trace Elements† (ppm)					
Be	--	14	20	--	--
Hg	--	.04	.016	--	--
Cd	--	<0.3	<0.3	--	--
Sb	--	0.2	19		
Se	--	--	--	--	--
Mo	--	6	8	--	--
Co	--	.40	.38	--	--
Ni	--	456	462	--	--
Pb	--	96	200	--	--
As	--	0.1	0.3	--	--
Cr	--	750	592	--	--
Cu	--	239	273	--	--
B	--	622	673	--	--
Zn	--	469	1600	--	--
V	--	301	181.	--	--
Mn	--	200	305	--	--
F	--	5	4.6	--	--

*Trace element balance for SASOL is presented in Table A-9.

†From Reference 10.

TABLE A-9. TRACE ELEMENT BALANCE FOR LURGI AT SASOL*
(PERCENT OF ELEMENT IN COAL)⁸

Element	Ash	Liquor	Tar	Oil	Total
Be	1	1.6	0.5	0.01	3
B	36	3.5	0.8	0.002	40
V	72	0.06	0.005	<0.001	72
Mn	154	0.36	0.005	<0.001	154
Ni	154	0.64	0.05	0.01	155
As	36	90	2.5	5.2	134
Cd	40	35	0.5	1.1	77
Sb	40	36	3	0.5	80
Ce	72	0.1	0.003	0.001	72
Hg	40	32	4.9	0.5	77
Pb	180	3.2	8.2	0.02	191
Br	3.6	32	0.05	--	36
F	54†	42†	0.08	0.003	96
Cl	51†	46†	0.24	0.008	97

*Analysis by spark source mass spectrometer (which can give a semi-quantitative analysis) for El Paso by SASOL.

†% distribution calculated on analyses as done by Sasol previously.

DATA GAPS AND LIMITATIONS

Even though the Lurgi gasifier has the most complete data of any gasifier because of its advanced development, the available data are not comprehensive in that not all streams (e.g., lock hopper vent gas) are addressed, and not all potential pollutants and toxicological and ecological properties are identified. An environmental data acquisition effort that would lead to generation of the needed data corresponds to EPA's phased level approach to multimedia environmental sampling and analysis.⁹

RELATED PROGRAMS

Environmental assessments of commercial-scale Lurgi SNG facilities have been prepared by El Paso Natural Gas for its proposed Burnham facility and by ANG Coal Gasification Company for its proposed North Dakota Coal Gasification Project. Documents on process and environmental considerations for other projects have also been released. Chief among these is the Wesco SNG facility. The Department of Energy (DOE) recently conducted tests at the British Coal Board's Lurgi plant at Westfield, Scotland. The tests involved operating the Lurgi gasifier in the slagging mode (this is the subject of another gasifier data sheet). EPA has released a report, Control of Emissions from Lurgi Coal Gasification Plants (EPA 450/2-78-012, March 1978), which is to provide information to States and regional EPA offices involved in setting standards for or evaluating impacts from proposed Lurgi gasification facilities.

REFERENCES

1. Handbook of Gasifiers and Gas Treatment Systems. Dravo Corp. ERDA FE-17772-11. February 1972.
2. The Lurgi Process: The Route to S.N.G. from Coal. (Presented at the Fourth Synthetic Pipeline Gas Symposium. Chicago. October 1972.)
3. Woodall-Duckham, Ltd. Trials of American Coals in a Lurgi Gasifier at Westfield, Scotland (final report). Crawley, Sussex, England. Research and Development Report No. 105, FE-105. November 1974.
4. Preliminary Economic Analysis of Lurgi Plant Producing 250 Million SCFD Gas from New Mexico Coal. Bureau of Mines. Morgantown, W.Va. Report No. ERDA-75-57. March 1976.
5. Gallagher, J. T. Political and Economic Justification for Immediate Realization of a Synfuels Industry, Third Annual International Conference on Coal Gasification and Liquefaction: What Needs to be Done Now. Pittsburgh, Pa. August 1976.
6. Kasper, S. Lurgi Gasification Process: Prospects for Commercialization, Symposium on Coal Gasification and Liquefaction. Pittsburgh, Pa. August 1974.
7. The Lurgi Pressure Gasification: Applicability. Lurgi Express Information Brochure Number 01145/6.75. January 1974.
8. Information Provided to the Fuel Process Branch of EPA's Industrial Environmental Research Laboratory (Research Triangle Park) by South African Coal, Oil and Gas Corporation, Ltd. November 1974.

9. Dorsey, J. A., and Johnson, L. D. Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1. EPA-600/2-77-115. June 1977.
10. Sather, N. F., et al. Potential Trace Element Emissions from the Gasification of Illinois Coal. Illinois Institute for Environmental Quality. Number 75-08. February 1975.

APPENDIX B

RECTISOL PROCESS

(SINGLE-ABSORPTION MODE)

GENERAL INFORMATION

1. Operating Principles: physical absorption of the sour components (H_2S , CO_2 , COS , mercaptans, etc.) of a gas stream using methanol as the sorbent. Selective regeneration can provide a rich sulfur-containing gas stream and a relatively pure CO_2 stream.
2. Development Status: commercially available.
3. Licensors/Developer: Lurgi Mineralöltechnik GmbH
American Lurgi Corporation
377 Rt. 17 South
Hasbrouck Heights, N.J.
4. Commercial Applications
 - Purification of low/medium-Btu gas produced from coal gasification. Gasification plants using the process include Sasolburg, South Africa; Westfield, Scotland; and Pristina, Yugoslavia.
 - Carbon dioxide removal and drying of coal-derived ammonia synthesis gas. One of the facilities using this process is located in Kutahya, Turkey.
 - Carbon dioxide removal from low-temperature fractionation feed gas. The locations of facilities using the process are not known.
 - Carbon dioxide and water removal from a feed gas to LNG plants. Plant location(s) are unknown.

PROCESS INFORMATION^{1 2 3 6}

1. Flow diagram (see Figure B-1, B-2, and B-3): the Rectisol process can be used in a variety of modes to achieve different treatment objectives. Only three operation modes that have been used or proposed appear most pertinent to coal conversion and are discussed here. The pertinent features of these operation modes are summarized in Table B-1.
2. Equipment: conventional absorbers, stripping columns, distillation columns, heat exchangers, separators, and regenerators.
 - Construction: vessels may be fabricated from carbon steel, dimensions dependent on application.
3. Feed Stream Requirements:^{*} gas should be cooled to reduce solvent losses; high pressures (close to 2.0 MPa or 300 psia) are usual. Gas temperatures between 253 K and 213 K ($-5^{\circ}F$ to $-75^{\circ}F$) are usual, depending on conditions.⁶

^{*}These conditions are for optimum performance; other input conditions can be handled with increased solvent losses and reduced efficiency.

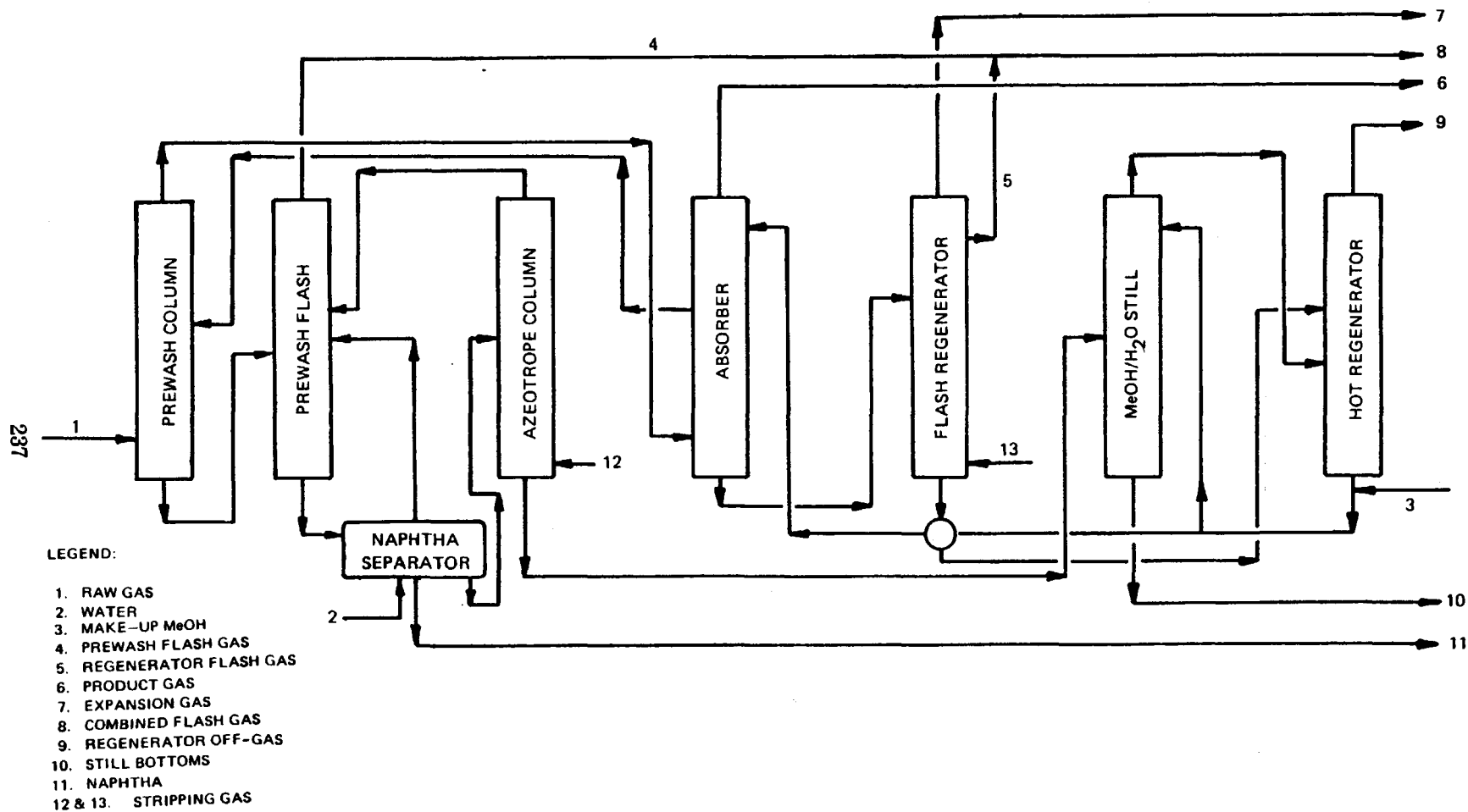


Figure B-1. Rectisol type A³ (removal of CO₂ from gas mixtures containing little or no H₂S).

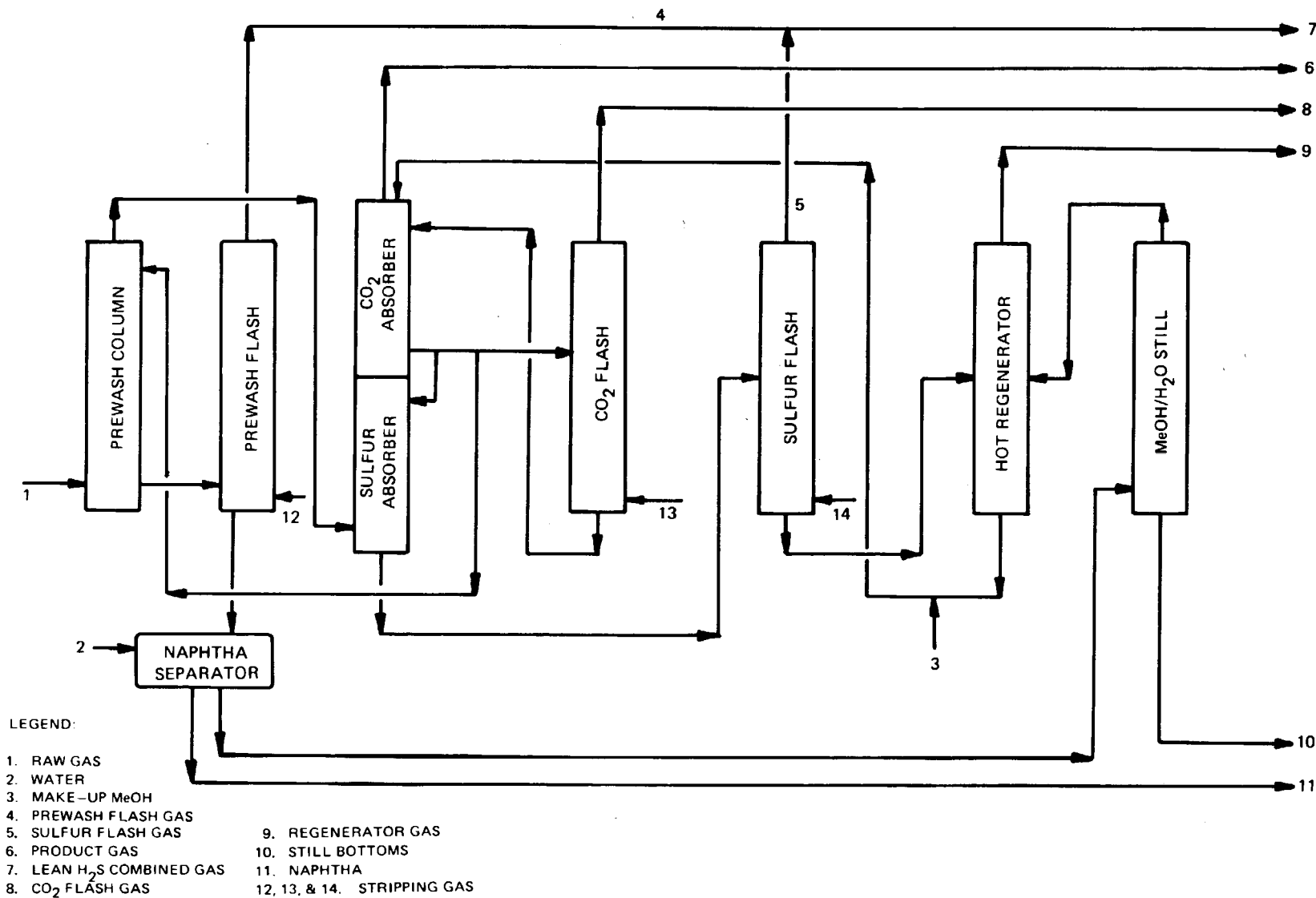


Figure B-2. Rectisol type B³ (removal of CO_2 and H_2S with separate recovery).

1. RAW GAS
2. WATER
3. MeOH
4. NH₃ COOLANT
5. NH₃ COOLANT
6. PRODUCT GAS
7. INTERMEDIATE GAS
8. REGENERATOR OFF-GAS
9. 5TH STAGE FLASH GAS
10. 6TH STAGE FLASH GAS
11. 1ST, 2ND, 3RD, 4TH STAGE FLASH GAS
12. AROMATICS
13. STILL BOTTOMS
14. CONDENSATE

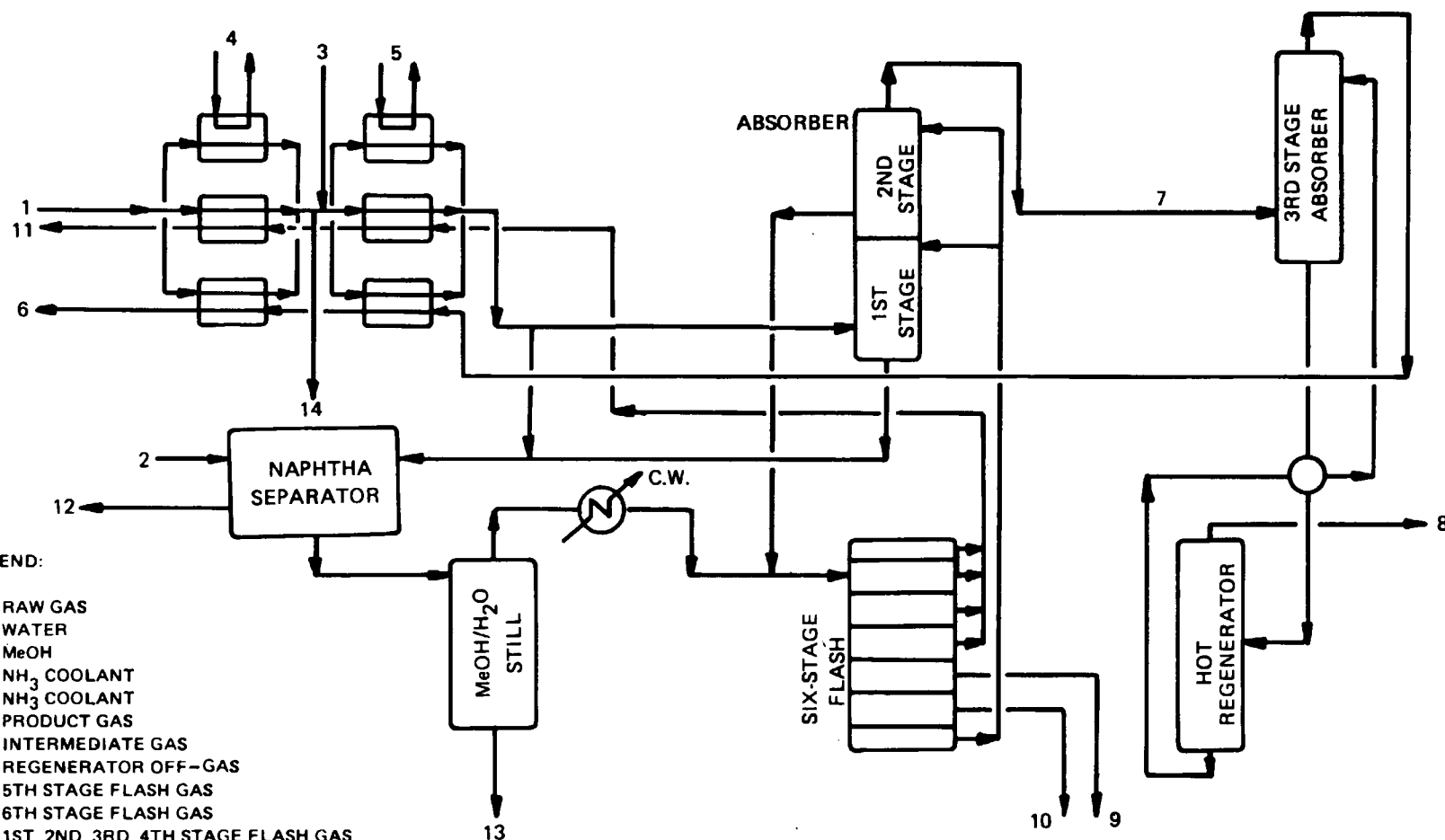


Figure B-3. Rectisol type C³ (removal of CO₂ and H₂S with separate recovery).

**TABLE B-1. PROCESS DESCRIPTIONS FOR RECTISOL TYPES A, B, AND C
OPERATING MODES**

Type	Process Application/ Treatment Objective	Process Description
A (Fig. B-1)	Removal of CO ₂ from gas mixture containing little or no sulfur.	A methanol stream rich in CO ₂ and H ₂ S is used in the prewash column to remove water, naphtha, ammonia and residual heavy hydrocarbons from the raw gas. The exit solvent enters the prewash flash column where a flash stream lean in H ₂ S and rich in CO ₂ is produced (Stream 4). The liquid bottoms from the flash vessel are routed to a separator where water (Stream 2) is added so that the naphtha and heavy hydrocarbons can be separated. In the main absorber raw gas contacts a pure methanol stream from the hot regenerator. A slipstream of saturated methanol is sent to the prewash column. The remaining methanol is sent to a flash regenerator where the absorbed gases are removed. Methanol from flash is sent to the hot regenerator where the final traces of CO ₂ and H ₂ S are removed. Water is removed from the prewash methanol in the methanol/water still with off gases going to the hot regenerator. Stripping gases (usually nitrogen) may be used.
B (Fig. B-2)	Simultaneous removal of CO ₂ and sulfur compounds with separate recovery.	Except for the use of a two-stage absorber and two separate flash columns, Type B Rectisol is very similar to Type A. The raw gas (after leaving the prewash absorber) is first contacted with a CO ₂ -saturated methanol stream. This first stage absorber removes H ₂ S. In the second stage a pure methanol stream removes CO ₂ . The methanol for first stage comes from the second stage absorber. The two methanol streams are flashed separately to create a stream rich in H ₂ S (No. 5) and a nearly pure CO ₂ stream (No. 8). Regeneration is the same as in the Type A.
C (Fig. B-3)	Same as Type B	The primary difference in Type C as compared to Type B is in the regeneration process. The first stage acts like the prewash in Type B with second and third stages similar to first and second in Type B. A multistage flash unit is used to desorb gases from first and second stage absorption. First stage methanol is first combined with heavy hydrocarbons and water removed from the raw gas and sent to the separator. The separator works in the same manner as the separators in Types A and B. The multistage flash reduces the regeneration requirements. The third stage methanol is handled in a conventional hot regenerator to provide a pure methanol for final absorption. A split stream regeneration section is also shown in Figure B-3. Similar gas cooling sections are used in Types A and B but are not shown on the figures.

4. Operating Parameters

- Absorption: 0.3-7.1 MPa (45 to 1066 psia) approximately 303 K (80° F).
- Regeneration: see discharge streams, Section 8.0.

5. Process Efficiency and Reliability

- CO₂ better than 97 percent.⁴
- H₂S better than 99.9 percent.⁴
- Reliability is considered high with a simple solvent and construction.

6. Raw Material Requirements

- Solvent: CH₃OH; purity - ?

Solvent losses can be estimated using equilibrium constants; however, considerable errors could be involved. No information available on solvent losses based on actual operating data.

7. Utility Requirements: ?

8. Miscellaneous: ?

PROCESS ADVANTAGES

- Lower energy consumption than conventional amine solvent acid-gas removal processes.²
- Can be adapted for removal of all impurities in one pass or for selective removal.²
- Production of a product gas with very low water content.²
- Noncorrosive nature of the solvent.³
- Unlimited solubility of methanol in water.³
- Chemical stability and low freezing point.³
- Good for high-pressure applications.

PROCESS DISADVANTAGES

- Complex flow scheme.²
- Solvent carryover losses may be high.²
- Not suited for operation at pressures below 1.1 MPa (165 psia).²

PROCESS ECONOMICS - ?

INPUT STREAMS

1. Gaseous

- Stream No. 1: Raw Gas--see Table B-2.
- Stream Nos. 12, 13, and 14: Types A and B stripping gas:^{†3}
When used, the stripping gas is nitrogen from an oxygen plant.

[†]This corresponds to the range from Type A and B facilities reported in Table B-2 from Reference 3.

TABLE B-2. RECTISOL GASEOUS INPUT STREAMS

Constituents/ Parameters	Stream Number Reference				
	1 ⁽⁵⁾ Type A	1 ⁽³⁾ Type A	1 ⁽³⁾ Type B	1 ⁽³⁾ Type B	1 ⁽⁴⁾ Type c
H ₂ *	40.05	58.4	62.31	61.59	63.74
CO	20.20	0.3	3.25	2.60	4.13
CH ₄	8.84	0.2	0.17	0.33	0.13
CO ₂	28.78	21.9	33.25	34.55	31.62
N ₂ + Ar	1.59	19.2	0.53	0.41	0.12
H ₂ S	4220 mg/Nm ³	--	0.49	0.52	0.26
COS	10 ppm	--	10 ppm	--	63 ppm
CS ₂	--	--	--	--	--
RSH	20 ppm	--	--	--	--
Thiophene	--	--	--	--	--
C ₂ ⁺	0.54	--	--	--	--
MeOH	--	--	--	--	--
Temp: °K (°F)	303 (86)	--	--	--	303 (86)
Pressure: MPa (psia)	2.5 (380)	2.4 (356)	3.2 (480)	7.1 (1066)	0.3 (45)
Rate: Nm ³ /hr (SCFM)	381,000 (236,000)	153,100 (94,300)	142,340 (88,250)	137,000 (84,940)	80,000 (49,600)

*All values, unless otherwise noted, are in volume percent.

Rate: 231,300 to 693,500 Nm³/hr (153,400 to 430,000 SCFM).

Temperature: ?

Pressure: 0.1 to 0.5 MPa (20 to 80 psia).

2. Liquid

- Stream No. 2: Water to Separator--quantity ?
- Stream No. 3: Methanol Makeup--quantity ?

INTERMEDIATE STREAMS

1. Gaseous

- Stream Nos. 4 and 5: Types A and B Flash Gases--?
- Stream No. 7: Type C Intermediate Gas--?

DISCHARGE STREAMS

1. Gaseous

- Stream No. 6: Product Gas--see Table B-3.
- Stream Nos. 7, 8, and 9: Types A and B Offgases--see Table B-4.
- Stream Nos. 8, 9, 10, and 11: Type C Offgases--see Table B-4.

2. Liquid

- Stream No. 10: Types A and B Still Bottoms--?
- Stream No. 11: Types A and B Hydrocarbons and Stream No. 12--Type C Hydrocarbons--?
- Stream No. 13: Type C Still Bottoms:⁴

Rate:	16 m ³ /hr
pH:	9.7
Phenol:	18 mg/L
Cyanide (as CN):	10.4 mg/L (includes thiocyanate)
Ammonia (as N):	42 mg/L
Sulfides (as S):	Trace
Oxygen absorbed:	286
COD:	1,606 mg/L
Conductivity:	1,111 μ mhos/cm
- Stream No. 14: Type C--?

DATA GAPS AND LIMITATIONS

The major limitation in the data is that not all input and discharge streams are characterized, and the characterizations are not comprehensive in that all potential pollutants and toxicological and ecological properties are not identified. An example is the total lack of data on MeOH carryover.

RELATED PROGRAMS - ?

REFERENCES

1. Sinor, J. E. Evaluation of Background Data Relating to New Source Performance Standards for Lurgi Gasification. EPA-600/7-77-057. June 1977.

TABLE B-3. RECTISOL PRODUCT GAS STREAMS

Constituents/ Parameters	Stream No.				
	6 ⁽⁵⁾ Type A	6 ⁽³⁾ Type A	6 ⁽³⁾ Type B	6 ⁽³⁾ Type B	6 ⁽⁴⁾ Type C
H ₂	57.30	74.8	94.08	94.92	93.58
CO	28.40	0.38	4.86	3.94	6.06
CH ₄	11.38	0.25	0.24	0.47	0.19
CO ₂	0.93	60 ppm	10 ppm	50 ppm	--
N ₂ + Ar	1.77	24.57	0.82	0.67	0.17
H ₂ S	0.05 mg/Nm ³ total sulfur	--	--	1 ppm	--
COS	--	--	--	--	--
CS ₂	--	--	--	--	--
RSH	--	--	--	--	--
Thiophene	--	--	--	--	--
C ₂ ⁺	--	--	--	--	--
MeOH	--	--	--	--	--
Temp: °K (°F)	288(59)	--	--	--	295(72)
Pressure: MPa (psia)	2.3(345)	2.2(327)	3.0(450)	6.9(1037)	2.9(440)
Rate: Nm ³ /hr (SCFM)	263,000 (163,000)	118,500 (73,500)	94,040 (34,300)	88,530 (54,890)	54,500 (33,800)

TABLE B-4. RECTISOL OFFGAS STREAMS

Constituents/ Parameters	Stream Number Reference														
	Type A ⁽³⁾		Type B ⁽³⁾			Type B ⁽³⁾			Type B ⁽⁴⁾			Type C ⁽⁴⁾			
	8	9	7	8	9	7	8	9	7	8	9	11	9	10	8
H ₂	0.4	--	0.15	0.79	--	0.76	--	--	0.33	--	--	21.4	2.6	0.14	--
CO	0.014	--	0.04	0.22	--	0.11	--	--	0.14	--	--	18.2	4.8	0.0	--
CH ₄	0.017	--	--	0.05	--	0.06	--	--	0.00	--	--	11.4	7.2	0.9	--
CO ₂	73.95	--	76.81	98.91	64.6	90.85	--	68.31	80.19	--	68.46	46.7	83.4	97.2	--
N ₂ + Ar	25.62*	--	23.0*	0.05	0.1	8.22*	--	1.92	19.34*	--	--	1.5	0.8	0.03	--
H ₂ S	--	--	2 ppm	2 ppm	35.2	5 ppm	--	29.77	<5 ppm	--	30.78	3176 ppm	4941 ppm	8824 ppm	--
COS	--	--	--	--	0.1	--	--	--	8 ppm	--	0.76	--	--	0.003	--
C ₂ ⁺	--	--	--	--	--	--	--	--	--	--	--	0.7	1.1	0.7	--
MeOH	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
CS ₂	--	--	--	--	--	--	--	--	--	--	--	--	--	0.0002	--
RSH	--	--	--	--	--	--	--	--	--	--	--	--	--	0.028	--
Thiophene	--	--	--	--	--	--	--	--	--	--	--	--	--	0.0002	--
Temp: °K (°F)	--	--	--	--	--	--	--	--	295(72)	--	322(121)	273(32)	273(32)	268(23)	--
Pressure: MPa (psia)	0.1(15)	--	0.1(15)	0.24(36)	0.24(36)	0.1(16)	--	0.2(28)	0.1(15)	--	0.5(73)	1.3(195)	0.46(70)	0.1(15)	--
Rate: Nm ³ /hr (SCFM)	45,090 (27,956)	--	41,480 (25,845)	14,130 (8,760)	1980 (1230)	50,280 (31,170)	--	2390 (1480)	30,800 (19,100)	--	673 (417)	4500 (2852)	15,000 (9,300)	98,000 (60,760)	--

*Includes N₂ stripper gas.

2. Kohl, A., and Riesenfeld, F. Gas Purification. Gulf Publishing Co. Houston, Texas. 1974.
3. Scholz, W. H. Rectisol: A Low-Temperature Scrubbing Process for Gas Purification. Advances in Cryogenic Engineering, 15. 1969.
4. Draft: Standards Support and Environmental Impact Statement Volume 1: Proposed Standards of Performance for Lurgi Coal Gasification Plants. November 1976.
5. South African Coal, Oil & Gas Corp., Ltd. Information Provided to the Fuel Process Branch of EPA's Industrial Environmental Research Laboratory, Research Triangle Park, N.C. November 1974.
6. Maddox, R. N. Gas and Liquid Sweetening. Campbell Petroleum Series. 1974.

(DUAL-ABSORPTION MODE)

GENERAL INFORMATION

1. Operating Principles: physical absorption of acid gases (CO_2 , H_2S , COS , CS_2 , etc.) using methanol. When operated in the dual-absorption mode, CO_2 -saturated methanol is used in the first absorption step to remove H_2S and other sulfur compounds. In the second absorption step, pure methanol is used for the absorption of CO_2 .
2. Development Status: commercially available.
3. Licensor/Developer: Lurgi Mineralöstechnik GmbH
American Lurgi Corporation
377 Rt. 17 South
Hasbrouck Heights, N.J.
4. Commercial Applications: a Rectisol of this type is installed at Modderfontein, South Africa, for purification of synthetic gas from coal for manufacture of ammonia.

PROCESS INFORMATION

1. Flow Diagram: see Figure B-4.¹
 - Process Description: CO_2 and H_2S are absorbed in separate columns with CO shift occurring between operations. In essence, two separate Rectisol units, each with its own stripper column (but with common still and regenerator) are employed. CO_2 -saturated methanol is used to absorb H_2S in the first absorber. Pure methanol from the regenerator is used in the CO_2 absorber.
2. Equipment: conventional absorbers, stripping columns, distillation columns, heat exchangers, and knockout drums.
 - Construction: vessels may be fabricated from carbon steel; dimensions depend on application.
3. Feed Stream Requirements: ?
4. Operating Parameters^{1 2 3}
 - Absorption: H_2S : 297 K (75° F) 3.0 MPa (440 psia).
 CO_2 : 213 K (-75° F) 4.9 MPa (720 psia).
 - Regeneration: ?

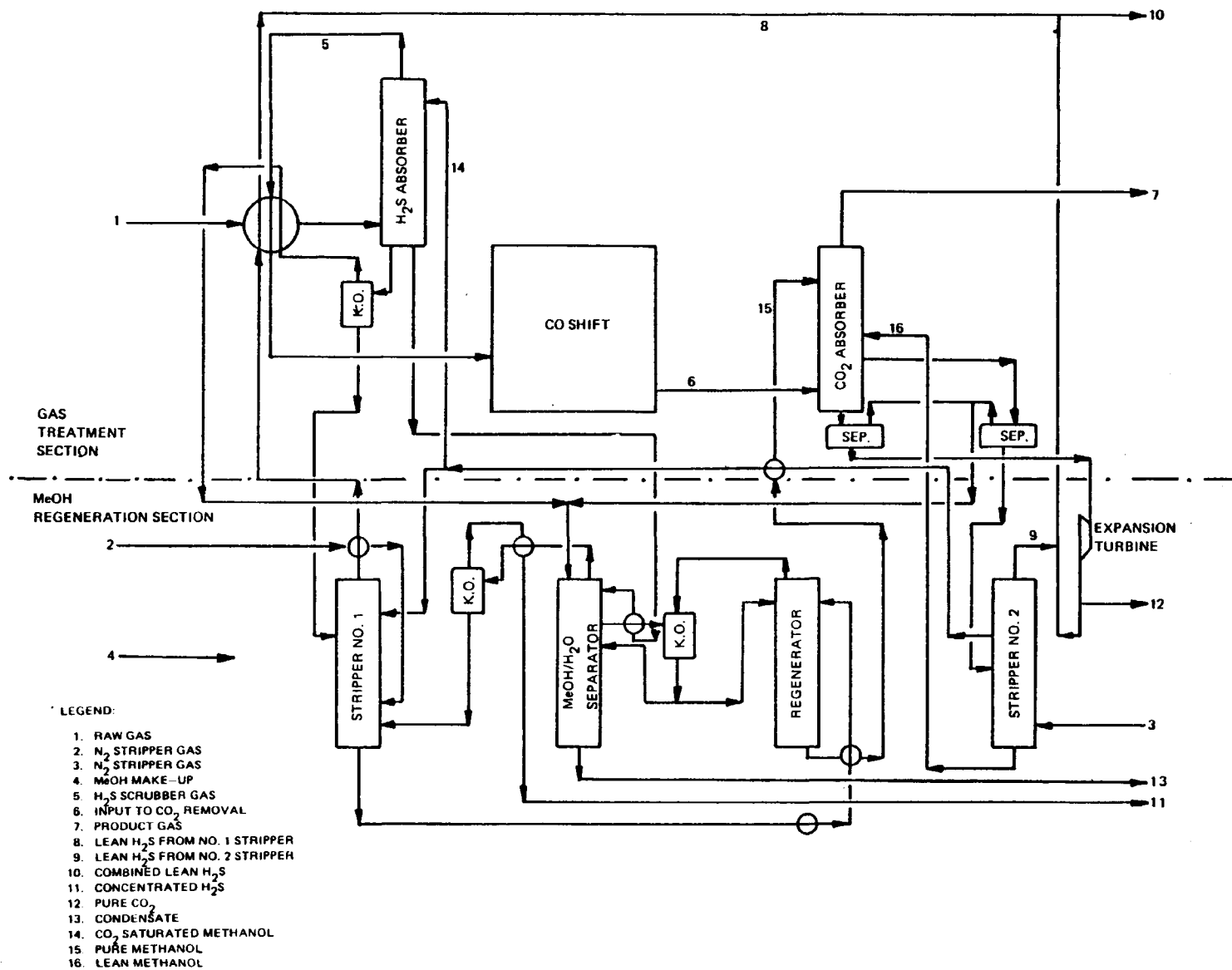


Figure B-4. Rectisol—dual-absorption flow diagram (as installed at Modderfontein, South Africa).

5. Process Efficiency and Reliability: removal of acid gases to a few micrograms per cubic meter. Reliability is high because of relatively simple operation.
6. Raw Material Requirements
 - Solvent: methanol
7. Utility Requirements: utility requirements are high because of large refrigeration requirements. Exact amounts are unknown.
8. Miscellaneous: ?

PROCESS ADVANTAGES

- A single solvent (methanol) is used for absorption of both CO_2 and H_2S .
- Noncorrosive environments.
- H_2S streams rich enough to be processed in a Claus unit can be obtained.
- Good selectivity between acid and product gases.
- Unlimited solubility of solvent in water.
- Solvent is chemically stable and has a low freezing point.

PROCESS LIMITATIONS

- Solvent retains heavy hydrocarbons.
- Solvent losses during regeneration may be high.
- High utility requirements.

PROCESS ECONOMICS - ?

INPUT STREAMS

Stream data are based on the Modderfontein plant.

1. Gaseous

A. Stream No. 1

<u>Composition, wt %</u>	<u>Ref. 1</u>	<u>Ref. 2</u>
CO_2	11.6	13.37
CO	55.02	54.45
H_2	31.2	30.00
N_2	1.0	0.95
Ar	0.5	0.54
CH_4	0.1	0.10
H_2S	0.5	0.59
		(includes COS)
COS	0.8	--
MeOH	0	0
Volume $\text{Nm}^3/(\text{scfm})$	91,700 (53,370)	--
Pressure, MPa (psia)	--	--
Temperature, K ($^{\circ}\text{F}$)	--	--

- B. Stream Nos. 2 and 3: nitrogen from air separation plant, rate unknown.

2. Liquid

A. Stream No. 4: methanol makeup, rate unknown.

INTERMEDIATE STREAMS

1. Gaseous

A. Stream No. 5

<u>Composition, wt %</u>	<u>Ref. 1</u>	<u>Ref. 2</u>
CO ₂	12.00	11.27
CO	54.60	56.02
H ₂	31.80	31.06
N ₂	1.00	0.98
Ar	0.50	0.57
CH ₄	0.10	0.10
H ₂ S	--	--
COS	--	--
MeOH	--	--
Volume, Nm ² /hr (scfm)	93,300 (58,370)	--
Pressure, MPa (psia)	3.0(440)	--
Temperature, K (°F)	298(75)	--

B. Stream No. 6

<u>Composition, wt %</u>	<u>Ref. 1</u>	<u>Ref. 2</u>
CO ₂	41.30	41.29
CO	3.00	3.00
H ₂	54.64	54.63
N ₂	0.70	0.64
Ar	0.30	0.37
CH ₄	0.06	0.07
H ₂ S	--	--
COS	--	--
MeOH	--	--
Volume, Nm ³ /hr (scfm)	140,000 (87,590)	--
Pressure, MPa (psia)	5.0(735)	--
Temperature, K (°F)	308(95)	--

C. Stream No. 8: ?

D. Stream No. 9: ?

DISCHARGE STREAMS

1. Gaseous

A. Stream No. 7

<u>Composition, wt %</u>	<u>Ref. 1</u>	<u>Ref. 2</u>
CO ₂	--	--
CO	4.60	5.02
H ₂	93.50	93.14
N ₂	1.20	1.12
Ar	0.60	0.61
CH ₄	0.10	0.11
H ₂ S	--	--
COS	--	--
MeOH	--	--
Volume, Nm ³ /hr (scfm)	80,000 (50,110)	--
Pressure, MPa (psia)	4.9(720)	--
Temperature, K (°F)	213(-75)	--

- B. Stream No. 10: ?
- C. Stream No. 12: mostly CO₂, trace constituents unknown.
- D. Stream No. 11

<u>Composition, wt %</u>	<u>Ref. 1</u>	<u>Ref. 2</u>
CO ₂	75.00	--
CO	--	--
H ₂	--	--
N ₂	--	--
Ar	--	--
CH ₄	--	--
H ₂ S	22.00	--
COS	3.00	--
MeOH	--	--
Volume, Nm ³ /hr (scfm)	21,000 (13,140)	--
Pressure, MPa (psia)	0.1(15)	--
Temperature, K (°F)	313(105)	--

2. Liquid

- A. Stream No. 13: ?

DATA GAPS AND LIMITATIONS

Limitations in the data for the selective absorption Rectisol relate primarily to the stream compositions. These limitations include the following:

- Input gas streams: few data on minor component concentrations. No data on N₂ stripper gas rates.
- Makeup methanol: no data on amount of makeup methanol required.
- Intermediate and product gas streams: limited data on minor components.
- Discharge gas streams: limited data on compositions of off-gas streams from the strippers and regenerator.
- Condensate stream: no data on compositions and rates of regenerator condensate stream.
- Operating parameters: utility requirements, regeneration parameters, etc., are not reported.

RELATED PROGRAMS

No known programs are presently undertaken to assess the discharges from this process.

REFERENCES

1. Staeger, H. Ammonia Production on the Basis of Coal Gasification. Chemical Industry Developments. 1973.
2. Schellberg, W. Coal-Based Ammonia Plants. ICI Operating Symposium Paper 21. 1974.
3. Goetze, E. K. Status of Coal Gasification Technology. FAI Symposium on Coal as Feedstock for Fertilizer Production. New Delhi. 1974.

ENVIRONMENTAL ASSESSMENT REPORT FOR WELLMAN-GALUSHA GASIFICATION SYSTEMS

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Abstract

Radian Corporation has just entered the fourth year of a 6-yr contract with the U.S. Environmental Protection Agency (EPA) to perform a comprehensive environmental assessment of low- and medium-Btu coal gasification technology. As part of that program, Radian has conducted a number of source test and evaluation programs at operating low-Btu gasification facilities in the United States. The results of those test programs, along with data collected from the open literature, vendors, process licensors, and other industry contacts, have been incorporated into an Environmental Assessment Report (EAR) for Wellman-Galusha low-Btu gasification systems. This paper presents the preliminary results and findings of the Wellman-Galusha EAR work. Included are:

- An overview of Wellman-Galusha low-Btu gasification systems,*
- Identification of waste streams and pollutants of major concern,*
- The status of environmental protection alternatives,*
- Future data needs and recommendations, and*
- Issues and areas of concern of EPA program offices.*

INTRODUCTION

In March 1976, Radian Corporation entered into a contract with the U.S. Environmental Protection Agency (EPA) to perform a comprehensive environmental assessment of low- and medium-Btu coal gasification technology. Originally a 3-yr effort, the low-Btu program has recently been extended for an additional 3 yr. Both the original program and the extension are being directed by the Fuel Process Branch of EPA's Industrial Environmental Research Laboratory (IERL) in Research Triangle Park,

North Carolina.

The initial activity of Radian's low-Btu assessment program involved a comprehensive information search aimed at compiling a data base for low- and medium-Btu gasification technology. While a significant amount of data was obtained, data gaps and areas of questionable or incomplete data were still identified.

In order to obtain the missing data, the second major phase of the low-Btu program—data acquisition—was initiated. This phase involved conducting source test and evaluation programs at a number of operating gasification facilities. To date, data acquisition test efforts have been conducted at three low-Btu gasification facilities in the United States and a medium-Btu facility in Yugoslavia.

The main purpose of this paper is to present a part of the results of the third phase of the low-Btu assessment program; i.e., the results communication phase. Several documents will be prepared over the next 3 yr in order to communicate the assessment program's results and findings. One type of document is the environmental assessment report, or EAR. The purpose of an EAR is to provide EPA administrators, program offices, and policy and planning with a document that represents the EPA Office of Research and Development's research input to standard-setting activities for gasification facilities. Each EAR addresses a unique segment of gasification technology. An EAR includes a detailed evaluation of process, waste stream, and control data collected from field testing programs; open literature; vendors; process licensors; and computer modeling activities. As such, an EAR is a data base for the subject technology.

In 1978, Radian initiated preparation of the first of four environmental assessments reports that will be prepared over the next 3 yr. This EAR addresses Wellman-Galusha low-Btu gasification systems. Incorporated into the Wellman-Galusha EAR are the process, waste stream, and control data collected by Radian at

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the three U.S. test sites. The preliminary results and findings of the Wellman-Galusha EAR are presented in the following text.

OVERVIEW OF WELLMAN-GALUSHA LOW-Btu GASIFICATION SYSTEMS

Wellman-Galusha gasifiers are one of the commercially available gasifiers used to produce low-Btu ($\sim 5.9 \times 10^6$ J/Nm³, 150 Btu/scf) gas from a variety of coal feedstocks. The Wellman-Galusha gasification systems examined in this report are described along with their status, industrial applicability, energy efficiency, costs, and commercial prospects.

System Description

Wellman-Galusha low-Btu gasification systems have three basic operations: coal pretreatment, coal gasification, and gas purification. Each operation includes processes with specific functions, inputs, and outputs. Figure 1 is a generalized flow diagram showing various combinations of operations and process modules for Wellman-Galusha gasification systems. Table 1 summarizes the input and output streams and the function associated with each process.

In this study, four coal feedstocks and three product gas specifications were considered:

- *Coal feedstocks*
 - Anthracite (0.6% S; 11.7% ash)
 - Low-sulfur HVA bituminous (0.7% S; 2.9% ash)
 - High-sulfur HVA bituminous (3.9% S; 8.4% ash)
 - Lignite (0.9% S; 8.3% ash)
- *Product gas specifications*
 - Can meet current NSPS for direct coal combustion
 - Can meet proposed NSPS for direct coal combustion
 - "Very clean" gas

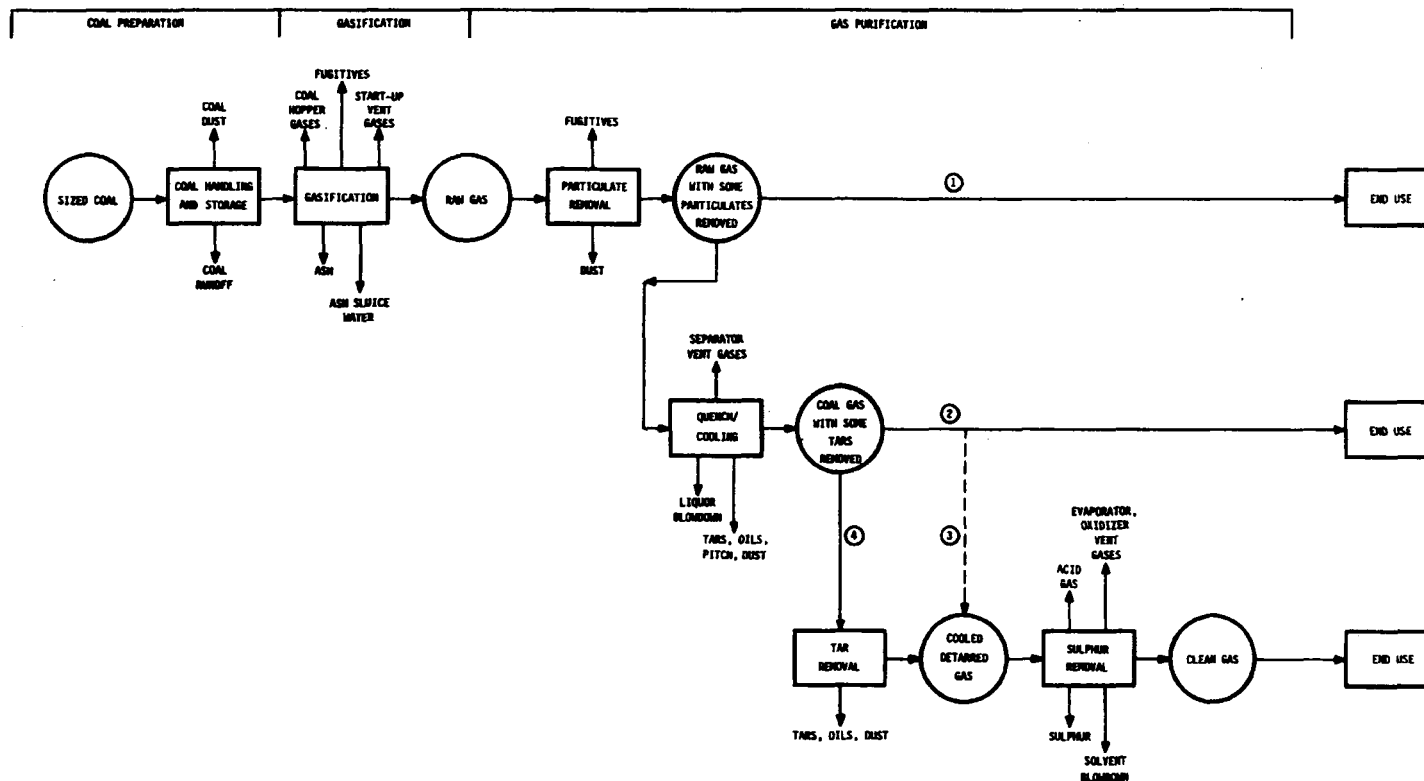
Combinations of these coals and product gas specifications were selected as the study bases. Those combinations resulted in three basic gasification systems being considered. The first system is typical of what would be required to produce fuel gas capable of complying with current New Source Performance Standards (NSPS) for direct combustion of low-sulfur coals (>0.7% S; HHV 30 MJ/kg or 13,000 Btu/lb). This system has only three process modules: coal

handling and storage, gasification, and particulate removal (hot cyclone). This system also represents currently operating facilities that use anthracite and low-sulfur HVA bituminous coals.

A variation of this first system has an additional process module: raw gas quenching and cooling. This additional module removes tars and oils from the raw product gas and reduces the potential for fouling of equipment used to transport the low-Btu product gas to its end use. This system is similar to a facility using Chapman (Wilputte) gasifiers to produce a low-Btu combustion gas for process heaters.

The second Wellman-Galusha gasification system is used to produce a clean gas from anthracite coal. This system contains the following process modules: coal handling and storage, gasification, gas quenching and cooling, and sulfur removal. In this system, the product gas is cooled to 316 K (110° F) before entering the Stretford sulfur-removal process. The Stretford sulfur-removal process is effective in removing H₂S, but organic sulfur species (i.e., COS, CS₂, etc.) will essentially remain intact in the product gas stream.¹ H₂S removal efficiencies greater than 99 percent have been achieved with residual outlet H₂S concentrations less than 10 ppmv.² An advantage of the Stretford process is that it not only removes H₂S but also converts the H₂S into elemental sulfur, which can be recovered as a byproduct.

The third system is used to produce a clean gas from the following coal feedstock: bituminous (HVA, or low-sulfur, and HVB, or high-sulfur) coal and lignite. In this system, the quenched and cooled product gas is sent to a tar/oil removal process followed by a sulfur removal process. An electrostatic precipitator (ESP) is used to remove tars and oils that would cause operating problems with the downstream sulfur removal process. As in the second system, the Stretford process was chosen for removal of sulfur species from the product gas. In addition, the Monoethanolamine (MEA) process was examined. The MEA process is capable of removing both H₂S and organic sulfur compounds. However, the sulfur removal efficiency is dependent upon the pressure of the product gas. For example, at 0.44 MPa (50 psig) residual sulfur concentrations of 16 ppmv can be achieved. At a higher pressure of approximately 1.5 MPa (200 psig), residual sulfur concentra-



KEY TO SYSTEMS

- ① GASIFICATION OF LOW-SULPHUR COALS (LESS THAN 0.7% SULPHUR FOR COALS WITH HEATING VALUES OF 30 MJ/KG OR 13,000 BTU/LB) TO PRODUCE A FUEL GAS ABLE TO COMPLY WITH CURRENT NSPS FOR THE COMBINATION OF COAL.
- ② GASIFICATION OF LOW-SULPHUR COALS TO PRODUCE A MOSTLY TAR-FREE FUEL GAS ABLE TO COMPLY WITH CURRENT NSPS.
- ③ GASIFICATION OF ANTHRACITE COALS TO PRODUCE A FUEL GAS ABLE TO COMPLY WITH PROPOSED NSPS FOR THE COMBUSTION OF COAL; GASIFICATION OF ANTHRACITE COALS TO PRODUCE A "CLEAN" GAS.
- ④ GASIFICATION OF LOW-SULPHUR BITUMINOUS, SUB-BITUMINOUS, AND LIGNITE COALS TO PRODUCE A FUEL GAS ABLE TO COMPLY WITH PROPOSED NSPS FOR THE COMBINATION OF COAL; GASIFICATION OF HIGH-SULPHUR COALS TO PRODUCE A FUEL GAS ABLE TO COMPLY WITH CURRENT AND PROPOSED NSPS FOR THE COMBINATION OF COAL; GASIFICATION OF ALL NON-ANTHRACITE COALS TO PRODUCE A "CLEAN" GAS.

Figure 1. Wellman-Galusha system process modules and multimedia discharges.

**TABLE 1. OPERATIONS/PROCESS MODULES IN WELLMAN-GALUSHA LOW-Btu
GASIFICATION SYSTEMS**

Operation/Process Module	Input Streams	Output Streams	Function	Remarks
Coal Pretreatment				
Coal Handling and Storage	Presized coal	Presized coal Coal dust Coal pile runoff water	Store and transport coal feedstock	Coal storage piles would contain a 30 day coal supply (2-12 Cg, 2000-13,000 short tons of coal for a plant producing 18-88 MW, 60-300 million Btu/hr of low-Btu gas).
Coal Gasification				
Fixed-Bed, Atmospheric Pressure, Dry Ash Gasifier - Wellman-Galusha	Presized coal Steam Air Ash sluice water	Raw product gas Coal hopper gases Fugitive gases Start-up vent gases Ash Ash sluice water	React coal with a mixture of steam and air to produce a raw low-Btu gas	Coals that have been used include anthracite and bituminous. Coal size specifications are 7.9 to 14.3 mm for anthracite and 26-51 mm for bituminous. Larger particle sizes can be used for more reactive coals.
Gas Purification				
Particulate Removal - Hot Cyclone	Raw product gas	Product gas Removed particulates	Remove large particulate matter from the hot, raw product gas	Total particulate removal efficiencies have been determined to be between 50-80%. Small particulate matter will not be removed. Collected particulates have characteristics similar to devolatilized coal particles.
Gas Quenching and Cooling	Product gas Quenching liquor	Quenched/cooled product gas Quench liquor Tars Oils Particulate matter	Remove tars and oils from the product gas and cool the product gas to approximately 316°K (110°F)	The amount of tars and oils removed is dependent upon the coal feedstock. Anthracite coal will produce essentially no tars, however, bituminous coal will produce a significant amount of tars. Emissions from the tar/liquor separator may contain potentially hazardous compounds. Spent quench liquor will require treatment before disposal.
Tar/Oil Removal - Electrostatic Precipitator	Cooled product gas	Cooled/detarred product gas Tars Oils	Remove tar and oil aerosols from the cooled product gas	ESP's have been used to remove tars and oils produced by two-stage, fixed-bed, atmospheric gasifiers and good removal of tars and oils have been demonstrated by ESP's used in sampling systems. Vent gases from tar/oil storage tanks may contain potentially harmful compounds and may need to be controlled.
Sulfur Removal - Stretford	Detarred product gas Stretford solution Air	Clean product gas Oxidizer vent gas Sorbent blowdown Sulfur	Remove H ₂ S from the detarred product gas	Other sulfur species (i.e., COS, CS ₂ , etc.) will not be removed from the product gas. If the HCN concentration is high, then a cyanide guard may be needed. Blowdown sorbent will require treatment before disposal. If the sulfur is to be disposed of, tests need to be performed (i.e., RCRA tests for solid wastes) to determine treatment and/or disposal techniques required.
Sulfur Removal - Monoethanolamine Process	Detarred product gas MEA solution	Clean product gas MEA blowdown Acid gases Sulfur from acid gas treatment processes Tail gases from acid gas treatment processes	Remove sulfur species and CO ₂ from the detarred product gas	Removal efficiency increases with increasing inlet gas pressure. Acid gases have to be treated to control sulfur emissions. MEA blowdown will require treatment before disposal.

TABLE 2. CURRENT WELLMAN-GALUSHA COAL GASIFICATION FACILITIES IN THE UNITED STATES

Company/Locations	Number of Gasifiers	Coal Feedstock	Gas Purification Process	Remarks
Glen-Gery Brick Co. • York, PA • Reading, PA • Shoemakersville, PA • Watsontown, PA	2 2 1 1	Anthracite, low sulfur (~ 0.7%)	• Hot cyclone	• Currently operational • Product gas used to fire brick kilns
National Lime and Stone Co. • Carey, OH	2	Bituminous low sulfur (~ 0.7%)	• Hot cyclone	• Currently operational • Product gas used to fire lime kiln • Lime partially removes sulfur from gas
Can Do, Inc. • Hazeltown, PA	2	Anthracite, low sulfur	• Hot cyclone	• Product gas to supply industrial park • To be operational in 1979
Bureau of Mines • Fort Snelling, MN	1	KY Bituminous CO Subbituminous WY or MT Sub-bituminous ND Lignite; (all coals low sulfur (<1% S))	• Hot cyclone • SO ₂ scrubbers (on combustion gas)	• Product gas to fire pilot iron pelletizing kiln • Excess product gas will be combusted • Operational in 1978
Pike County • Pikeville, KY	2	Bituminous, low sulfur (0.6-1.2%)	• Hot cyclone • Gas quench/cooling • Tar/liquor separation • Stretford sulfur removal • Dehydration • Electrostatic precipitators	• To be operational in 1979 • Product gas to fire boilers and process heaters
Aluminum Refinery • PA	1	Anthracite, low sulfur (~ 0.7%)	• Hot cyclone	• To be operational in 1979 • Product gas to fire process furnaces • Five gasifiers may be added later

tions of less than 4 ppmv are attainable.^{3,4} As mentioned above, the Stretford process also converts the removed sulfur species into elemental sulfur. Unfortunately, the MEA process does not have this advantage. Instead, it produces an acid-gas stream that requires further treatment, for example, in a Claus unit.

Status

Wellman-Galusha gasifiers have been commercially available since 1941. Approximately 150 gasifiers have been installed worldwide. In the United States, eight Wellman-Galusha gasifiers are currently being used to produce a low-Btu gas from anthracite and low-sulfur bituminous coals. Table 2 summarizes the locations, processes, and coal feedstocks for each plant.

Industrial Applicability

Wellman-Galusha gasification systems have been used to provide a low-Btu fuel gas and a synthesis gas for ammonia production. A summary of past applications is given in Table 3.

In the near term, Wellman-Galusha gasifiers will be used primarily to produce a fuel gas for onsite use. Potential uses of the product low-Btu

gas include fuel to provide direct heat for such processes as brick and lime kilns; fuel for small industrial boilers; and, possibly, synthesis gas for ammonia production. Production of gas for offsite use will probably not be significant because of the cost of transporting atmospheric pressure, low-Btu gas.

Energy Efficiency

The energy efficiency of Wellman-Galusha gasification systems will be a significant factor affecting commercialization potential. However, this factor becomes less critical when compared to use of natural gas, which may be either unavailable or too expensive.

The following two kinds of energy efficiencies are used to describe gasification systems:

$$\eta_{cg} = \frac{(Q_g)_{out}}{(Q_c)_{in}} \times 100$$

and

$$\eta_T = \frac{(Q_T)_{out}}{(Q_T)_{in}} \times 100$$

TABLE 3. PAST USERS OF GAS PRODUCED BY WELLMAN-GALUSHA GASIFIERS^a

• chemical plants	• aluminum and stainless steel manufacturers
• glass plants	• ordinance plants
• steel mills	• tin plate mills
• magnesium manufacturers	• lime plants
• silk mills	• brick plants
• bakeries	• zinc smelters
• wire mills	• iron ore processors
• foundries	• fertilizer plants
• potteries	

^aSpecific uses varied from heat treating (in glass and steel mills) to synthesis gas (for synthetic fertilizer manufacture). Materials gasified included charcoal, coke, anthracite and bituminous coals.

where η_{cg} is the coal/gas efficiency (in percent), η_T is the overall thermal efficiency (in percent), $(Q_g)_{out}$ is the output product gas energy, $(Q_c)_{in}$ is the input coal energy, $(Q_T)_{out}$ is the total output energy (product gas + byproducts + steam), and $(Q_T)_{in}$ is the total input energy (coal + steam + electricity).

Calculated energy efficiencies for the Wellman-Galusha systems considered in this report are shown in Table 4. These calculated efficiencies show that the types of processes used, byproducts produced, and the nature of the coal feedstock affect the coal/gas and overall thermal-energy efficiencies of the system.

Capital and Operating Costs

Capital investment requirements and operating costs were calculated for the following Wellman-Galusha gasification systems producing 17.6 MW (60×10^6 Btu/hr) and 87.9 MW (300×10^6 Btu/hr) of product low-Btu gas:

- System 1 produces a hot raw product gas.
- System 2 produces a desulfurized product gas (down to 10 ppmv H_2S but retaining all organic sulfur) using a Stretford sulfur-removal process.
- System 3 produces a desulfurized product gas (~ 200 ppmv total sulfur) using an MEA sulfur-removal process operating at 0.21 MPa (30 psia).
- System 4 produces a desulfurized product gas (~ 10 ppmv total sulfur) using an MEA sulfur-removal process operating at 1.6 MPa (230 psia).

Tables 5 and 6 summarize the capital investment requirements and operating costs for Wellman-Galusha gasification systems using various coal feedstocks. The cost data shown are for systems without environmental controls.

As shown in Tables 5 and 6, the product gas costs are dependent upon coal feedstock, product gas specifications (tar/sulfur content), and plant size. Product gas costs for producing a hot raw gas for onsite use (System 1) range between \$1.90 and \$3.60 per GJ (\$2.00 and \$3.80 per 10^6 Btu) depending upon the coal feedstock and plant size. For systems using a Stretford sulfur-removal process, product gas costs range from \$3.30 to \$5.60 per GJ (\$3.50 to \$5.90 per 10^6 Btu), again depending upon the coal feedstock and plant size. If an MEA sulfur-removal process is used to remove gaseous sulfur species, product

gas costs would range from \$3.80 to \$6.20 per GJ (\$4.00 to \$6.50 per 10^6 Btu) depending upon the sulfur content of the clean product gas and the plant size.

For most of the gasification systems, the major component of the annualized costs is the coal feedstock cost. For systems using anthracite coal, the coal costs represent 36 to 56 percent of the total costs of the product gas. For systems using low-sulfur bituminous coal, coal costs are between 36 and 70 percent of the product gas costs, and for high-sulfur bituminous coal, coal costs are 28 to 42 percent.

Commercial Prospects

In the near term, low-Btu gas from fixed-bed atmospheric-pressure gasifiers like the Wellman-Galusha will be used primarily as a substitute fuel by industries threatened with natural gas curtailments. The low-Btu gas will principally be considered for use as a fuel gas in onsite furnaces, heaters, kilns, and small boilers. Its substitution for natural gas will most likely occur when the costs of retrofitting for use of the low-Btu gas are small and the low-Btu gas requires minimal purification.

In both new and retrofit applications, coal gasification is mainly competing with the alternative of direct coal combustion. Factors affecting the selection of coal gasification or direct coal combustion include the suitability of the coal conversion technology for satisfying the needs of the specific end use, the cost of the technology, the cost and difficulty of retrofitting, the cost of environmental controls, and the cost of the coal.

The increased commercialization of low-Btu gasification systems like the Wellman-Galusha depends on the demonstration of the environmental acceptability of the various gasification systems. Although commercially available controls seem to be adequate, some of the controls (such as sulfur removal) have not been adequately demonstrated on coal gasification systems. The cost of these controls are also uncertain.

Gasification systems featuring Wellman-Galusha gasifiers are most suitable for relatively small applications, with fuel demands ranging from about 8.8 to 88 MW (30 million to 300 million Btu/hr). Energy demands greater than about 88 MW may be better served by gasification systems using gasifiers with larger capac-

**TABLE 4. CALCULATED ENERGY EFFICIENCIES OF VARIOUS WELLMAN-GALUSHA
GASIFICATION SYSTEMS**

Coal Feed Type	For Systems Producing a Hot Product Gas			For Systems Producing Quenched/Clean Gas at 317°K (110°F)	
	Typical Raw Gas Temperature	Coal/Gas Efficiency ^a , %	Overall Thermal Efficiency ^b , %	Coal/Gas Efficiency ^a , %	Overall Thermal Efficiency ^b , %
Anthracite	700°K (800°F)	91	90	83 ^c	84 ^c
Low-S HVA Bituminous	840°K (1050°F)	93	92	68 ^c	82 ^c
High-S HVB Bituminous	640°K (700°F)	NA ^g	NA ^g	70 ^c 61 ^d 62 ^e	83 ^c 72 ^d 64/61 ^{e,f}
Lignite	420°K (300°F)	NA ^g	NA ^g	78 ^c	89 ^c

^aCoal/gas efficiency is calculated as: output product gas energy divided by input coal energy.

^bOverall thermal efficiency is calculated as: total output energy (product gas + by-products + steam) divided by total input energy (coal + steam + electricity).

^cThese systems produce a cooled, cleaned product gas and feature the Stretford process for sulfur removal.

^dThese systems produce a cooled, cleaned product gas (<200 ppmv total sulfur) by using an amine (MEA) absorption process to remove sulfur species. In these systems, some of the product low-energy gas is assumed to be used to meet the energy requirements of the amine process. Alternately, by-product tar may be used to meet at least part of these energy requirements.

^eThese systems produce a "very clean" gas (<10 ppmv total sulfur) by using an amine absorption system (MEA) to remove sulfur species.

^fThe first efficiency is for the 16MW (54.7x10⁶ Btu/hr) system which uses an electric motor to drive the gas compressor. The second efficiency is for the 80.1 MW (273.5x10⁶ Btu/hr) system which uses a steam turbine to drive the gas compressor.

^gNot applicable - Given the coal quality data which were assumed for purposes of conducting this assessment, these coals cannot be used in systems in which the raw product gas is burned directly.

TABLE 5. CAPITAL INVESTMENT REQUIREMENTS AND ANNUALIZED COSTS OF UNCONTROLLED WELLMAN-GALUSHA GASIFICATION SYSTEMS PRODUCING NOMINALLY 17.6 MW (60 × 10⁶ Btu/HR) OF PRODUCT LOW-Btu GAS (LATE-1977 DOLLARS)^a

	Coal Feedstock/Type of Product Gas						
	Anthracite		Low Sulfur Bituminous		High Sulfur Bituminous (Cold Gas)		
	Hot Gas ^b	Cold Gas ^c	Hot Gas ^b	Cold Gas ^c	Stretford ^c	MEA (200 ppmv) ^d	MEA (neg.) ^e
Capital Investment Requirements ^f , \$1,000	3,250	6,110	1,730	5,200	5,500	3,890	4,700
Design Plant Capacity, MW	19.9	18.3	24.9	18.2	18.2	15.7	15.9
Annual Operating Factor	90%	90%	90%	90%	90%	90%	90%
Annualized Costs, \$1,000/yr							
Operating and Maintenance Costs							
Coal ^g	1,040	1,040	919	919	702	702	702
Labor/Overhead (@ \$15.00/man-hr)	131	197	66	131	131	131	131
Electricity (@ \$0.04/kWh)	16	48	18	79	118	225	643
Steam ^h	-	(17)	-	-	-	-	-
Chemicals	-	8	-	8	63	55	55
Maintenance (@ 6% of direct equipment costs)	149	276	74	233	248	175	210
Taxes, Insurance, and GSA Costs (@ 4% of depreciable investment)	117	229	58	194	207	143	171
Capital Related Charges ⁱ	602	1,116	326	950	1,003	715	867
TOTAL Annualized Costs, \$10 ³ /yr	2,055	2,897	1,461	2,514	2,472	2,146	2,779
Average Gas Costs, \$/GJ	3.64	5.58	2.07	4.87	4.78	4.82	6.16

^a Each system has a basic capacity of 17.6 MW (60 × 10⁶ Btu/hr) of tar/oil-free product gas at 43.3°C (110°F). The actual total energy supplied to the end-user though is as indicated. Differences in the indicated useful energy supplied and the basic capacity of 17.6 MW (60 × 10⁶ Btu/hr) are a result of 1) energy credits taken for the sensible heat and/or tar/oil content of the product gas for the hot gas systems, and 2) use of a portion of the product gas to supply energy to the stripper reboiler in the systems that use the MEA process.

^b These systems use only a cyclone for product gas purification and deliver a hot product gas to the end user.

^c These systems use the Stretford process to remove H₂S from the cooled product gas. Residual H₂S levels are nominal 10 ppmv. Organic sulfur compounds, such as COS and CS₂, are not removed by the Stretford process.

^d This system uses the MEA process operating at 0.21 MPa (30 psia) to remove sulfur species from the cooled product gas. Residual sulfur species amount to the equivalent of 200 ppmv H₂S.

^e This system uses the MEA process operating at 1.6 MPa (230 psia) to remove sulfur species from the cooled product gas. Negligible sulfur species are left in the product gas.

^f In estimating capital investment requirements, a spare gasifier/cyclone unit is included for all systems and cooling liquor pumps are spared 100%.

^g Assumed coal properties and delivered costs are: Anthracite: 29.7 MJ/kg (12,800 Btu/lb) and \$50/metric ton (\$45/short ton)
Low sulfur bituminous: 33.2 MJ/kg (14,300 Btu/lb) and \$40/metric ton (\$36/short ton)
High sulfur bituminous: 29.0 MJ/kg (12,500 Btu/lb) and \$28/metric ton (\$25/short ton)

^h Steam costs were assumed to be \$0.011/kg (\$5/10³ lb). Steam credits were taken as \$1/GJ (\$1.05/10⁶ Btu).

ⁱ Basis for capital related charges:

Utility financing method	100% equity financing
Late-1977 dollars without inflation	15% after tax return on equity
25-year economic project lifetime	46% federal income tax rate
4% per year straightline depreciation of depreciable investment	10% pretax return on working capital

**TABLE 6. CAPITAL INVESTMENT REQUIREMENTS AND ANNUALIZED COSTS OF
UNCONTROLLED WELLMAN-GALUSHA GASIFICATION SYSTEMS
PRODUCING NOMINALLY 87.9 MW (300 × 10⁶ Btu/hr)
OF PRODUCT LOW-Btu GAS (LATE 1977 DOLLARS)^a**

	Coal Feedstock/Type of Product Gas						
	Anthracite		Low Sulfur Bituminous		High Sulfur Bituminous (Cold Gas)		
	Hot Gas ^b	Cold Gas ^c	Hot Gas ^b	Cold Gas ^c	Stretford ^c	MEA (200 ppmv) ^d	MEA (neg.) ^e
Capital Investment Requirements ^f , \$1,000	13,300	19,700	4,770	13,100	14,200	11,600	14,000
Design Plant Capacity, MW	99.6	91.4	99.7	91.1	90.8	78.5	79.7
Annual Operating Factor	90%	90%	90%	90%	90%	90%	90%
Annualized Costs, \$1,000/yr							
Operating and Maintenance Costs							
Coal ^g	5,198	5,198	3,676	4,595	3,510	3,510	3,510
Labor/Overhead (@ \$15.00/man-hr)	524	657	263	394	394	394	394
Electricity (@ \$0.04/kWh)	81	238	72	396	590	1,125	334
Steam ^h	-	(86)	-	-	-	-	3,390
Chemicals	-	40	-	40	315	274	274
Maintenance (@ 6% of direct equipment costs)	596	871	189	563	617	499	582
Taxes, Insurance, and GSA Costs (@ 4% of depreciable investment)	468	713	149	465	512	406	474
Capital Related Charges ⁱ	2,476	3,640	916	2,436	2,614	2,165	2,625
TOTAL Annualized Costs, \$10 ³ /yr	9,343	11,271	5,265	8,889	8,552	8,373	11,583
Average Gas Costs, \$/GJ	3.30	4.34	1.86	3.44	3.32	3.76	5.12

^aEach system, except the one producing a hot product gas from low sulfur bituminous coal, has a basic capacity of 87.9 MW (300 × 10⁶ Btu/hr) of tar/oil-free product gas at 43.3°C (110°F). The actual total energy supplied to the end-user though is as indicated. Differences in the indicated useful energy supplied and the basic capacity of 87.9 MW (300 × 10⁶ Btu/hr) are a result of 1) energy credits taken for the sensible heat and/or tar/oil content of the product gas for the hot gas systems, and 2) use of a portion of the product gas to supply energy to the stripper reboiler in the systems that use the MEA process. For the hot gas, low sulfur bituminous system, the tar/oil-free product gas rate is 70.3 MW (240 × 10⁶ Btu/hr). But, the sensible heat and tar/oil content of the hot product gas raise the total system capacity to 100 MW (341 × 10⁶ Btu/hr). This capacity was used in the cost analysis because it is comparable to the capacity of the other systems examined.

^bThese systems use only a cyclone for product gas purification and deliver a hot product gas to the end user.

^cThese systems use the Stretford process to remove H₂S from the cooled product gas. Residual H₂S levels are nominal 10 ppmv. Organic sulfur compounds, such as COS and CS₂, are not removed by the Stretford process.

^dThis system uses the MEA process operating at 0.21 MPa (30 psia) to remove sulfur species from the cooled product gas. Residual sulfur species amount to the equivalent of 200 ppmv H₂S.

^eThis system uses the MEA process operating at 1.6 MPa (230 psia) to remove sulfur species from the cooled product gas. Negligible sulfur species are left in the product gas.

^fIn estimating capital investment requirements, a spare gasifier/cyclone unit is included for all systems and cooling liquor pumps are spared 100%.

^gAssumed coal properties and delivered costs are: Anthracite: 29.7 MJ/kg (12,800 Btu/lb) and \$50/metric ton (\$45/short ton)
Low sulfur bituminous: 33.2 MJ/kg (14,300 Btu/lb) and \$40/metric ton (\$36/short ton)
High sulfur bituminous: 29.0 MJ/kg (12,500 Btu/lb) and \$28/metric ton (\$25/short ton)

^hSteam costs were assumed to be \$0.011/kg (\$5/10³ lb). Steam credits were taken as \$1/GJ (\$1.05/10⁶ Btu).

ⁱBasis for capital related charges:

Utility financing method	100% equity financing
Late-1977 dollars without inflation	15% after tax return on equity
25-year economic project lifetime	46% federal income tax rate
4% per year straightline depreciation of depreciable investment	10% pretax return on working capital

ities (for example, pressurized gasifiers).

Systems featuring two to four gasifiers and gas purification facilities will require 18 to 24 mo from initial feasibility studies to full-scale operation.⁵ McDowell-Wellman can deliver Wellman-Galusha gasifiers 6 to 8 mo from the date of order.⁶

Wellman-Galusha gasification systems will be most widely applied in the industrial areas of the Northeast and Midwest. States in those regions have large reserves of bituminous coal.

WASTE STREAMS AND POLLUTANTS OF MAJOR CONCERN

Wellman-Galusha low-Btu gasification systems are sources of gaseous, liquid, and solid waste streams. Also associated with these systems are process and byproduct streams that may contain toxic substances. The multimedia waste streams and pollutants of major concern are summarized in Tables 7 through 9. Process and byproduct streams that may contain potentially toxic compounds are summarized in Table 10.

Gaseous emissions from Wellman-Galusha systems contain a significant amount of pollutants that may have harmful health and ecological effects. Gaseous pollutants (CO , H_2S , HCN , NH_3 , and light hydrocarbons) from the coal feeder and gasifier pokeholes need to be controlled. Startup vent gases will contain compounds found in the raw product gas (CO , sulfur species, light hydrocarbons, tars, and oils), which will require control before venting to the atmosphere. Vent gases from the byproduct tar recovery process will contain significant amounts of potentially harmful pollutants and will, therefore, need to be controlled. Emissions from sulfur removal processes are not yet characterized since there are currently no sulfur recovery processes being used with fixed-bed, atmospheric pressure, low-Btu gasification systems.

The amount of liquid effluents from Wellman-Galusha systems will be limited to blowdown streams, ash sluice water, and coal pile runoff. Of these effluents, the blowdown streams will contain significant quantities of potentially harmful constituents. Ash sluice water and coal pile runoff will contain compounds leached from the ash and coal, which may effect health and the environment.

Solid waste streams from Wellman-Galusha systems will consist of ash, collected particulates, sulfur, and blowdown from the MEA sulfur-removal process. Ash and sulfur may contain leachable constituents that may be potentially harmful. Collected particulates resemble devolatilized coal and therefore may be classified as a solid combustible material. MEA blowdown sludge contains potentially harmful constituents and needs to be treated before disposal.

The byproduct tar and quench liquor represent process streams that contain partially harmful organic and inorganic compounds. Worker exposure and accidental releases of these streams should be carefully controlled.

It should be emphasized that the chemical characteristics and potential biological effects of the various streams present in a gasification facility are highly dependent upon the coal feedstock and processes used. For example, tars will not be produced when anthracite coal is gasified; however, process condensate may contain light oils.

STATUS OF ENVIRONMENTAL PROTECTION ALTERNATIVES

The assessment of the status of environmental protection alternatives involves identifying and evaluating control alternatives to determine the most effective control alternatives and the costs and energy impacts of those alternatives. The secondary waste streams from the most effective control alternatives are also compared to existing and proposed regulations and to the multimedia environmental goals (MEGs).⁷

Most Effective Control Alternatives

The criteria used to identify the most effective control alternatives are applicability to treating waste streams from low-Btu gasification systems, control effectiveness, development status, and secondary waste streams. Costs and energy considerations are *not* considered in the selection of the most effective controls. Table 11 shows the most effective control alternatives to treat the multimedia waste streams and potential toxic substances associated with Wellman-Galusha gasification systems.

**TABLE 7. GASEOUS WASTE STREAMS AND POLLUTANTS OF MAJOR CONCERN FROM
WELLMAN-GALUSHA LOW-Btu GASIFICATION SYSTEMS**

<u>Operation Process</u>	<u>Gaseous Waste Stream</u>	<u>Pollutants of Major Concern</u>	<u>Remarks</u>
<u>Coal Preparation</u>			
Coal Storage and Handling	Coal dust	Particulate matter similar in composition to the coal feedstock.	Bituminous coal gave slightly positive results for the Ames test. Anthracite coal results were negative.
<u>Coal Gasification</u>			
Wellman-Galusha Gasifier	Coal feeder vent gases	Gaseous species in the product gas (CO, H ₂ S, NH ₃ , HCN, light hydrocarbons).	High levels of CO were found in the coal hopper area.
	Start-up vent gases	Raw product gas constituents. Particulate matter (coal dust, tar, oil aerosols) and gaseous species (CO, H ₂ , H ₂ S, COS, NH ₃ , HCN, light hydrocarbons, etc.). Organics of concern include fused aromatic hydrocarbons, heterocyclic nitrogen, sulfur and oxygen compounds, carboxylic acids, amines, sulfonic acids, sulfoxides, phenols, thiols, benzene, and substituted benzene hydrocarbons. Inorganics of concern include CO, ethylene, Cr, Hg, U, V, Al, P, As, Cu, Cd, H ₂ S, CO ₂ , HCN, Li, Tl, Si, Pb, Sb, SO ₂ , CS ₂ , Cl, Ti, Zr, Fe, Co, Ni, Ag and Zn.	The amount of tars and oils will depend upon the coal feedstock. Bituminous coals will have a significant amount of tars where anthracite will not. Tars from the gasification of bituminous coals gave positive results on the Ames test.
	Fugitive emissions (pokehole gases)	Gaseous species in the product gas (CO, H ₂ S, NH ₃ , HCN, light hydrocarbons).	Emissions of tars and oils will occur when pokehole valves are open; however, the major emissions from the pokeholes will be from gaseous species in the product gas leaking from the pokehole valves.
<u>Gas Purification</u>			
Gas Quenching and Cooling (Tar/Liquor Separation)	Separator vent gases	Organics of concern include fused aromatic hydrocarbons, amines, heterocyclic nitrogen and sulfur compounds, ethylene, phenols, methane, and carboxylic acids. Inorganics of concern include CO, NH ₃ , NO ₂ , CO ₂ , Cr, Ag, V, Cu, P, Li, As, Fe, Ni, and U.	These pollutants of concern are associated with bituminous coals.
Sulfur Removal-Stretford	Evaporator and oxidizer vent gases	Volatile compounds in the Stretford liquor (H ₂ O, CO ₂ , N ₂ , O ₂ , and possibly NH ₃).	This stream has not been sampled because no Stretford processes are currently used to remove sulfur species from low-Btu gas.
Sulfur Removal-MEA	Acid gas stream	CO ₂ , H ₂ S, COS, CS ₂ , mercaptans, and light hydrocarbons.	This stream is sent to a sulfur recovery unit consisting of a Claus process followed by a Claus tail gas clean-up process to remove the sulfur species in the acid gas stream. This stream has not been sampled since MEA processes have not been used to remove sulfur species from low-Btu gas.

TABLE 8. LIQUID WASTE STREAMS AND POLLUTANTS OF MAJOR CONCERN FROM
WELLMAN-GALUSHA LOW-Btu GASIFICATION SYSTEMS

Operation Process	Liquid Waste Stream	Pollutants of Major Concern	Remarks
<u>Coal Preparation</u>			
Coal Handling and Storage	Coal pile runoff	Contain leachable organics and inorganics.	The composition of this stream will depend upon the coal feedstock and site-specific conditions (i.e. pH of leachate).
<u>Coal Gasification</u>			
Wellman-Galusha Gasifier	Ash sluice water	Inorganics of major concern include P, Ti, V, Cu, Fe, Ba, Cd, Cr, CN ⁻ , Li and Ni. Organic concentrations of 65 mg/l have been found; however, it is not certain whether these were present in the plant's service water used to sluice the ash from the gasifier.	The amount of sluice water is low and highly variable. Negative Ames tests were obtained with low to nondetectable results indicated for the cytotoxicity and rodent acute toxicity tests.
<u>Gas Purification</u>			
Gas Quenching and Cooling	Process condensate	May contain organic and inorganic pollutants found in the quench liquor (see Table 10).	The amount of process condensate produced will depend upon the system operation and type of processes used.
Sulfur Removal- Stretford	Solvent blowdown	Thiosulfate and thiocyanate salts.	The amount of these salts produced will depend upon the sulfur and cyanide content of the cooled product gas entering the Stretford process.

**TABLE 9. SOLID WASTE STREAMS AND MAJOR POLLUTANTS OF CONCERN FROM
WELLMAN-GALUSHA LOW-Btu GASIFICATION SYSTEMS**

<u>Operation Process</u>	<u>Solid Waste Streams</u>	<u>Pollutants of Major Concern</u>	<u>Remarks</u>
<u>Coal Gasification</u>			
Wellman-Galusha Gasifier	Gasifier ash	Inorganics of major concern include Be, P, Fe, Ca, Al, Li, Ba, Se, Pb, Cs, Cu, Ti, Cd, Sb, V, Co, U, Mg, Sr, Si, Hg, Zr, F, Rb, As, Mn, Cr, Ni, Th, Al, Bi, Ag, Y. Total extractable organics in the ash is low ranging from 40-116 µg/g. Organics of potential concern include phthalate esters, phenols, nitrophenols, and fused aromatic hydrocarbons.	Results from the Ames, cytotoxicity, and rodent acute toxicity tests for ash produced from gasifying anthracite and bituminous coals were negative, low or nondetectable. Effects on soil microcosms were also low.
	Ash leachate (anthracite coal)	Inorganics of concern include P, Zn, Cd and Ag.	Results from the Ames, cytotoxicity and rodent acute toxicity tests of leachate from ash produced from gasifying anthracite coal were negative, low or nondetectable.
<u>Gas Purification</u>			
Particulate Removal- Hot Cyclone	Collected particulate matter	Inorganics of major concern include Ni, Pb, P, Mn, Fe, Cu, Ba, Sb, Ti, Cr, Ca, Al, V, Li, Mg, Zr, Co, As, Si, Se, Be, Cd, Ag, Th, Zn, F, Ga, Hf, Hg, Sr, Tl, Y. Low concentrations (40 to 800 µg/g) of extractable organics have been determined. Organics of concern include phthalate esters, phenols, nitrophenols, amines, cresols.	Negative results from the Ames test have been obtained with low to nondetectable results from cytotoxicity and rodent acute toxicity tests. High effects on soil microcosms were found. Collected particulates resemble devolatilized coal with carbon contents ranging from 70 to 80%.
	Collected particulate matter leachate (anthracite coal)	Inorganics of major concern include Mn, Pb, Li, Zn, Al, Cd, Co, Cu and Fe.	Negative Ames test results were obtained and nondetectable cytotoxicity test results.
Sulfur Removal- Stretford	Sulfur	May contain organics and inorganics including thiocyanate and thiosulfate salts.	No data are currently available on the chemical and biological aspects of the recovered sulfur.
Sulfur Removal- MEA	MEA sludge	Degradation products including oxazolidon-2, 1-(2-hydroxyethyl) imidazolidone-2, diethanol urea, dithiocarbamates, thiocarbamides and other high molecular weight nonregenerable compounds.	No data are currently available on the characteristics (chemical or biological) of MEA sludge.

**TABLE 10. POTENTIAL TOXIC STREAMS AND COMPOUNDS OF MAJOR CONCERN FOR
WELLMAN-GALUSHA LOW-Btu GASIFICATION SYSTEMS**

<u>Operation Process</u>	<u>Potential Toxic Stream</u>	<u>Compounds of Major Concern</u>	<u>Remarks</u>
<u>Gas Purification</u>			
Gas Quenching and Cooling	By-product tar and oils	Organics of major concern include fused aromatic hydrocarbons, benzene, substituted benzene hydrocarbons, heterocyclic nitrogen, sulfur and oxygen compounds, carboxylic acids, aliphatic hydrocarbons, phenols and amines. Inorganics of concern include Cu, Pb, Sb, Cr, Cd, Ba, Hg, V, Mg, and As.	Tar will be produced from bituminous and lignite coals. Positive Ames test results have been obtained. Safe handling and controlling tar leaks procedures are required.
	Quench liquor	Organics of major concern include phenols, fused aromatic hydrocarbons, heterocyclic nitrogen and sulfur compounds, carboxylic acids, thiols, glycols, and epoxides. Inorganics of concern include NH ₃ , cyanides, P, Se, As, F, Cl, Ca, Fe and Cd.	Results from aquatic tests indicated a high potential effect on aquatic species. Health effects tests were low; however, because of the chemical characteristics of the quench liquor, safe handling and control of leaks are required.

TABLE 11. SUMMARY OF MOST EFFECTIVE EMISSION, EFFLUENT, SOLID WASTES, AND TOXIC SUBSTANCES CONTROL ALTERNATIVES

Waste Stream	Most Effective Control Technology
<u>Air Emissions</u>	
• Fugitive dust from coal storage	• Covered bins
• Fugitive dust from coal handling	• Asphalt and polymer coatings
• Coal feeding system vent gas	• Enclosed equipment, collect gas and recycle to gasifier inlet air or treat with baghouse
• Ash removal system vent gas	• Collect gas and recycle to gasifier inlet air or combine with product gas
• Start-up emissions	• No control necessary in a properly designed system
• Fugitive emissions and pokehole gases from gasifier	• Incinerator
• Fugitive emissions from hot cyclone	• Adherence to good operating and good maintenance procedures
• Separator gas	• Same as for gasifier
• MEA acid gas	• Combine with product gas
• Stretford oxidizer vent gas	• Recycle to gasifier
• Stretford evaporator vent gas	• Stretford
	• Claus with tail gas cleanup
	• None required with existing applications. However, viability of this approach needs to be confirmed in a gasification process application.
	• Same as for oxidizer vent gas
<u>Liquid Effluents</u>	
• Water runoff	• Use covered bins for coal storage
• Ash sluice water	• Contain, collect and reuse for process needs
• Process condensate	• Collect and recycle to ash sluice system
	• Containment and treatment at hazardous waste facility

(Continued)

TABLE 11 (continued)

(Continued)

Waste Stream	Most Effective Control Technology
• Stretford blowdown	• Containment and treatment at hazardous waste facility • Reductive incineration at high temperature
<u>Solid Wastes</u>	
• Ash • Cyclone dust • Recovered sulfur • MEA blowdown	• Secured landfill • Combustion in incinerator or coal-fired boiler • Purify for sale or disposal • Containment and treatment at hazardous waste facility
<u>Toxic Substances</u>	
• Tars and oils	• Combustion in boiler or furnace

^aBased only on effectiveness in eliminating or reducing emissions.

Cost and Energy Considerations

Costs of the "best available" candidate control methods (identified in Table 11) are summarized in Table 12. Most of the control alternatives have negligible costs when compared to the costs of the product low-Btu gas. The most costly control alternatives are those for treatment of the MEA acid-gas stream and process condensate. The most costly control methods are also the largest energy consumers. Tars and oils represent a large energy credit (~25 percent of the product gas energy content), depending upon the coal feedstock.

One method to reduce the costs and energy consumption of process condensate treatment is to reduce the size of the condensate stream. This can be accomplished by drying the coal before gasification (the dryer offgas may contain large amounts of coal volatiles). Alternatively, the size of the stream can be reduced by minimizing the amount of steam fed to the gasifier.

Impacts on Air Quality

The potential air quality impacts of gaseous waste streams from Wellman-Galusha low-Btu gasification facilities were estimated and compared to the following air standards and guidelines:

- New Source Performance Standards (NSPS) for stationary sources,
- National Emissions Standards for Hazardous Air Pollutants (NESHAP),
- National Ambient Air Quality Standards (NAAQS), and
- State and Federal emission standards.

The air quality impact of specified pollutants (CO, H₂S, COS, NH₃, HCN, NO_x, SO_x, and non-CH₄ hydrocarbons) in gaseous waste streams from Wellman-Galusha systems using a low- and high-sulfur bituminous coal was estimated by an atmospheric dispersion model. The waste streams considered were coal feeder gases, tar/quench liquor separator vent gases, and Claus tail gas incinerator gases (high-sulfur case only).

Table 13 compares maximum ground-level concentrations of CO, nonmethane hydrocarbons, NO_x, and SO_x with the NAAQS. With the exception of nonmethane hydrocarbons, the predicted pollutant concentrations for both the low- and high-sulfur coals are below the

NAAQS. Carbon monoxide concentrations do not exceed the NAAQS; however, they are relatively high. H₂S concentrations were also modeled and compared to the Texas ambient air standards. As shown, H₂S concentrations for the high-sulfur coal case exceed the Texas standard.

The major source of nonmethane hydrocarbon emissions is the separator vent. Recycling the separator vent gas to the product gas would give an 85 to 98 percent reduction in the ground-level concentrations of nonmethane hydrocarbons. This would also significantly reduce the ground-level concentrations of CO, H₂S, NH₃, HCN, and COS, since the separator vent is the major source of these pollutant emissions.

In summary, the gaseous emissions from a well-controlled Wellman-Galusha gasification facility should not significantly impact air quality. This implies that the separator vent gases are recycled to the product gas.

Impacts on Water

The quantity of liquid waste streams from a Wellman-Galusha gasification facility will be small; however, the concentration of various constituents in those waste streams may exceed effluent standards. The liquid effluents associated with a Wellman-Galusha system are water runoff from coal storage, ash sluice water, process condensate, and blowdown from the Stretford process. Water runoff may contain constituents exceeding effluent standards. The concentration of those constituents will be variable and highly site- and coal-specific.

Table 14 shows the constituents in the ash sluice water, process condensate, the Stretford blowdown that have been found or estimated to exceed the most stringent effluent standards and minimum acute toxicity effluent (MATE) values given in the MEGs. The amount and type of organic compounds found in the process condensate will vary depending upon the coal feedstock. High levels of organics will be present when bituminous and lignite coals are used. Low levels of organics will be present when anthracite coals are gasified.

Impacts on Land

Under the Resource Conservation and Recovery Act (RCRA), EPA has issued

TABLE 12. SUMMARY OF MAJOR COSTS AND ENERGY CONSUMPTION OF ALTERNATIVE CONTROL METHODS

Operation Process	Waste Stream Media Waste Stream	Control Method	Control Costs (\$/GJ) ^a	Energy Consumption (J/J) ^b
<u>Coal Preparation</u>				
Coal Handling and Storage	<u>Gaseous Emissions</u>			
	• Fugitive dust	• Covered bins • Asphalt and polymer coatings • Enclosed equipment, collection systems	<0.01 <0.01 <0.01	• Negligible • Negligible • Negligible
	<u>Liquid Effluents</u>			
	• Coal pile runoff	• Covered bins • Collection and reuse	<0.01 <0.01	• Negligible • Negligible
<u>Coal Gasification</u>				
Wellman-Galusha Gasifier	<u>Gaseous Emissions</u>			
	• Coal feeding vent gases	• Collection and recycle to gasifier inlet air or product gas	<0.01	• Negligible
	• Ash removal vent gases	• None required	—	—
	• Start-up vent gases	• Flare or incinerator	<0.1	• NA ^c
	• Fugitive emissions (pokehole gases)	• Good maintenance and operating practices ^d	—	—
	<u>Liquid Effluents</u>			
	• Ash sluice water	• Collection and reuse	<0.01	• Negligible
	<u>Solid Wastes</u>			
	• Ash (low-S Bituminous)	• Secured landfill Without fixation	0.01-0.02(0.01-0.03)	• Negligible
	• Ash (high-S Bituminous)	• Secured landfill With fixation	0.02-0.06(0.04-0.08)	• Negligible
	- Stratford		0.03-0.07(0.05-0.10)	• Negligible
	- MEA ^e		0.03-0.06(0.04-0.10)	• Negligible
	- MEA (Stringent) ^f		0.04-0.10(0.07-0.15)	• Negligible
	• Ash (Anthracite)		0.04-0.10(0.07-0.15)	• Negligible
	• Ash (Lignite)		0.04-0.10(0.07-0.15)	• Negligible
<u>Gas Purification</u>				
Particulate Removal- Hot Cyclone Gas Quenching and Cooling	<u>Solid Wastes</u>			
	• Collected particulates	• Combustion	<0.01	• NA ^g
	<u>Gaseous Emissions</u>			
	• Quench liquor/tar separator vent	• Combine with the product gas	<0.01	• Negligible
	<u>Liquid Effluents</u>			
	• Process Condensate	• Containment and treatment off-site in a hazardous waste treatment facility		
	- High-S Bituminous		0.40-0.59	• NA ^h
	• Stratford		0.88-1.32	• NA ^h
	• MEA ^e		1.16-1.69	• NA ^h
	• MEA (Stringent) ^f		1.43-2.01	• NA ^h
	- Lignite			
	• Process Condensate	• Evaporation on-site		
	- High-S Bituminous		0.06-0.07	0.019
	• Stratford		0.12-0.14	0.042
	• MEA ^e		0.16-0.18	0.055
	• MEA (Stringent) ^f		0.18-0.20	0.065
	- Lignite			
Sulfur Removal- Stratford	<u>Gaseous Emissions</u>			
	• Oxidizer vent gas	• None required	—	—
	• Evaporator vent gas	• None required	—	—
	<u>Liquid Effluents</u>			
	• Blowdown solvent	• Reductive incineration	NA	NA
	<u>Solid Wastes</u>			
	• Sulfur	• Secured landfill		
	- Low-S Bituminous		0.002-0.009	• Negligible
	- High-S Bituminous		0.02-0.37	• Negligible
	- Anthracite		0.002-0.009	• Negligible
	- Lignite		0.005-0.020	• Negligible
Sulfur Removal- MEA	<u>Gaseous Emissions</u>			
	• Acid gas	• Stratford acid gas removal		
	- 15 MW product gas		1.2-1.6	0.007
	- 74 MW product gas		0.6-0.8	0.007
	• Acid gas	• Claus without tail gas cleanup		
	- 15 MW product gas		0.5-0.6	0.008
	- 74 MW product gas		0.2	0.008
	<u>Solid Wastes</u>			
	• MEA Blowdown	• Containment and treatment at a hazardous waste facility	<0.01	NA ^h
	• Sulfur	— Same as the Stratford sulfur removal case —		

NA - Data not available for calculation of energy consumptions.

^a Costs are annualized costs per GJ of cooled, detarred product gas.

^b Energy consumptions are J of energy required by the control method per J of cooled, detarred product gas.

^c Energy consumption will depend upon the materials (coke, coal, wood, oil, etc.) used to start up the gasifier and the composition of the gas during the start up time period.

^d Good maintenance and operating procedures should already be defined and included in the units operating costs.

^e MEA produces a product gas to meet proposed NSPS for coal combustion (36 ng/J, 0.2 lb/Stu).

^f MEA (stringent) produces a "clean" product gas containing 5 ng/Nm³ (10 ppw) of sulfur species.

^g Combustion characteristics of the collected particulates have not been determined.

^h Data are not available on the energy consumption of treating process condensate at an off-site hazardous waste treatment facility.

TABLE 13. COMPARISON OF PREDICTED POLLUTANT CONCENTRATIONS TO THE NAAQS AND STATE OF TEXAS H₂S AMBIENT AIR STANDARDS

Pollutant	Low-Sulfur Coal ^a			High-Sulfur Coal ^b			NAAQS (µg/m ³)	
	Predicted Concentrations (µg/m ³) 24-h	3-h	1-h	Predicted Concentrations (µg/m ³) 24-h	3-h	1-h	Primary Standards	Secondary Standards
CO	2,300	9,800	13,700	2,300	9,800	13,700	10,000 (8-h) ^c	10,000 (8-h) ^c
Non-CH ₄ Hydrocarbons	650	2,800	3,900	650	2,800	3,900	160 (3-h) ^{c,d}	160 (3-h) ^{c,d}
NO _x	20	70	90	20	70	90	100 (aam)	100 (aam)
SO _x	NA	NA	NA	110	380	560	365 (24-h) ^c	1,300 (3-h) ^c
<u>State of Texas Regulations</u>								
H ₂ S	10	50	70	90	390	540	122 µg/m ³	

NA - Not applicable, SO_x emissions are from the high-sulfur case using an incinerator to combust the Claus unit's tail gases.

aam - Annual arithmetic mean.

^aFor the low-sulfur coal case, a Stretford sulfur removal process is used.

^bFor the high-sulfur coal, an MEA sulfur removal process is used followed by a Claus process and a Claus tail gas incinerator.

^cConcentration not to be exceeded more than once a year.

^d6:00 a.m. to 9:00 a.m.

**TABLE 14. LIQUID EFFLUENTS FROM WELLMAN-GALUSHA LOW-Btu GASIFICATION
SYSTEMS EXCEEDING THE MOST STRINGENT EFFLUENT
STANDARDS AND MATE VALUES**

Liquid Effluent	Constituents Exceeding Most Stringent Effluent Standards	Constituents Exceeding Health and Ecological MATE Values in the Multimedia Environmental Goals
Ash Sluice Water	Fe, Cr, CN ⁻ and suspended solids	P, Fe, Ti, Ba, La, Li, Cd, Cu, CN ⁻ , Ni and V
Process Condensate ^a (Bituminous Coal)	NH ₃ , As, Cl ⁻ , CN ⁻ , B, F ⁻ , Fe, Phenols, P, Se, SO ₄ ⁼ , BOD, COD, and suspended solids	Phenols, Fused Aromatic Hydrocarbons, Heterocyclic Nitrogen and Sulfur Compounds, Carboxylic Acids, Thiols, Glycols, Epoxides, NH ₄ , CN ⁻ , P, Se, As, F ⁻ , Cl ⁻ , Ca, Fe and Cd
Stretford Blowdown	Fe	Vanadate, Fe, EDTA and possibly Thiocyanates and Thiosulfates

MATE: Minimum Acute Toxicity Effluent

^aProcess condensate produced from gasifying anthracite coal should not contain the high amounts of organic constituents found in process condensate from gasifying bituminous or lignite coals.

guidelines for the land disposal of solid wastes (40 CFR 241). These standards set minimum levels of performance for any solid-waste land disposal site. The guidelines apply to the land disposal of all solid material. Additional standards have been proposed for hazardous solid wastes (40 CFR 250).

The solid waste streams from a Wellman-Galusha gasification facility that will be regulated under the RCRA are: gasifier ash, cyclone dust, sulfur cake, and MEA blowdown. Table 15 shows the characteristics of these solid waste streams and how the proposed RCRA regulations may apply. All of the solid waste streams may be classified as hazardous wastes under the proposed RCRA regulations.

Product/Byproduct Impacts

The product gas and byproduct tar produced by Wellman-Galusha facilities may be regulated by the Toxic Substances Control Act (TSCA) of 1976. However, polychlorinated biphenols (PCBs) and chlorofluorocarbons are the only specific substances for which regulations have been issued.

The product low-Btu gas may contain toxic substances even after extensive purification. The byproduct tar does contain substances and positive Ames test results for mutagenicity have been obtained.

Radiation and Noise Impacts

Wellman-Galusha low-Btu gasification facilities may have radiation and noise impacts. Some radioactive species in the coal may be concentrated in the entrained particulate matter in the raw product low-Btu gas and in the ash. Process blowers and turboblowers, coal conveyors, coal bucket elevators, and pumps are sources of potential noise impacts in Wellman-Galusha facilities.

DATA NEEDS AND RECOMMENDATIONS

Data needs and recommendations for obtaining those data are divided into the following categories:

- Gaseous, liquid, and solid waste stream characterizations and control;
- Process and process streams; and
- Health and environmental impact assessments.

The data needs for the multimedia waste streams and the process and process streams associated with Wellman-Galusha gasification systems are summarized in Tables 16 and 17, respectively. In general, data associated with the gasification of high-sulfur bituminous coal are currently not available. Since existing and planned commercial Wellman-Galusha gasification plants are low-sulfur bituminous and anthracite coals, data on high-sulfur coals may have to be obtained from bench-scale units. Data are not available on the performance of sulfur recovery processes and waste streams from those processes. These data may be obtained if a Stretford sulfur-removal process is included in the Pike County gasification facility.

Data needs associated with performing health and environmental assessments include data required by existing and proposed regulations, and data required to assess health and environmental (air, water, and land) impacts of nonregulated pollutants or streams. The data needs for existing and proposed environmental regulations mainly involve pollutant-specific determinations (i.e., consent decree pollutants, solid waste leaching tests defined in 40 CFR 251), bioassay tests (i.e., proposed in the RCRA [40 CFR 250]), and accurate pollution control costs. Also, long-term monitoring of specified pollutants is required to assess the effectiveness of a control technique.

Data requirements for assessing the health and environmental impacts of nonregulated pollutants and streams will involve pollutant-specific determinations, long-term monitoring, and biological testing (including both acute and chronic tests for health and ecological effects). The specific methodologies to be used in performing these impact assessments are still under development. Therefore, the specific data needs are not totally defined.

ISSUES AND AREAS OF CONCERN BY PROGRAM OFFICES

The EPA program offices' issues and areas of concern for Wellman-Galusha low-Btu gasification technology are briefly discussed here. The basic issues and areas of concern include:

- *Wellman-Galusha gasification technology*
At what stage should existing standards apply to a developing technology?
When will the technology be commercialized?

TABLE 15. SOLID WASTES FROM WELLMAN-GALUSHA LOW-Btu GASIFICATION
SYSTEMS THAT WILL BE REGULATED BY THE RCRA
(20 CFR 241)

Solid Waste Stream	Characteristics of the Waste Stream that may be Classified as Hazardous
Gasifier Ash	High levels of trace elements are present and may be leached from the ash.
Cyclone Dust	High levels of trace elements are present. The dust contains high levels of carbon (70-90%) and may be classified as ignitable.
Sulfur Cake	The sulfur will contain various components such as vanadium salts, thiocyanates, and thiosulfates.
MEA Blowdown	This stream will contain oxazolidin-2, 1-(2-hydroxyethyl) imidazolindone-2; diethyl urea; dithiocarbamates; thiocarbamides; and other high molecular weight compounds resulting from the formation of nonregenerable complexes.

TABLE 16. SUMMARY OF WASTE STREAM CHARACTERIZATION AND CONTROL DATA NEEDS AND PLANNED ACTIVITIES TO OBTAIN THOSE DATA

<u>Waste Stream Media</u> Waste Stream	<u>Additional Characterization Needed</u>	<u>Control Technology Performance Needed</u>	<u>Planned Activities to Obtain Data Needs</u>
<u>Gaseous Emissions</u>			
Coal feeder vent gas	Compounds present for gasification of high-sulfur coal	Effectiveness and actual cost of recycling this stream to the gasifier inlet air	This control will be evaluated by Radian and ORNL at the University of Minnesota (Duluth) (UMD) Foster Wheeler/Stoic gasification facility
Start-up vent gas	Chemical characteristics during the start-up period for various start-up materials (i.e. coke, wood, oil, etc.)	Effectiveness and energy requirements using a flare to control these gases. Currently there are no good techniques for evaluating the control effectiveness of flares	The Wellman-Galusha test facility at the U.S. Bureau of Mines at Ft. Snelling Minn. has a start-up vent flare that may be available for testing
Pokehole gases	Compounds present for gasifying bituminous (high- and low-sulfur) coals	Effectiveness of injecting an inert gas (i.e. steam) into the pokehole during the poking operation Effectiveness of using automatic pokers	None The UMD facility will use automatic pokers
Tar/quench liquor separator vent gases	Chemical and biological characteristics for gasifying high-sulfur bituminous, anthracite and lignite coals	Effectiveness of recycling to the product gas	The UMD facility will use this for their tar storage tank. Vent gases will be characterized by Radian and ORNL
Stretford oxidizer vent gases	Chemical characterization	None should be required	The Pike County Wellman-Galusha facility may have a Stretford sulfur removal process. This stream will be characterized by Radian and ORNL. Other potential test sites are currently being pursued by Radian.
MEA acid gas stream	Chemical characterization	Effectiveness of using a Claus and tail gas cleanup process for sulfur removal	No MEA processes are planned for removing sulfur from low-Stu gas at atmospheric pressure
<u>Liquid Effluents</u>			
Ash sluice water	Chemical and biological characterizations for effluent guideline standards and comparison to the MEG's for high-sulfur bituminous and lignite coals	Effectiveness of collection and reuse of the ash sluice water	Ash sluice water for the gasification of lignite at the Ft. Snelling facility will be characterized by Radian
Process condensate	Chemical and biological characterizations for effluent guidelines and comparison to the MEG's for high-sulfur bituminous, anthracite and lignite coals	Effectiveness of concentrating process condensate by forced evaporation	Laboratory tests may be performed to evaluate the gaseous emissions generated by forced evaporation
Stretford blowdown	Chemical and biological characterizations for effluent guidelines and comparison to the MEG's for high- and low-sulfur bituminous, anthracite and lignite coals	Effectiveness of reductive incineration	Reductive incinerations may be used at the Pike County facility
<u>Solid Wastes</u>			
Gasifier ash	Chemical and biological characterizations for high-sulfur bituminous and lignite coals. Leaching studies are needed to determine if the ash is classified as hazardous by the RCRA	Control requirements will be defined by the RCRA based on chemical and biological characteristics	Leaching tests for lignite ash are planned. Other leaching tests for low-sulfur bituminous ash may also be performed
Cyclone dust	Chemical and biological characterizations of dust collected from gasifying high- and low-sulfur bituminous and lignite coals are needed for the RCRA	Control requirements will be defined by the RCRA based on chemical and biological characteristics Effectiveness of combusting the dust may be required	Leaching tests for lignite are planned. Other leaching tests for low-sulfur bituminous coal may be performed Laboratory tests may be performed to evaluate dust combustion characteristics
Sulfur	Chemical and biological characterizations of sulfur are needed for the RCRA	Control requirements will be defined by the RCRA based on chemical and biological characteristics	Sulfur produced by the Stretford process will be characterized if a Stretford process is used at Pike County or if another test site can be obtained.
MEA blowdown	Chemical and biological characterizations are needed for the RCRA	Control requirements will be defined by the RCRA based on chemical and biological characteristics	No MEA processes are currently planned to remove sulfur from atmospheric low-Stu gas streams

**TABLE 17. PROCESS AND PROCESS STREAM DATA NEEDS AND PLANNED
ACTIVITIES TO OBTAIN THOSE DATA**

Process	Data Needs	Planned Activities
Wellman-Galusha Gasifier	Fate of pollutants (sulfur species, nitrogen species, tars and oils) for various gasifier operating conditions and coal feedstocks. Operating conditions that need to be evaluated include steam/air ratio, coal throughput, and bed depth. High-sulfur bituminous coal has not been tested since all commercial facilities use low-sulfur bituminous and anthracite coals.	Research Triangle Institute and North Carolina State University will be performing parametric studies on bench-scale gasifiers using various coal feedstocks.
Particulate Removal - Hot Cyclone	Collection efficiencies of hot cyclones are needed since the particulates not removed will affect downstream gas purification processes and the raw gas combustion process characteristics and flue gases.	Particulate removal efficiency studies for the hot cyclone at the UMD facility are planned.
Gas Quenching/Cooling	Fate and distribution of sulfur species, nitrogen species, tars, oils and particulate matter are needed. The quenched and cooled gas characteristics will affect the performance and design of downstream purification processes.	The Pike County facility may have a gas quenching/cooling process. The Chapman facility may be used to evaluate this process.
Tar Removal - Electrostatic Precipitation	Tar removal effectiveness needs to be determined since residual tar/oil aerosols will affect the performance and design of downstream sulfur removal processes.	The tar/oil removal effectiveness will be determined at the UMD gasification facility.
Sulfur Removal - Stretford	Sulfur removal effectiveness needs to be determined. There are currently no data on the performance of the Stretford process used to remove H ₂ S from low-Btu gas.	Stretford process performance will be evaluated by EPA and DOE if a Stretford unit is used at Pike County. Other test sites are currently being identified.
End Use - Combustion	Combustion gases from burning hot raw gas, quenched gas and desulfurized gas are needed along with tar combustion gases.	Combustion gases will be characterized at the Ft. Snelling and UMD facility.

- *Waste streams from Wellman-Galusha facilities*

What are the potentially harmful pollutants in gaseous, liquid, and solid waste streams, including potential fugitive emissions?

What are the emission rates of those pollutants?

What potentially harmful pollutants in those streams are not currently regulated?

What are the health and ecological effects of those pollutants and streams?

- *Pollution control technology*

What technologies have been demonstrated in controlling gaseous, liquid, and solid waste streams from Wellman-Galusha facilities?

What are the economics and energy usage associated with controlling those streams?

Each program office needs representative and accurate data concerning:

- Chemical, physical, and biological characteristics of the waste streams to air, water, and land;
- Technology required to control those waste streams; and
- Chemical, physical, and biological characteristics of fugitive emissions resulting from the processing, storage, and transport of waste streams, products, and byproducts.

The waste stream and fugitive emission data must be able to stand up to a traditional peer review and court review before the data are used for recommending standards. Control technology data should be obtained on demonstration-scale control equipment.

The following text contains a summary of the specific issues and areas of concern by each EPA program office.

Office of Air Quality Planning and Standards (OAQPS)

OAQPS prepares a Standards Support and Environmental Impact Statement (SSEIS) document to back up its regulatory activity. These SSEISs address specific source categories, and each document contains the following items:

- The process or processes and associated air emissions;
- Emission control techniques, including process modifications and "add-on" control equipment;
- Environmental impacts to air, water, and

land resulting from air emissions and the control of those emissions; and

- Energy and economic impacts associated with controlling air emissions.

Accurate, well-documented data for emission measurements are needed to prepare an SSEIS, along with representative data concerning control equipment performance.

All methods used to measure emissions must be documented. Where EPA reference methods are used, citation of the appropriate part of Appendix A, 40 CFR 60, is sufficient. Any new methods or modifications of the standard sampling and/or analysis methods must be clearly defined and discussed. Confidence intervals on the data obtained from modified or new methods are required along with a discussion concerning the representativeness of those data with respect to long-term emissions.

As part of the SSEIS, OAQPS needs accurate data concerning control technology performance, costs, and energy usage. These data also include water pollution control and solid waste disposal when there are liquid and solid waste streams resulting from an air pollution control device. If possible, data on control technology should be collected on demonstration-size units.

The following OR&D inputs are desired by OAQPS:

- Development and evaluation of continuous monitoring devices for selected pollutants in air emissions,
- Identification of other potentially harmful pollutants in air emissions,
- Assessment of a control technology's performance in controlling potentially harmful pollutants, and
- Evaluation of control technology performance, costs, and energy usage.

Results from the above inputs need must be discussed in detail and to be well documented.

Office of Water Planning and Standards (OWPS)

OWPS has data needs and requirements similar to those of OAQPS, except with respect to effluent streams. Effluent measurements to determine the presence and concentration of the 129 priority pollutant species are needed. These measurements should be performed by techniques established as adequate for standards support. Other standard measurements,

such as total suspended solids, biological oxygen demand, pH, etc., are also needed along with the identification of other potentially harmful species in process effluents.

Accurate control technology performance and economic and energy usage data are inputs needed by the OWPS. If possible, these data should be obtained from demonstration-size processes. Sampling and analysis techniques and control technology performance data must be thoroughly discussed and well documented.

Office of Solid Waste (OSW)

OSW has issued proposed regulations establishing the criteria for methods of testing for and handling and disposal of hazardous wastes. Their present needs from OR&D for Wellman-Galusha gasification technology are minimal. However, the application of the test methods and identification of hazardous waste streams from the various processes in Wellman-Galusha gasification systems will provide necessary data for the various cognizant enforcement and monitoring agencies at the local, State, and Federal levels.

Office of Toxic Substances (OTS)

OTS needs information on toxicity and exposure potential of pollutants in the product and byproduct streams associated with Wellman-Galusha facilities to guide its regulatory efforts. Although OTS will rely on the other program offices (OAQPS, OWPS, and OSW) to regulate waste streams and residuals, it will probably serve in an advisory capacity to guide efforts of these offices relative to toxic substances.

Office of Radiation Planning (ORP)

ORP may consider in FY80 the radiation hazards posed by the operation of Wellman-Galusha gasification facilities as well as other synthetic fuels plants. Radon 222 in air emissions from these plants, or as fugitive emissions from coal piles and ash piles associated with plant operation, would be one concern. Another concern would be the Radium 226 trace impurities in coal pile runoff. A key question for ORP is: Providing that Radon 222 is found to be a hazard in conventional combustion technology, would synthetic fuels plants function as an ef-

fective control technology? From ORP's point of view, OR&D environmental assessments must include measurement of Radon 222 and Radium 226.

Gross α and β measurements on waste streams are not adequate to fulfill ORP needs. Gamma-ray spectrometry followed by U^{235} , Th^{232} , and K^{40} elemental analysis are required. Accurate particle size distribution data from emission sources are also needed.

Office of Enforcement (OE)

The needs of the Office of Enforcement are very similar to those of OAQPS and OWPS. If OE is to advise on the issuance of permits, or in some cases, issue permits, for Wellman-Galusha plant operation, it must have a comprehensive view of Wellman-Galusha low-Btu gasification technology.

Many of the EPA program offices' general and specific issues and areas of concern can be addressed for Wellman-Galusha low-Btu gasification systems. However, because of a limited budget and a limited number of available test sites having best available control technology, the data collected on gaseous, liquid, and solid waste stream characteristics (chemical, physical, and biological) and technologies to control those streams must be prioritized. Priorities will be based upon the program offices' R&D needs and standards support schedule that are defined in the *Standards Support Plan for Synthetic Fuels*, to be published by IERL/RTP of the Office of Research and Development.

REFERENCES

1. Kohl, A. C., and F. C. Riesenfeld. *Gas Purification* (second edition). Houston, Gulf Publishing Co., 1974.
2. Williams, Dale, and A. F. (Buzz) Zey. Personal Communication, J. F. Pritchard & Co. August 1 1978.
3. Sigmund, Paul. Personal Communication, 5 and 7. Union Carbide Corp. June 1978.
4. Perry, Charles R. Basic Design and Cost Data on MEA Treating Units. In: *Proceedings of the 1967 Gas Conditioning Conference University of Oklahoma, April 4-5, 1967, Norman 1967*. P. C1-C9.
5. Chem, C. L., and T. L. McCaleb. Coal Processing: Low Btu Gas as an Industrial Fuel.

Chem Eng Progr. 73(6):82-88. (1977).

6. Woodruff, David D. Personal Communication. McDowell-Wellman Engineering Co. December 19 1977.
7. Cleland, J. G., and G. L. Kingsbury. *Multimedia Environmental Goals for En-*

vironmental Assessment, Volumes I and II. Research Triangle Institute. Research Triangle Park, NC. Report No. EPA-600-7-77-136a, b, EPA Contract No. 68-02-2612. November 1977.

FATE OF PHENOLS DURING THE GASIFICATION OF COAL

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Abstract

An investigation of the engineering relationships governing the production of phenols during coal gasification processing is described. Experiments were conducted on bench, PDU, and pilot plant-scale facilities to assess the impact of initial formation and subsequent decomposition phenomena on observed levels of phenolic compound production. Experimental efforts included:

- Bench-scale investigation of the decomposition characteristics of select phenolic compounds in the homogeneous gas phase and over fixed beds of lignite char and limestone acceptor solids,*
- PDU-scale experimentation on the Pittsburgh Energy Technology Center's Synthane PDU gasifier to assess the effects of changing initial devolatilization conditions on the formation of phenols from coal, and*
- Pilot-scale investigation of coupled formation/decomposition phenomena via probe sampling of the spatial chemical composition within the CO₂-acceptor pilot plant gasifier in the vicinity of the fresh coal feed location.*

Integrating the results of these three separate experimental studies facilitates an understanding of phenolic compound behavior during coal gasification. Major behavioral characteristics identified indicate that:

- Phenols are formed inherently during the devolatilization stage of coal processing;*
- Production of phenols, which are highly susceptible to thermal and catalytic decomposition, is controlled by physical and operational characteristics of the gasification process that could enhance thermal and catalytic cracking, and*

- Conditions responsible for enhancing reduction of phenolic compound production do not adversely affect production of the primary product of coal gasification.*

INTRODUCTION

Phenolic compounds comprise a family of aromatic hydrocarbons produced during coal gasification. They report to aqueous and hydrocarbon condensates (when produced) and are removed from raw gasifier product gas during quenching operations. Production of phenolic effluents during gasification processing is highly variable and is a strong function of both gasification process conditions and quench system operation. This apparent variability, both between and within individual processes, provides the incentive to investigate the relationships that govern production of phenols during coal gasification.

Given the current status of coal gasification research in the United States, it is clear that the environmental acceptability of a process must be determined based on data from subcommercial facilities. As a result, a substantive engineering basis is needed to properly obtain and interpret environmental data taken at PDU and pilot-plant scales of development. In view of the fact that significant changes in operating conditions can occur in scaling to commercial-size facilities, data must be obtained that permit adequate decoupling of process variable interactions so quantitative projections of phenolic compound production can be made. The accuracy of these projections affects the design and operation of all modes of processing downstream of the primary gasification system.

An experimental strategy is developed that effectively uses three different experimental scales of process development. Production is qualitatively segregated into initial formation

*Speaker.

and subsequent secondary reaction steps within the gasification environment. The choice of experimental efforts reflects the desire to study these phenomena individually and in a highly coupled manner. The primary data base needed to delineate the pathway governing production of phenols in coal gasification processing is generated from these experiments.

PHENOLIC COMPOUND PRODUCTION DURING COAL GASIFICATION

Phenols are of primary interest in coal gasification processing. Although produced in small quantities relative to the major product of gasification, their presence is important in specifying particular modes and configurations of downstream raw product gas processing. When produced in sufficient quantities, they can represent a valuable byproduct of gasification. If byproduct recovery is uneconomical or production is limited, they represent an effluent that must be eventually processed. The amount, type, and physical characteristics of phenols produced during coal gasification determines the physical and chemical nature of the processing scheme required.

Basic Production and Processing Patterns of Phenols

The general pattern of phenolic compound production and processing is illustrated in Figure 1. Phenols produced during gasification exit the gasifier with the raw product gas and are removed during quenching operations. They report to both aqueous and hydrocarbon condensates, when produced, because of their partial solubility in water and the aromatic nature of the compounds. Relative quantities of condensates produced are a strong function of gasification process conditions.

Two basic options are available for processing phenolic condensates: byproduct recovery of crude phenols, and destructive treatment of phenols. Crude phenols can be recovered from either aqueous or hydrocarbon condensates. Solvent extraction and distillation are two frequently used recovery techniques. In the event that byproduct recovery is not feasible, phenols in both aqueous and hydrocarbon condensates can be destructively treated. Aqueous condensates containing high levels of phenolic

material can be processed via biological oxidation in the presence of bacterial organisms. Reduction of phenols in hydrocarbon condensates can be accomplished by injection of tar back into the gasifier, which is frequently done for commercial fixed-bed gasification technology.

Variable Phenolic Compound Production Rates

Data summarized in Table 1 indicate substantial variation in measured phenolic compound production rates, both within and across processing concepts. Given the widely different processes represented, this is not surprising. Large changes in macroscopic operating conditions and physical gasifier geometries must affect the production of phenols. In addition, variabilities within processes should be expected if significant differences in operating conditions can be effected.

Phenol Production Variation Across Processes—

Processes listed in Table 1 are significantly different, both physically and operationally. Differences exist in operating temperatures and pressure, contacting geometry, and coal type. These differences are summarized in Table 2 based upon characteristics of operating pilot-plant facilities.

The type of gas-solid contacting varies considerably, implying substantial differences in modes of mixing. Pressure and temperature variations are considerable, with the latter segregated to specify the initial thermal conditions the coal meets upon entering the gasification environment. Coal type is indicated more from an operational viewpoint because neither CO₂-Acceptor nor the slagging fixed bed facilities can operate on bituminous coals.

The most obvious difference in production of phenols occurs for the CO₂-Acceptor process (see Table 1), where production is fully two to three orders of magnitude less than for any other process. Differences in processing conditions are also evident. Most notably, pressure and initial coal devolatilization temperature are consistently higher and lower, respectively, for all other processes. Further cross-process comparisons are difficult because of considerable observed variability within processes.

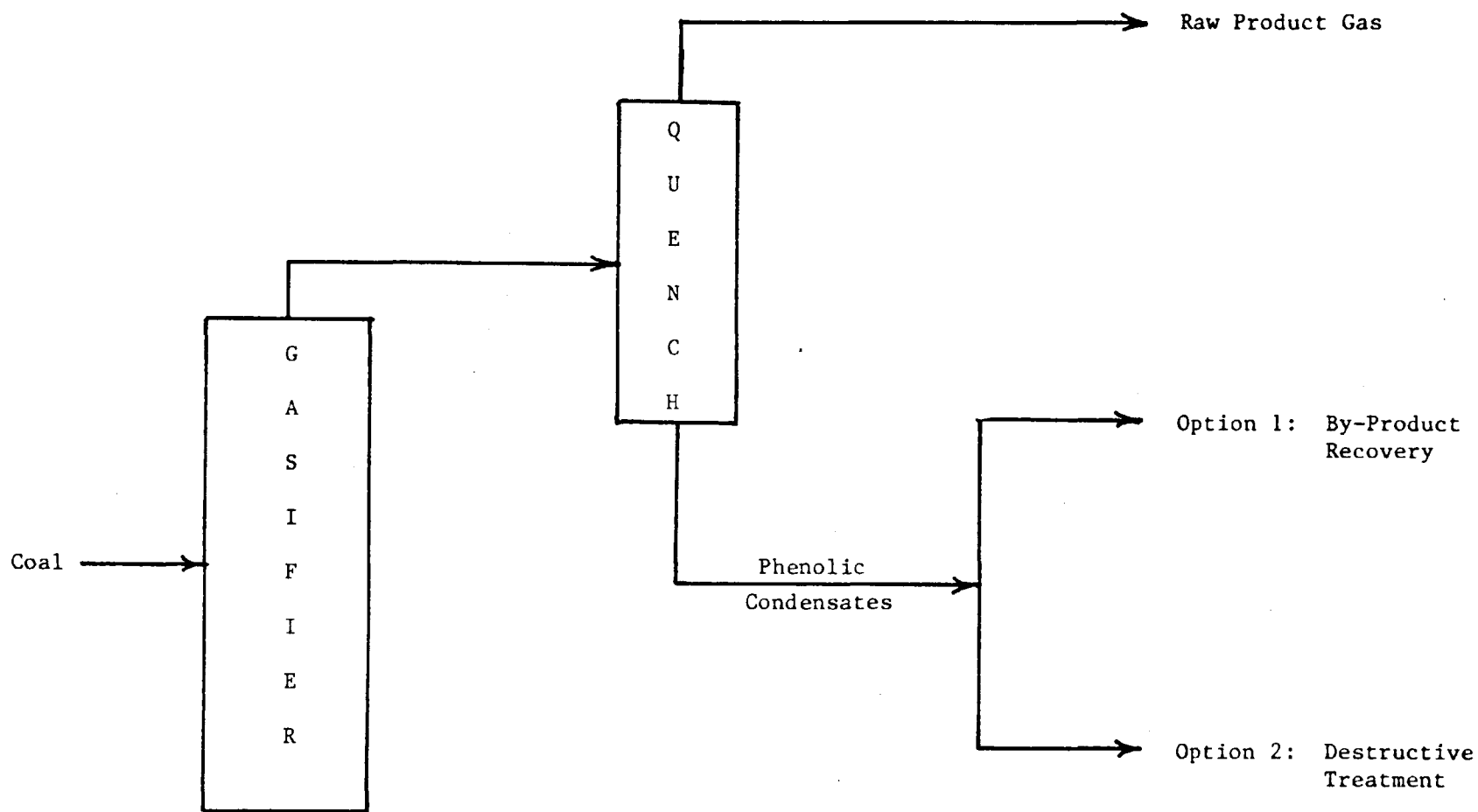


Figure 1. Basic production and processing patterns of phenols during coal gasification.

Phenol Production Variation Within Processes—

Differences in phenol production rates within individual processes are significant and suggest that changes in processing conditions can also significantly affect production. The complexity of pilot-plant systems, operationally and physically, precludes straightforward analysis of this behavior. However, results of experimentation conducted on the Synthane Pilot Development Unit (PDU) dramatically illustrate that production of phenols is substantially reduced simply by feeding coal deeper into the gasifier.⁸

Although production of phenols and hydrocarbon tars decreased substantially as coal was injected deeper into the gasifier (see Table 3), the extent of these observed reductions differed. Alteration of coal feed geometry significantly changed process variables such as temperature, vapor residence time, gas-solid contacting, and coal heating rates. Changing from free-fall (i.e., gravity feed through solids disengaging zone) to shallow bed-injection (i.e., feed directly into the fluidized bed) of coal resulted in major increases in all variables except residence time. Residence time was the only vari-

able to increase substantially as coal was fed deeper into the fluidized bed. Coupling of hydrocarbon production reductions and process variable changes suggested:

- Phenol production was reduced by increasing temperature and residence time, consistent with thermal cracking mechanisms, and
- Hydrocarbon tar production was reduced primarily by changing initial coal devolatilization conditions (i.e., coal heating rates, gas-solid contacting).

STRATEGIC EVALUATION OF PHENOLIC COMPOUND PRODUCTION PATTERNS

As a result of the demonstrated variability in production of phenols, determination of basic production patterns for phenols during coal gasification was considered desirable. Production of phenols, as well as of any other effluent, is a manifestation of two distinct phenomena: initial formation from coal followed by subsequent secondary reactions within the gasification environment. Proper delineation of these characteristics required minimizing the inherent complexity of the individual reacting systems. Ex-

TABLE 1. SUMMARY OF RANGES OF PHENOLIC COMPOUND PRODUCTION FROM COAL GASIFICATION PROCESSES

<u>Process</u>	<u>Phenol Production^(a), lb/ton MAF coal</u>
Bigas	-
CO ₂ -Acceptor	< 0.01
Hygas ^(b)	1-16
Slagging Fixed Bed ^(c)	10-30
Synthane PDU	1-12

Footnotes:

- Data from Reference 1, except where noted.
- Includes data from Reference 2.
- Data from References 3-7.

TABLE 2. SUMMARY OF COAL GASIFICATION PILOT-PLANT OPERATING CONDITIONS

Process	Coal Type ^(a)	Contacting Geometry	Pressure, atm	Temperature ^(b) , °C	
				Devolatilization ^(c)	Gasification
Bigas	NR	Entrained Flow	69	925-1200	1650
CO ₂ -Acceptor	Lignite and Subbituminous	Fluidized Bed	11	815	815
Hygas	NR ^(d)	Staged Fluidized Beds ^(e)	69	425-650	870
Slagging Fixed Bed	Lignite and Subbituminous	Fixed Bed	< 30	175	1650
Synthane PDU	NR ^(d)	Fluidized Bed	< 40	400 - 700	870

Footnotes:

- (a) Coal types include lignite, subbituminous and bituminous, with NR referring to no restrictions.
- (b) Temperatures represent averages, accurate to within at least ± 10 percent. Wide temperature variations are noted.
- (c) Initial temperature condition to which coal is subjected.
- (d) Use of bituminous coal requires an oxidative thermal pretreatment step.
- (e) Coal is devolatilized in an upflow entrained-flow riser tube.

TABLE 3. COMPARATIVE STEADY-STATE PRODUCTION RATES FOR PHENOLS AND TAR: FREE-FALL, SHALLOW, AND DEEP-BED INJECTION OF NORTH DAKOTA LIGNITE^(a)

Coal Injection Geometry	Phenols		Tar	
	Production, lb/ton MAF coal	Percent Reduction ^(b)	Production, lb/ton MAF coal	Percent Reduction
Free-Fall	11.9 ± 1.3	71	74.1 ± 27.	86
Shallow Bed	3.5 ± 1.9		10.1 ± 5	
Deep Bed	0.5 ± 0.6		6.3 ± 2.2	

Footnotes:

(a) Source: Reference 8.

(b) Reduction achieved by injecting coal deeper into the gasifier.

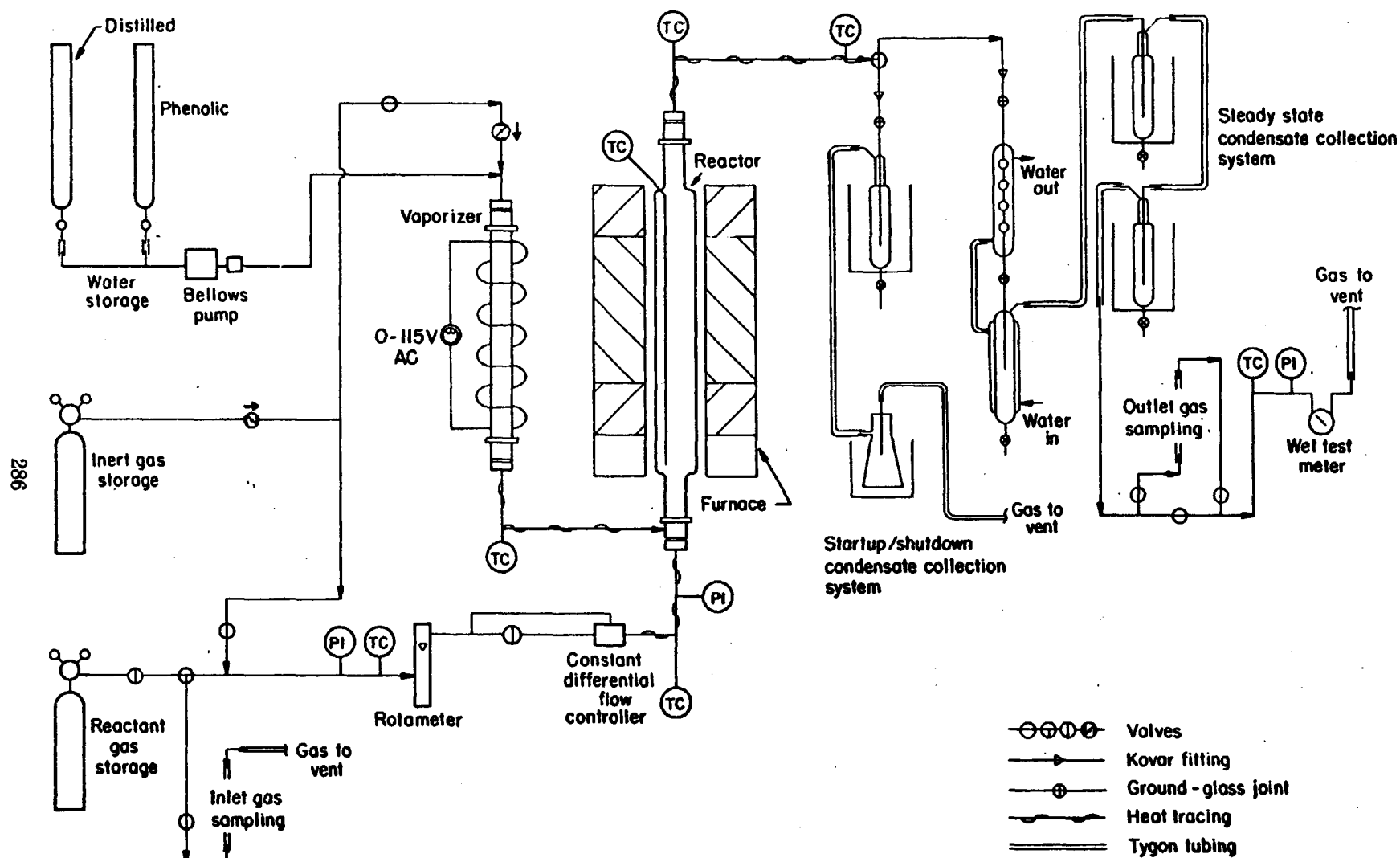


Figure 3. Thermal decomposition reactor—basic bench-scale equipment train.

composition on rates of phenol decomposition and the nature of the decomposition products. The range of process conditions in these experiments included:

- Reactor temperatures from 300° to 975° C, with primary emphasis on the range 750° to 900° C;
- Reaction gas residence times of 2 to 4 s; and
- Hydrogen partial pressures of 0.0, 0.2 and 0.5 atm, each at a constant water partial pressure of approximately 0.5 atm.

Such homogeneous thermal decomposition rate measurements at atmospheric pressure provided a distinctly conservative estimate of potential phenolic compound decomposition rates in the presence of char at system pressure. Experimentation under well-controlled conditions also provided quantitative decomposition kinetics for the most prevalent single compound in coal gasification aqueous condensates.

Homogeneous Ortho-Cresol Decomposition—

Ortho-cresol was chosen as a second phenolic compound in these studies because cresols are the largest class of phenolic compounds in coal gasification wastewaters, with ortho-cresol the most reactive of the cresols.^{9 10 14} The range of experimental conditions included:

- Reactor temperatures from 600° to 900° C, and
- Reaction gas residence times of 2 to 4 s.

Hydrogen and water partial pressures were maintained at approximately 0.2 and 0.5 atm, respectively. These studies, in conjunction with studies of phenol, would define a "decomposition envelope" for approximately 80 + percent of the phenolic compounds typically found in coal gasification aqueous condensates.

Heterogeneous Phenol Decomposition—

Char solids occupy significant portions of coal gasifiers. In addition, the CO₂-Acceptor process required the use of a lime-bearing acceptor. Experiments were conducted to evaluate separately the decomposition of phenol in the presence of fixed beds of North Dakota lignite char from the Synthane PDU and lime-bearing acceptor from the CO₂-Acceptor gasifier. Similar conditions of residence time, water, and hydrogen partial pressures were used at reactor temperatures ranging from 350° to 750° C. Such ex-

periments permitted assessment of the relative magnitudes of reaction rates in the presence of potentially catalytic solid surfaces typical in coal gasification processes.

Formation Characteristics of Phenols—

A series of six gasification trials were conducted on the Synthane PDU (see Figure 4) to examine the sensitivity of phenolic effluent production and composition to critical changes in devolatilization process parameters. Variations in gas-solid contacting and heating/diffusion rates were effected by altering coal injection geometry and mean coal particle size, respectively. The relative effects of thermal/catalytic decomposition, identified during bench-scale experimentation, were minimized by injecting fresh coal on top of the fluidized bed. This mode of coal injection provided devolatilization conditions similar to previous shallow and deep bed-injection trials,⁸ while essentially eliminating residence time of devolatilized species in the hot fluidized bed.

Gas-Solid Contacting—

Gas-solid contacting in the Synthane PDU was varied by utilizing both free-fall and top bed-injection of North Dakota lignite coal. Free-fall injection of coal permitted devolatilization to occur in a relatively dilute, unmixed environment. Top bed-injection of coal onto the gasifier's fluidized bed produced the intense gas-solid mixing thought to enhance secondary reactions of devolatilized species with hot char surfaces. Because residence time of devolatilized species in the hot fluidized bed was minimized, the impact of devolatilization conditions was effectively isolated.

Coal Particle Size—

Variation of coal particle size influenced rates of coal heating and diffusion of devolatilized species from the coal particles. Transient transport by either of these mechanisms (generally described in terms of the Fourier number) contains the same functional dependencies (i.e., proportional to diameter squared). Particle sizes used in this study produced initial heating and diffusion rates that differed by more than an order of magnitude. Initial heating rates (i.e., assuming an isothermal coal particle) were 4,000° and 84,000° C/s for 220 (i.e., 20 × 100 mesh) and 50 (i.e., 70 percent through 200 mesh)

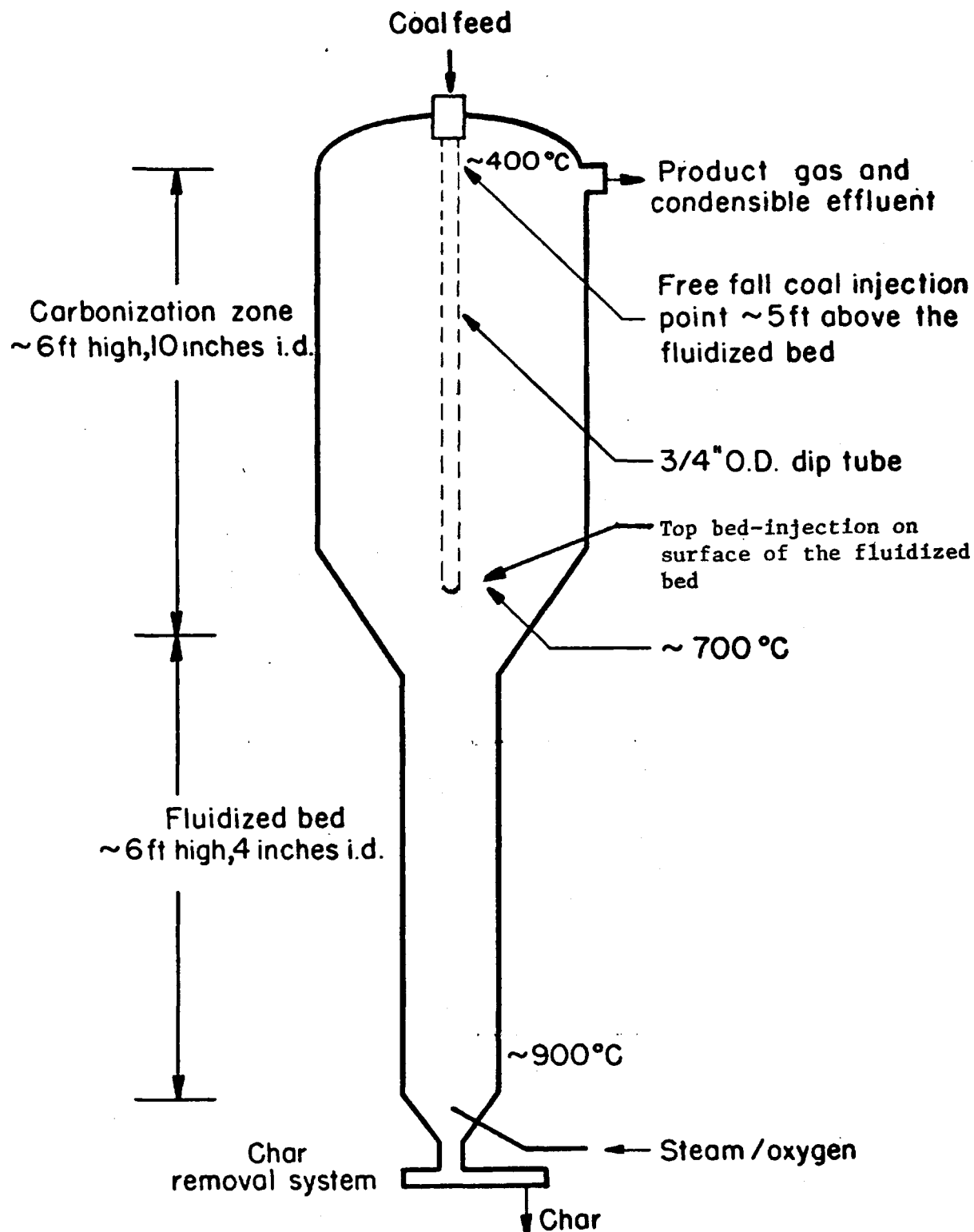


Figure 4. Basic configuration and coal feed locations of the Synthane PDU gasifier.

micron coal particles, respectively. Overall heating rates (i.e., coal particle reaches 95 percent of reactor temperature) were 200° and 3,000° C/s, respectively. The range and order of magnitude changes in these rate processes were sufficient to identify the combined effects of heating and diffusion rates on phenolic compound formation during coal devolatilization.

Operation of the Synthane PDU during gasification of such widely varying coal particle sizes required maintenance of either constant carbon conversion or fluidizing conditions (i.e., gas-solid contacting). Because coal devolatilization is a rapidly occurring phenomenon, it should not be affected by levels of carbon conversion typical in the Synthane PDU (i.e., 50 to 95 percent). As a result, "constant" fluidization conditions were maintained throughout these gasification trials as defined by Damon.¹⁵ Operating velocities necessary to achieve these fluidization conditions were 10.4 and 3.7 cm/s, for mean particle sizes of 220 and 50 microns, respectively. Selection of fluidization velocities in these trials was based solely on the operating constraints of the Synthane PDU gasifier.

Coupled Formation/Decomposition Characteristics of Phenols

Negligible quantities of hydrocarbon tars, oils, and phenols were produced from the CO₂-Acceptor pilot-plant gasifier. Coal was injected at the base of the gasifier's fluidized bed, operating at 11.5 atm and 815° C. Volatile species released from the coal had to travel through over 8 m of a fluidized char bed to exit with the product gas. In view of the complexities governing production of phenols during coal gasification, formation and decomposition were impossible to decouple by measuring external production characteristics.

This experiment was designed to investigate phenol production characteristics on a large-scale gasification system. The inherent coupling of formation and decomposition phenomena made it an attractive site for strategically designed experiments where both phenomena could be observed. This was accomplished by sampling the spatial chemical composition of the gasifier in the vicinity of fresh coal feed. Sampling probes able to withstand the severe gasifier conditions were designed to quantitatively remove process gas from within the three-phase

gasifier environment. Complete characterization of process gas samples provided data on both phenols and hydrocarbon tars/oils, as well as for inorganic effluents (e.g., hydrogen cyanide and ammonia), and CO₂-Acceptor gasifier process dynamics (i.e., steam-carbon gasification kinetics and fluid mechanical behavior).¹⁶ A schematic of the base of the CO₂-Acceptor gasifier and the three longitudinal probe locations is shown in Figure 5.

Formation of Phenols—

Effective segregation of phenolic compound formation within the CO₂-acceptor gasifier required sampling in the immediate vicinity of the location of fresh coal feed. As a result, a primary location for a sampling probe necessarily had to be opposite this point in the gasifier. Then, sampling could occur progressively closer to the fresh coal feed location through an approach from the opposite side of the gasifier. The sampling point closest to fresh coal feed was approximately 25 cm above, offset by 16° (see Figure 5).

Decomposition of Phenols—

Sampling probes were located at various levels around the coal feed location to track the fate of phenols within the gasifier following their release during coal devolatilization. Since gas and solid mixing patterns within the gasifier were not known a priori, two additional probes were located approximately 56 cm above and 36 cm below the coal feed location. Probe entry into the gasifier was offset by 110° and 225° for top and bottom probes, respectively. Combined with the capability to perform a radial traverse, the environment within the gasifier could be effectively sampled.

PATHWAYS TO PRODUCTION OF PHENOLS IN COAL GASIFICATION PROCESSING

Results of these investigations cover essentially the full range of parameters for each individual effort. Bench-scale phenolic compound decomposition studies were previously presented for the initial phenol work,¹⁷ and for later ortho-cresol and solids experiments.^{16 18 19} Results of experimentation on the Synthane PDU were reported for characterization of all effluent and product species.^{1 16} Process gas and

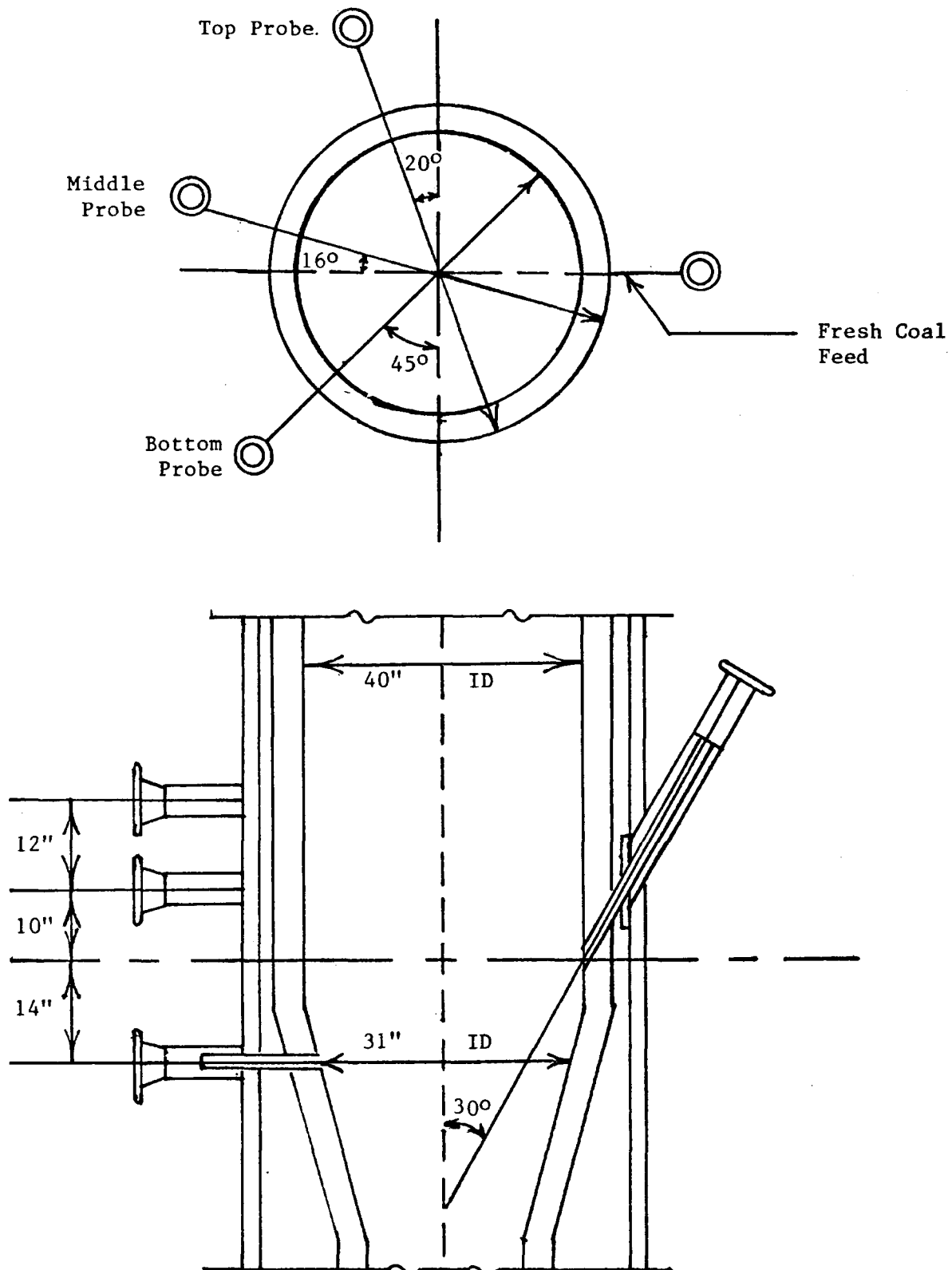


Figure 5. Radial and longitudinal probe orientations in the CO_2 -acceptor gasifier bed.

environmental characteristics within the CO₂-acceptor gasifier have also been analyzed and reported.¹⁶ The following discussion evaluates experimental results that help delineate the formation and decomposition patterns of phenols during coal gasification.

Delineation of Formation Characteristics of Phenols

Bulk Formation of Phenols—

Results of experimental investigations conducted on the Synthane PDU point distinctly to inherent formation of phenols during coal devolatilization. Data summarized in Table 4 indicate essentially invariant production of total phenols (i.e., 8 ± 3 , 7 ± 4 and 6 ± 1 lb/ton MAF coal) over the full range of varying coal devolatilization conditions. In contrast, note that changes in devolatilization conditions result in significantly reduced production of hydrocarbon tars and oils. In the case of the CO₂-Acceptor gasifier, probe sampling at the point nearest fresh coal feed (i.e., ~25 cm above coal feed) identified levels of phenols of 1 to 2 lb/ton MAF coal. This is in contrast to levels of phenols fully three orders of magnitude lower (see Table 1) as measured in the raw product gas. The release of phenols from coal, based upon observed characteristics in the Synthane PDU, must necessarily occur through the lower end of the coal's thermal processing (i.e., less than 650° C).

Phenolic Compound Homologues Formed During Coal Gasification—

The types of phenolic compounds present in aqueous condensates cannot be determined simply by characterization of total phenols, measured colorimetrically. Selected condensate samples from both the CO₂-Acceptor and Synthane PDU gasifiers were analyzed via direct aqueous injection gas chromatography to assess the types of compounds produced. Results were significant from an analytical standpoint as well as for delineating phenolic compound formation characteristics.

Comparison of Phenolic Compound Production Levels from Total Colorimetric and GC Analyses—Data from experimentation on the Synthane PDU suggest a negative bias in determining phenols by the colorimetric technique.

Results, summarized below, include data from runs CHPFL-284 and 285 (free-fall coal injection) and CHPFL-287 and 288 (top bed coal injection, 220 and 50 micron particle diameters, respectively):

Coal feed geometry	Ratio colorimetric/GC
Free-fall	0.61 ± 0.02 (4)
Top bed	0.74 ± 0.02 (4)

On the average, only 61 to 74 percent of total phenolic material measured gas chromatographically is detected in the colorimetric determination. This behavior is significant because the colorimetric technique, an accepted standard method for determination of phenols in gasification wastewaters, does not detect between 26 and 39 percent of the aqueous phenols present in these aqueous condensates.

Primary Phenol Homologues Formed During Coal Gasification—The only phenolic compounds detected in these experimental investigations were single aromatic ring phenols (i.e., phenol, cresols, and xylenols) present in Synthane PDU aqueous condensate. Phenol and cresols were the only phenols detected in condensates from probe sampling in the CO₂-Acceptor gasifier. Unfortunately, formation was not decoupled entirely in the CO₂-Acceptor probe studies, and hydrocarbon condensates produced in the Synthane PDU were not analyzed for phenols. However, published data for the Synthane PDU and the Grand Fork's Slagging Fixed Bed gasifiers, where both aqueous and hydrocarbon condensates were analyzed for phenols, were available and are summarized below:

Run	Phenolic compound production ¹⁶		
	lb/ton MAF coal		Single rings, percent
	Single ring	Multi-ring	
Synthane PDU ¹⁸			
CHPFL-111	13	5	71
CHPFL-118	13	3	83

TABLE 4. SUMMARY OF STEADY-STATE CONDENSIBLE HYDROCARBON PRODUCTION LEVELS FOR GASIFICATION OF NORTH DAKOTA LIGNITE IN THE SYNTHANE PDU

<u>Trial No.</u>	<u>Coal Feed Geometry</u>	<u>Mean Particle Size, microns</u>	<u>Condensible Hydrocarbon Production, lb/ton MAF coal</u>		
			<u>Tar</u>	<u>Oils</u>	<u>Phenols</u>
CHPFL-284	Free-Fall	50	$13 \pm 3^{(b)}$	$54 \pm 11^{(c)}$	8 ± 3
CHPFL-285			$(\bar{6})$	$(\bar{2})$	
CHPFL-288	Top Bed	50	$0.4 \pm 0.4^{(d)}$	49 ± 38	7 ± 4
CHPFL-289			$(\bar{6})$		
CHPFL-286	Top Bed	220	0.3 ± 0.2	$4^{(d)}$	6 ± 1
CHPFL-287			$(\bar{4})$		

Footnotes:

- a) Minimum total phenols as phenol, determined colorimetrically.
- b) Values in parentheses are number of data points averaged.
- c) Data for CHPFL-285 only.
- d) Includes single data points for either CHPFL-286 or 289.

Run	Phenolic compound production ¹⁶		
	lb/ton MAF coal		Single rings, percent
	Single ring	Multi- ring	
GFETC SFB			
RA-21 ^{5 7}	27	4	88
RA-31 ⁶	29	4	89
RA-40 ⁶	19	4	82

These data show that single aromatic ring phenols are by far the most predominant phenolic compound type formed from coal during gasification processing. Single aromatic ring phenols comprise 71 to 83 percent of Synthane PDU phenolic condensates. The Grand Fork's Slagging Fixed Bed gasifier produces from 82 to 89 percent single aromatic ring material for the data shown.

Correspondence of the Pattern of Phenolic Compound Formation with State-of-the-Art Coal Chemistry—

Ironically, one must address decomposition of coal itself to explain the formation of phenols from coal. In effect, candidate reactions responsible for phenolic compound formation from a hypothetical chemical structure of the coal "molecule" are proposed. As a result, the present understanding of specific chemical groupings and their orientation in the coal "molecule" makes this prognostication speculative at best.

Based on the behavior identified, certain conclusions can be drawn in addressing formation of phenols from coal.

- Phenolic compound production from gasification systems that minimize thermal decomposition (i.e., Lurgi, Slagging Fixed Bed, Synthane) varies by less than a factor of 2 to 3, regardless of coal rank;
- Coal oxygen content varies by as much as an order of magnitude between lignite and bituminous (on a moisture- and ash-free basis); and
- Phenolic effluents from coal gasification processes typically contain less than 2 percent of the coal's original oxygen (on a moisture-and ash-free basis).

What should be noted is the apparent invariability in phenolic compound production compared to the significant variability in coal

oxygen content. Drastic swings in coal oxygen content do not result in similar variability in phenolic compound production. The small amounts of coal oxygen that report as phenolic effluents only hamper accurately tracking the fate of coal oxygen during formation of phenols.

Delineation of Decomposition Characteristics of Phenols

The major conclusion from these experimental investigations is that production of phenols during coal gasification is controlled primarily by decomposition processes. Phenolic compounds are susceptible both to thermal and catalytic decomposition, although not to the same extent. The unique atmosphere present in coal gasification processing (i.e., high relative H₂ and H₂O partial pressures) precisely determines the decomposition pathway for the formed phenolic compounds. Experimentation across bench-, PDU-, and pilot plant-scale processes amply supports this behavior.

Relative Phenolic Compound Reactivity—

A significant data base is reported that defines the decomposition of phenolic compounds, specifically the methyl-phenols. Dealkylation rates of phenols increase with increasing molecular weight (i.e., additional alkyl substitution).¹⁴ Xylenols as a compound class are more reactive than cresols.⁹ Of the three isomeric cresols, meta-cresol is the least reactive and ortho-cresol is the most reactive.^{10 14}

Homogeneous Gas Phase Decomposition of Phenol and Ortho-Cresol—Experimental results confirm that substantially quantitative decomposition of phenol and ortho-cresol can be achieved by homogeneous gas phase reaction above 900° and 825° C, respectively. Data on the relationship of decomposition to reaction temperature and vapor residence time for phenol and ortho-cresol are shown in Figures 6 and 7, respectively. As anticipated, experimental results show that decomposition depends strongly on reaction temperature and vapor residence time. Greatest increases in phenol decomposition occur at temperatures between 750° and 900° C. In contrast, similar increases occur for ortho-cresol decomposition between less than 600° and 825° C, suggesting increased reactivity of ortho-cresol relative to phenol.

Observed decomposition rates are independent of hydrogen partial pressure for phenol. The effects of changing hydrogen partial pressure on ortho-cresol decomposition were not investigated.

Heterogeneous Decomposition of Phenol—

Experimental results indicate significantly different behavior for lignite char and lime-bearing acceptor solids (see Figure 8). Substantially complete decomposition of phenol occurs for reaction over fixed beds of lignite char from the Synthane PDU at temperatures as low as 600° C in less than 2 s. Greatest increases in phenol decomposition occur between 400° and 600° C. In contrast, decomposition of phenol over fixed beds of lime-bearing acceptor is only slightly higher than that observed during homogeneous gas phase reaction at the same temperature. Only 11 percent decomposition occurs at a temperature where complete decomposition occurs in the presence of lignite char. It is expected that the high surface area of the lignite char (i.e., ~ 360 m²/gm), as opposed to that for the lime-bearing acceptor (i.e., ~ 1 m²/gm), is responsible for providing the potential for a catalytically enhanced reaction.

Relative Reactivity of Phenol and Ortho-Cresol—Based on the demonstrated independence of phenol decomposition on hydrogen partial pressure, first-order kinetics of phenol decomposition were developed similar to that for decomposition of unsubstituted aromatic hydrocarbons.²⁰ The rate-controlling step in the reaction sequence was the initial thermal decomposition of the aromatic ring. First-order rate constants for both homogeneous and heterogeneous decomposition were plotted individually as a function of reciprocal absolute temperature. Arrhenius parameters were calculated by a least-squares linear fit of the first-order rate constants. Ortho-cresol data were similarly treated, as the reaction appears first order for large relative molar ratios of hydrogen to ortho-cresol (i.e., fully 300:1 in these experiments).¹⁰ Analysis results are summarized in Table 5.

Arrhenius parameters summarized in Table 5 are used to determine reactivities of ortho-cresol relative to phenol during homogeneous decomposition and those for phenol, heterogeneous relative to homogeneous decomposition. As shown in Table 6, ortho-cresol is 4 to 15 times

more reactive than phenol under typical gasification temperatures. Considering that ortho-cresol is no more than twice as reactive as meta-cresol (i.e., at ~ 700° C),¹⁰ phenol is the least reactive of the phenols. Most notable is the approximate three order of magnitude rate enhancement for decomposition of phenol over fixed beds of lignite char.

Effect of Reaction Atmosphere on the Decomposition Pathway of Phenols—

Two distinct characteristics of phenolic compound reaction products were demonstrated throughout the course of bench-scale experimentation:

- No dehydroxylation products (i.e., benzene or toluene) were ever detected in more than trace quantities during either phenol or ortho-cresol decomposition experiments, and
- Substantial quantities of heavy hydrocarbon tars were formed only in the absence of hydrogen during these experiments.

The first result was not surprising considering the excessive amounts of water present in the reacting system (i.e., fully 1000:1 on a molar basis) relative to the phenols. Excessive quantities of water essentially act to stabilize the phenolic hydroxyl to dehydroxylation reactions.^{21, 22} The presence of hydrogen in the reacting atmosphere acts to prevent repolymerization of free radicals formed during the decomposition reactions. In this particular instance, amounts of hydrogen relative to phenols were fully 300:1 on a molar basis.

Results of this experimental program, combined with previously demonstrated decomposition characteristics of higher phenols (i.e., cresols and xylenols), define a precise reaction pathway for decomposition of phenols in coal gasification:

- Methyl-phenols formed from coal undergo successive dealkylation to the next lowest phenolic compound until phenol is produced. Phenol decomposes via pathways similar to those for unsubstituted aromatic hydrocarbons.²⁰
- Minimal amounts of heavy hydrocarbon tars are formed.

The unique atmosphere present in coal gasification processes is primarily responsible for determining phenolic compound decomposition characteristics. Quantities of hydrogen and steam present in reaction gases are fully hun-

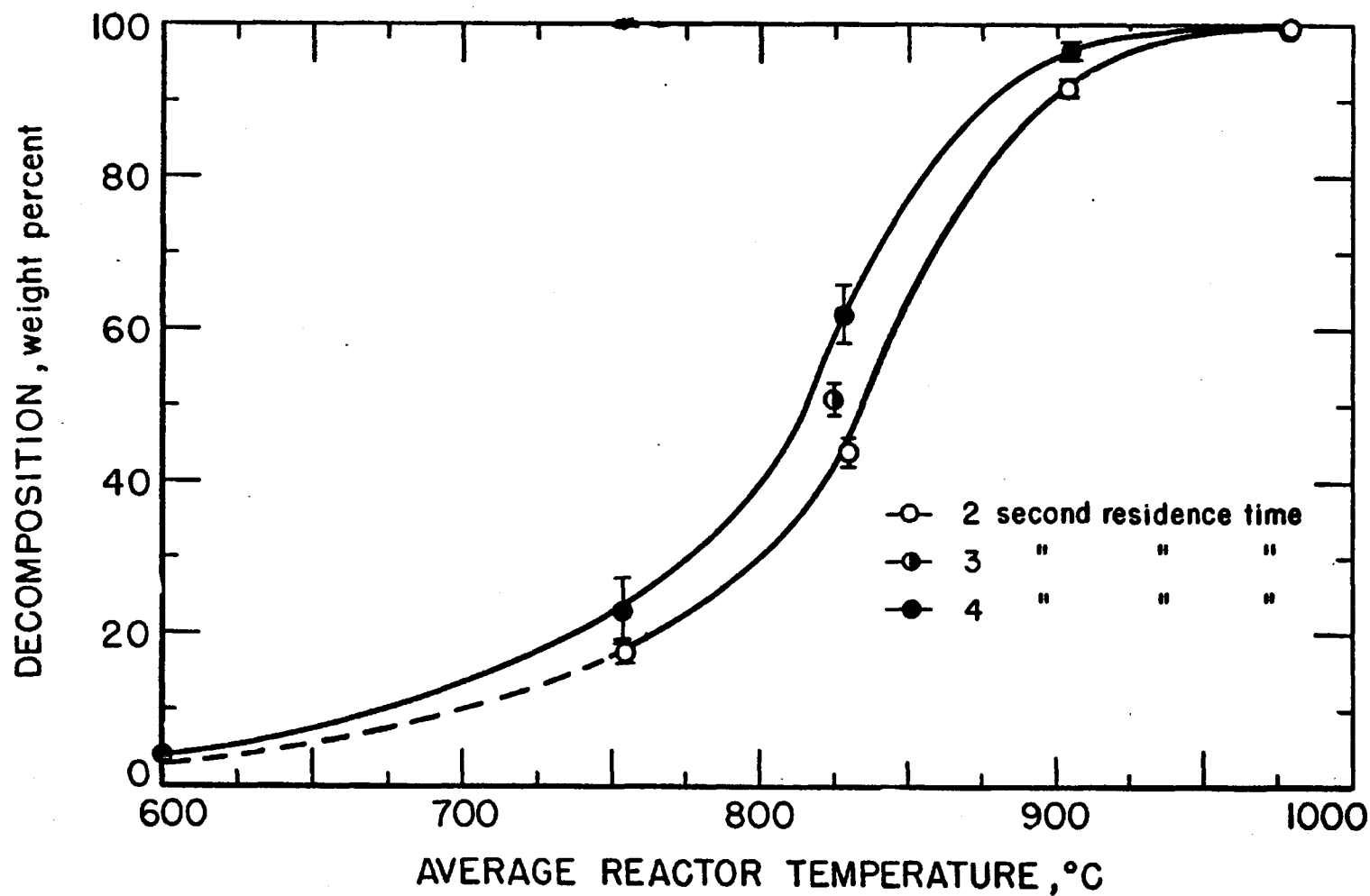


Figure 6. Measured phenol decomposition as a function of average temperature for 2, 3, and 4 s nominal residence times.

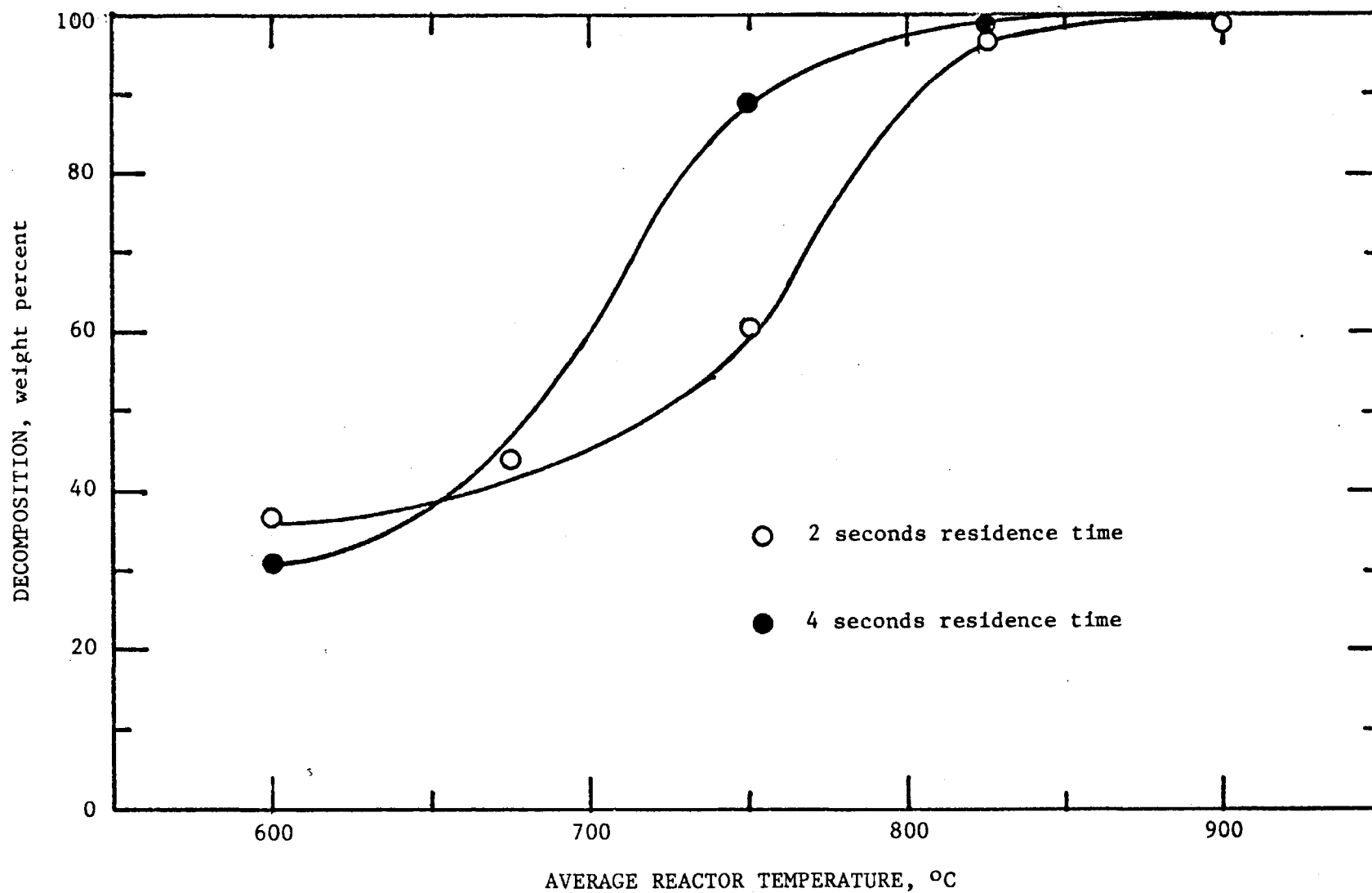


Figure 7. Measured ortho-cresol decomposition as a function of average reactor temperature for 2 and 4 s nominal residence time.

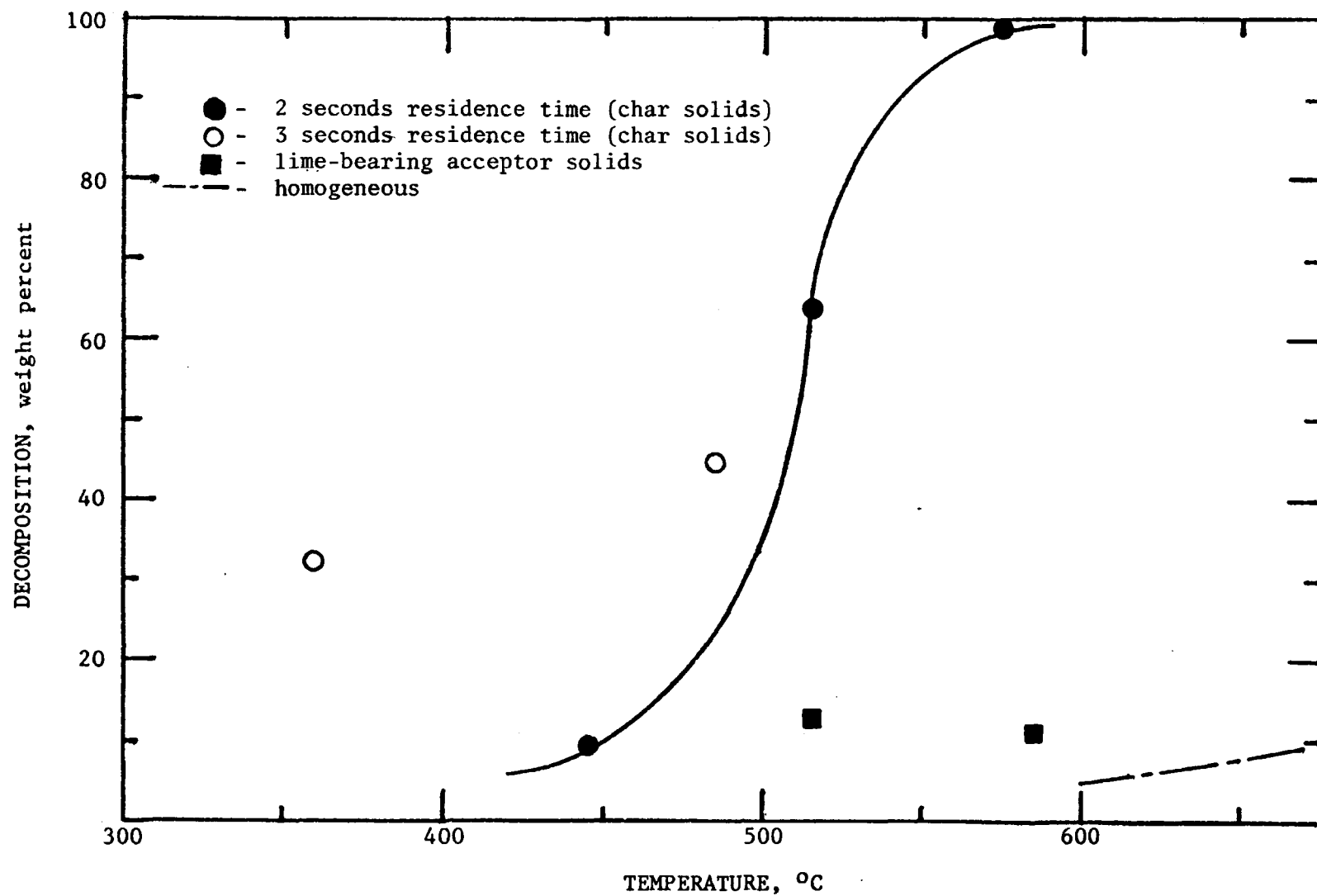


Figure 8. Measured phenol decomposition in the presence of lignite char and limestone acceptor solids as a function of temperature.

TABLE 5. SUMMARY OF PHENOL AND ORTHO-CRESOL FIRST-ORDER DECOMPOSITION KINETIC PARAMETERS

Reaction	Frequency Factor, $\ln A$	Activation Energy, kcal/gmole	Coefficient of Determination, r^2
Homogeneous Phenol (25) ^(a)	16.5	39.1	0.96
Homogeneous Ortho-Cresol (9)	11.0	23.2	0.97
Heterogeneous Phenol (4)	19.8	31.9	0.997

(a) Number of data points.

TABLE 6. COMPARATIVE RATE CONSTANTS FOR PHENOL AND ORTHO-CRESOL DECOMPOSITION

Temperature, °C	Phenol	Homogeneous
	$k_{\text{hetero}}/k_{\text{homo}}$	$k_{\text{o-cresol}}/k_{\text{phenol}}$
600	1840	40
700	1200	15
800	840	7
900	630	4

dreds of times higher (as high as 1,000:1 for steam) on a molar basis.

Pathway to the Production of Phenols During Coal Gasification

Production of phenols during coal gasification is a complex function of gasifier configuration, reaction conditions, and probably the chemistry of the coal processed. The pattern underlying production of these effluents includes initial formation followed by subsequent decomposition within the gasification environment. The primary pathway explaining production of phenols during coal gasification is illustrated in Figure 9 and consists of:

- **Formation:** Phenols are formed inherently

from coal, primarily as single aromatic ring species. The formation of phenols is not expected to alter significantly as a result of different processing concepts. Similarly, coal type (at least among those currently utilized) should not affect formation characteristics to a major extent.

- **Decomposition:** Thermal and/or catalytic cracking phenomena controls production characteristics of phenols. Sequential decomposition of phenols occurs by dealkylation through lower homologues to phenol, which decomposes to primarily gaseous species. The rate of decomposition of phenols is significantly enhanced by the presence of char solids. The rate-limiting step in the reaction sequence is the final decomposition of the compound phenol.

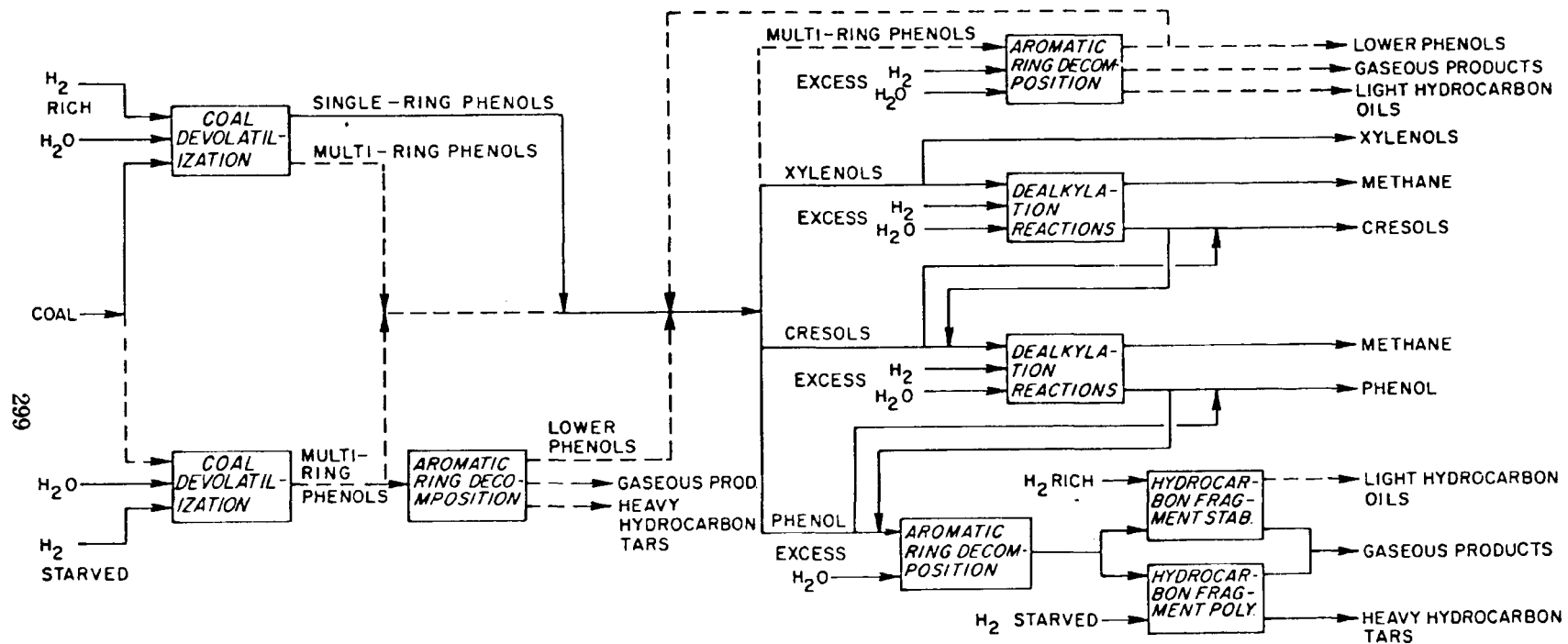


Figure 9. Pattern of phenolic compound production in coal gasification processing.

IMPLICATIONS AND FUTURE WORK

Necessary and quantitative data were generated during the course of this experimental investigation, which effectively defines the decomposition characteristics of phenols under typical gasification conditions. The studies, combined with previous work in the literature, provide a stepping stone for launching a variety of additional experimental investigations. However, the following issues must be resolved:

- The effects of variations in process gas steam content must be addressed. The demonstrated role of steam in delineating a specific decomposition pathway for phenols should be evaluated at lower steam-to-phenol molar ratios.
- The relative effects of amount and type of solid surface in enhancing phenol decomposition rates need to be addressed. The source of catalytic activity on the char surface in addition to definition of precise modes of gas-solid mixing during gasification need to be defined.

Implications of strategy and quantitative experimentation performed in this work have significant impact upon the assessment and design of coal conversion technology. From these studies, it is evident that experimental determination of effluent production characteristics at a single experimental scale is inadequate. A particular scale of development provides either too little information (i.e., an incomplete characterization) or behavior that is too highly coupled to measure without resorting to complex sampling techniques. Judicious choice of experiments across a range of process scales can provide the information necessary to synthesize quantitative effluent production patterns amenable to process scaleup.

Quantitatively, the demonstrated sensitivity of hydrocarbon effluent production (including phenols) to changes in processing conditions provides an alternative to the conventional strategy of post-gasification effluent treatment. Relationships previously developed, along with those developed in the course of these studies, can be used to control production of undesirable hydrocarbon effluents. This strategy can be implemented during process development, on scaleup to commercial facilities, or for development of generically similar novel processing technologies.

ACKNOWLEDGMENTS

Results presented herein reflect cooperative efforts between Carnegie-Mellon University and a range of personnel. The authors wish to thank the Pittsburgh Energy Technology Center for their support and assistance during bench-scale phenolic compound decomposition experiments and the Synthane PDU gasifier trials. The authors also wish to thank Conoco Coal Development Company and Stearns-Roger, Inc., for assistance in performing the CO₂-Acceptor gasifier probe studies.

REFERENCES

1. Nakles, D. V. *Significance of Process Variables on Liquid Effluent Production in Coal Gasification* (Ph.D. thesis). Carnegie-Mellon University. Pittsburgh, Pa. 1978.
2. Jonardi, R. J., L. J. Anastasia, M. J. Massey, and R. H. Karst. *Hygas Environmental Characterization: Data Synthesis, Analysis and Interpretation—Tests 37-64* (interim report FE-2433-25 from the Institute of Gas Technology). U.S. Department of Energy. February 1979.
3. *Quarterly Technical Progress Report, Grand Forks Energy Research Center*. U.S. Energy Research and Development Administration. GFERC/QTR-76/5. November 1976. p. 16-32.
4. Ellman, R. C., B. C. Johnson, H. H. Shobert, L. E. Paulson, and M. M. Fegley. *Current Status of Studies in Slagging Fixed-Bed Gasification at the Grand Forks Energy Research Center*. (Presented at the Ninth Biennial Lignite Symposium. Grand Forks. May 1977.
5. Fillo, J. P., and M. J. Massey. *Analysis of RA-21 Effluent Data: GFERC Slagging Fixed Bed Gasifier* (interim report FE-2496-24 from Carnegie-Mellon University). U.S. Department of Energy. April 1978.
6. Johnson, B. C., M. M. Fegley, R. C. Ellman, and L. E. Paulson. *Gasification of North Dakota Lignite in a Slagging Fixed-Bed Gasifier*. Grand Forks Energy Technology Center, U.S. Department of Energy. 1978.
7. Paulson, L. E., H. H. Shobert, and R. C. Ellman. *Sampling, Analysis, and Characterization of Effluents from the Grand Forks Energy Research Center's Slagging Fixed-*

- Bed Gasifier. *Am Chem Soc Div Fuel Chem Preprints*. 23(2):107. 1978.
8. Nakles, D. V., M. J. Massey, A. J. Forney, and W. P. Haynes. *Influence of Synthane Gasifier Conditions on Effluent and Product Gas Production*. Pittsburgh Energy Research Center, U.S. Department of Energy. Pittsburgh, Pa. PERC/RI-75/6. December 1975.
 9. Wells, G. L., and R. Long. Thermal Dealkylation-Hydrocracking of Alkyl Phenols. *Ind Eng Chem Process Des Develop* 1(1):73. 1962.
 10. Davies, G. A., and R. Long. The Kinetics of the Thermal Hydrocracking of Cresols. *J Appl Chem*. 15:117. 1965.
 11. Schmidt, C. E., A. G. Sharkey, and R. A. Friedel. *Mass Spectrometric Analysis of Product Water from Coal Gasification*. Pittsburgh Energy Research Center, U.S. Department of Energy. Bureau of Mines Report TPR No. 86. 1974.
 12. Ho, C. H., B. R. Clark, and M. R. Guerin. Direct Analysis of Organic Compounds in Aqueous Byproducts from Fossil Fuel Conversion Processes: Oil Shale Retorting, Synthane Coal Gasification and COED Coal Liquefaction. *J Environ Sci Health*. A11(7):481. 1976.
 13. White, C. M., and C. E. Schmidt. Analysis of Volatile Polar Organics in Untreated By-product Waters from Coal Conversion Processes. *Am Chem Soc Div of Fuel Chem Preprints*. 23(2):134. 1978.
 14. Jones, B. W., and M. B. Neuworth. Thermal Cracking of Alkyl Phenols— Mechanism of Dealkylation. *Ind Eng Chem*. 44(11):2872. 1952.
 15. Damon, D. A. *Aspects of Fine Particle Fluidization* (M.S. thesis). Carnegie-Mellon University. Pittsburgh, Pa. 1972.
 16. Fillo, J. P. *An Understanding of Phenolic Compound Production During Coal Gasification Processing* (Ph.D. thesis). Carnegie-Mellon University. Pittsburgh, Pa. 1979.
 17. Fillo, J. P., M. J. Massey, J. P. Strakey, D. V. Nakles, and W. P. Haynes. *Decomposition Characteristics of Phenol Under Synthane Gasifier Conditions*. Pittsburgh Energy Research Center, U.S. Department of Energy. Pittsburgh, Pa. PERC/RI-77/6. April 1977.
 18. Fillo, J. P., and M. J. Massey. *Studies of Phenolic Compound Decomposition Under Synthane Gasifier Conditions* (quarterly technical progress report, April-June, 1978 from Carnegie-Mellon University). Pittsburgh Energy Research Center, U.S. Department of Energy. July 1978.
 19. Fillo, J. P., and M. J. Massey. *Studies of Phenolic Compound Decomposition Under Synthane Gasifier Conditions* (quarterly technical progress report, July-September, 1978 from Carnegie-Mellon University). Pittsburgh Energy Technology Center, U.S. Department of Energy. November 1978.
 20. Virk, P. S., L. E. Chambers, and H. N. Woebke. Thermal Hydrogasification of Aromatic Compounds. In: *Coal Gasification*, Massey, L. G. (ed.). Washington, D.C. American Chemical Society, 1974.
 21. Given, P. H. Reactions of Alkyl Phenols Over Cracking Catalysts—I. Comparison of Catalysts and Study of Reaction Conditions. *J Appl Chem*. 7:172. 1957.
 22. Saha, N. C., N. G. Basak, and A. Lahiri. Hydrogenolysis of Higher Phenols to Lower Homologues Part I— Factors Affecting Hydrogenolysis. *J Sci Ind Res*. 19B:67. 1960.

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PREDICTIONS ON THE DISPOSITION OF SELECT TRACE CONSTITUENTS IN COAL GASIFICATION PROCESSES

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Abstract

Many factors may affect the formation and disposition of minor and trace constituents in coal gasification processes; e.g., the coal feed-stock, the gasification conditions, and the gas-processing conditions. Adequate knowledge of the forms and amounts of these constituents and the controlling factors that dictate their final disposition would be desirable for the complete design of a full-scale plant. However, the current data base is weak for some of the more volatile inorganic trace constituents that may be gasified with the coal.

In this paper, theoretical projections are made on the amount and final disposition during coal gasification of volatile trace constituents formed from arsenic, boron, lead, selenium, and mercury present in coals. Note that these predictions are theoretical; they are intended to provide insight into what might occur in coal gasification processes, to provide direction for future experimental work for improving the data base on these constituents, and to indicate areas where further investigations would prove useful for the design of full-scale processes.

The results of these studies indicate that high recoveries of these trace inorganics are to be expected, with low discharge to the environment, in most coal gasification process designs.

INTRODUCTION

Certain minor and trace inorganic constituents found in coal undergo chemical transformations during gasification. Some of these reactions produce compounds that are volatile under gasification conditions and leave the gasifier as part of the raw gasifier product gas.

Present environmental assessment studies are concerned with the disposition of potentially toxic substances. However, because of the enormous number of possible substances that may

be present, emphasis has been on elemental material balances around the primary gasifier and quench system. For some elements, closing the material balance is difficult because a significant fraction of the material may be part of the quenched product gas. In most cases, the quantity of these elements in the quenched product gas is estimated by difference because these materials are difficult to analyze. Further, the analytical techniques often used for trace inorganics are not of high accuracy. Sampling is also difficult in certain cases because of absorption or reaction of these volatile materials in the sample containers. However, knowledge of the compounds present and their approximate concentrations would simplify some of these analytical problems. Then, through further experimental investigations, knowledge of the disposition of these volatile constituents, which are important both from an environmental viewpoint and a processing viewpoint, can be increased.

As an indication of what might occur to certain elements in coal during gasification, a theoretical analysis has been performed on the formation and disposition of compounds containing arsenic, selenium, boron, lead, and mercury. These elements were chosen for this study because earlier work had indicated that they were the most likely elements to be removed from the coal during gasification.¹ Much of the theoretical analysis is based on engineering estimates and should not be taken as hard data. Rather, this analysis should provide a starting point for more definitive future investigations.

BEHAVIOR OF THE SELECT TRACE ELEMENTS UNDER GASIFICATION CONDITIONS

Processes Analyzed

The major differences between available coal gasification processes are the operating condi-

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tions and the amount and distribution of hydrocarbons produced. Gasification processes operate under reducing conditions, and the major constituents produced, other than hydrocarbons, are H_2 , CO , CO_2 , H_2O , H_2S , and NH_3 . In this study the transformations that the select elements may undergo were investigated as influenced by the operating conditions of three gasification processes. The three processes selected were the Koppers-Totzek process, the Lurgi process, and the Hygas® SNG process with steam-oxygen. Brief descriptions of these processes follow.

Koppers-Totzek Process—

In this process, pulverized coal is reacted at low pressure and high temperatures ($> 1,800$ K) with steam and oxygen in an entrained bed with cocurrent gas/solids contacting. A simplified diagram of the gasifier is shown in Figure 1. The high gasification temperature assures nearly complete gasification of the carbon in the feed coal. Approximately 50 percent of the ash in the coal flows down the gasifier walls as molten slag and drains into a slag quench tank. The remainder of the ash leaves the gasifier as fine particles entrained in the exit gas. These particles are solidified at the gasifier exit by water sprays and are subsequently separated from the scrubber water and disposed of with the solidified slag.

The high operating temperature and low operating pressure of this process produce a raw product gas from the gasifier primarily comprised of H_2 , CO , CO_2 , and steam with minimal amounts of hydrocarbons and tars. A typical product gas is shown in Table 1.

Lurgi Process—

The Lurgi process employs a gravitating bed of coal with continuous countercurrent gas flow, as shown in Figure 2. Coal is fed intermittently to the top of the reactor through pressurized lockhoppers, while oxygen and steam are mixed and fed into the bottom of the gravitating coal bed. Gas temperature ranges from 590 K at the top of the gasifier to 1,280 K at the bottom of the gasifier. Normal operating pressures are 20 to 32 atm, and coal residence time is approximately an hour. Typical raw product gas from the gasifier is shown in Table 1. The major difference in the product gas from that of the Koppers-Totzek process is that roughly 19 per-

cent of the feed carbon reacts to form methane and ethane rather than carbon oxides. Approximately 12 percent of the feed carbon results in tar, fatty acids, phenols, and BTX production.

Hygas Process—

The Hygas process uses three separate reaction stages for gasifying coal. A diagram of the gasifier is shown in Figure 3. Coal is fed to the gasifier as a slurry made with either aromatic oil or water. The oil or water is vaporized in a fluidized bed (the slurry dryer) in the top of the gasifier using heat available in the product gas from the top reaction stage. The dried coal is then gravity fed to the first stage, entrained, and reacted in a low-temperature reactor stage (LTR) with product gas from the lower sections of the reactor. The operating temperature for this section of the gasifier is usually between 920 and 1,060 K. The reacted coal from the first stage is then disengaged from the gases and gravity fed to the fluidized-bed second-stage hydrogasifier (the high-temperature reactor), where it is reacted with product gas from the lowest stage of the gasifier at temperatures between 1,030 and 1,170 K. Finally, the reacted coal from the second stage is gravity fed to the lowest stage of the gasifier, the SOG (steam-oxygen gasifier), where the remaining carbon in the coal is reacted with high-pressure steam and oxygen at temperatures between 1,170 and 1,280 K. The normal operating pressure of the Hygas process is 69 to 100 atm. A typical raw product gas from this gasification process is shown in Table 1. In this process, methane and ethane account for 27 percent of the feed carbon, while 8 percent or less of the feed carbon produces BTX and phenol with minimal production of tars and fatty acids.

Trace Element Chemistry During Gasification

With the background above, the analysis of the transformations that arsenic-, selenium-, boron-, lead-, and mercury-containing compounds might undergo during gasification follows.

Arsenic Chemistry—

Arsenic concentrations in U.S. coals range from 0.5 ppm to 93 ppm, with an average of 14 ppm. The major form of arsenic in coal was

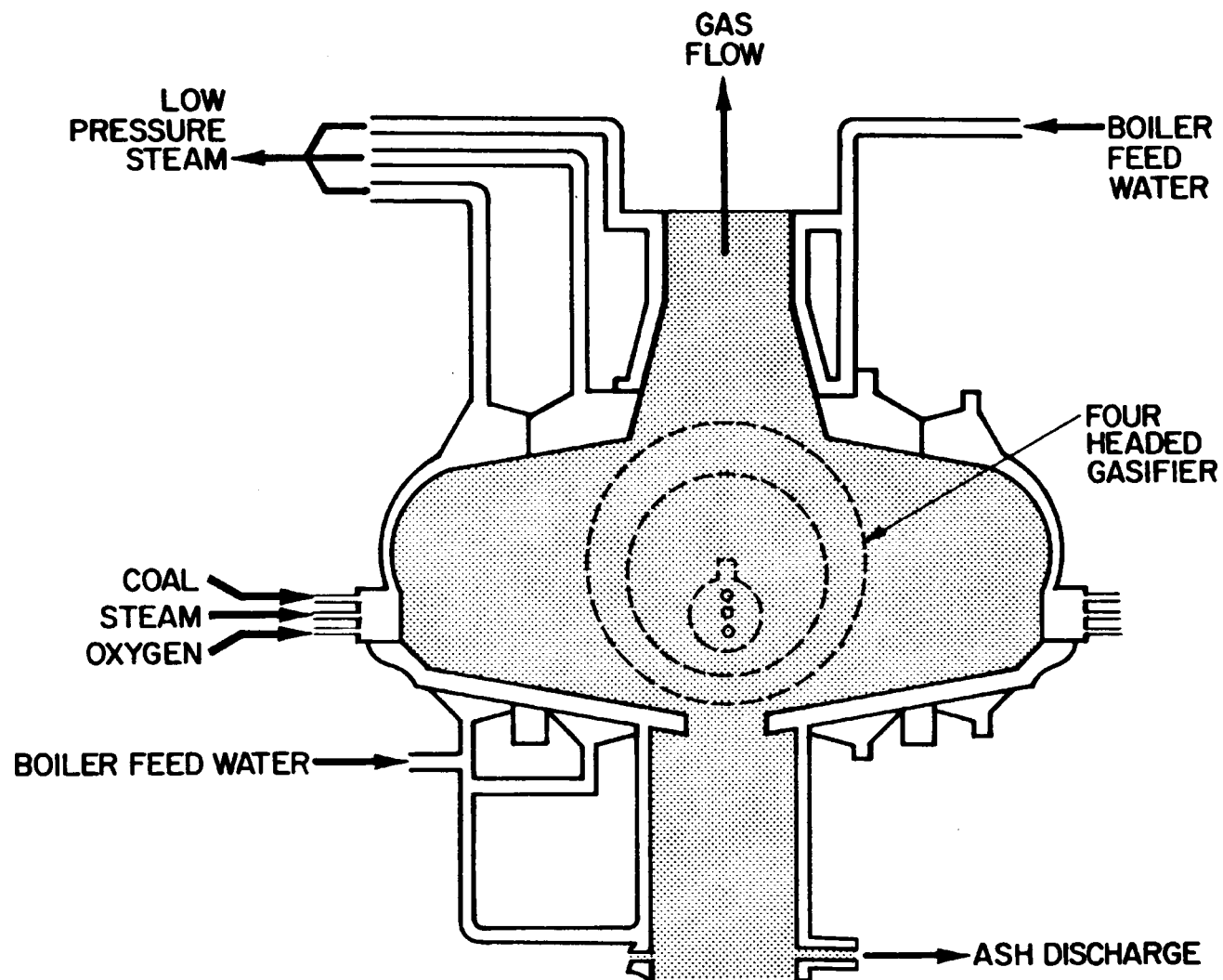


Figure 1. Koppers-Totzek gasifier.

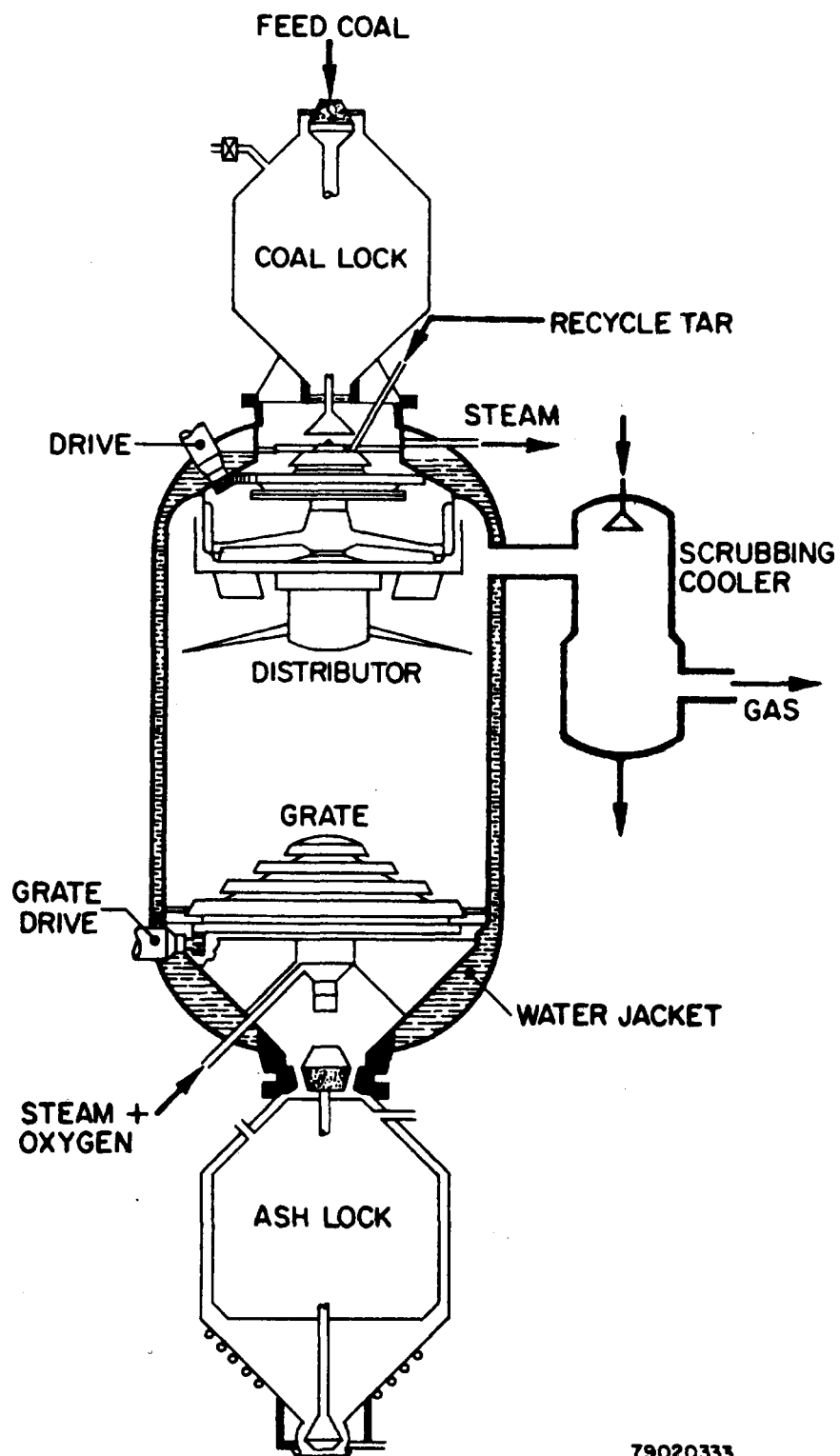
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TABLE 1. OPERATING CHARACTERISTICS OF THE KOPPERS-TOTZEK, LURGI, AND
HYGAS STEAM-OXYGEN GASIFIERS USING SUBBITUMINOUS COAL

	Koppers-Totzek ²	Lurgi ³	HYGAS ⁴
Pressure, atm	2-3	20-32	69-100
Temperature, K	1800-2000	590 (top) 1260 (bottom)	590 (top) 920-1060 (1st stage) 1030-1170 (2nd stage) 1170-1280 (SOG)
<u>Product Gas, mole fraction</u>			
H ₂ O	0.0801*	0.4659	0.4265†
H ₂	0.3039	0.2172	0.1500
CO	0.5428	0.0800	0.0843
CO ₂	0.0651	0.1638	0.1950
N ₂	0.0052	0.0005	0.0003
CH ₄	--	0.0591	0.1248
C ₂ -C ₅	--	0.0045	0.0064
BTX	--	0.0023	0.0068
H ₂ S	0.0026	0.0026	0.0023
COS	0.0002	0.0002	0.0001
NH ₃	0.00003	0.0032	0.0034
HCN	0.00002	0.000002	0.00006
HCl	0.0001	0.00002	0.00002
C ₆ H ₅ OH	--	0.0004	0.0005
Tar	--	0.1660 g/g-mol	--
Fatty Acids	--	0.0167 g/g-mol	--
g-mol/g-coal	0.0778	0.1165	0.0969

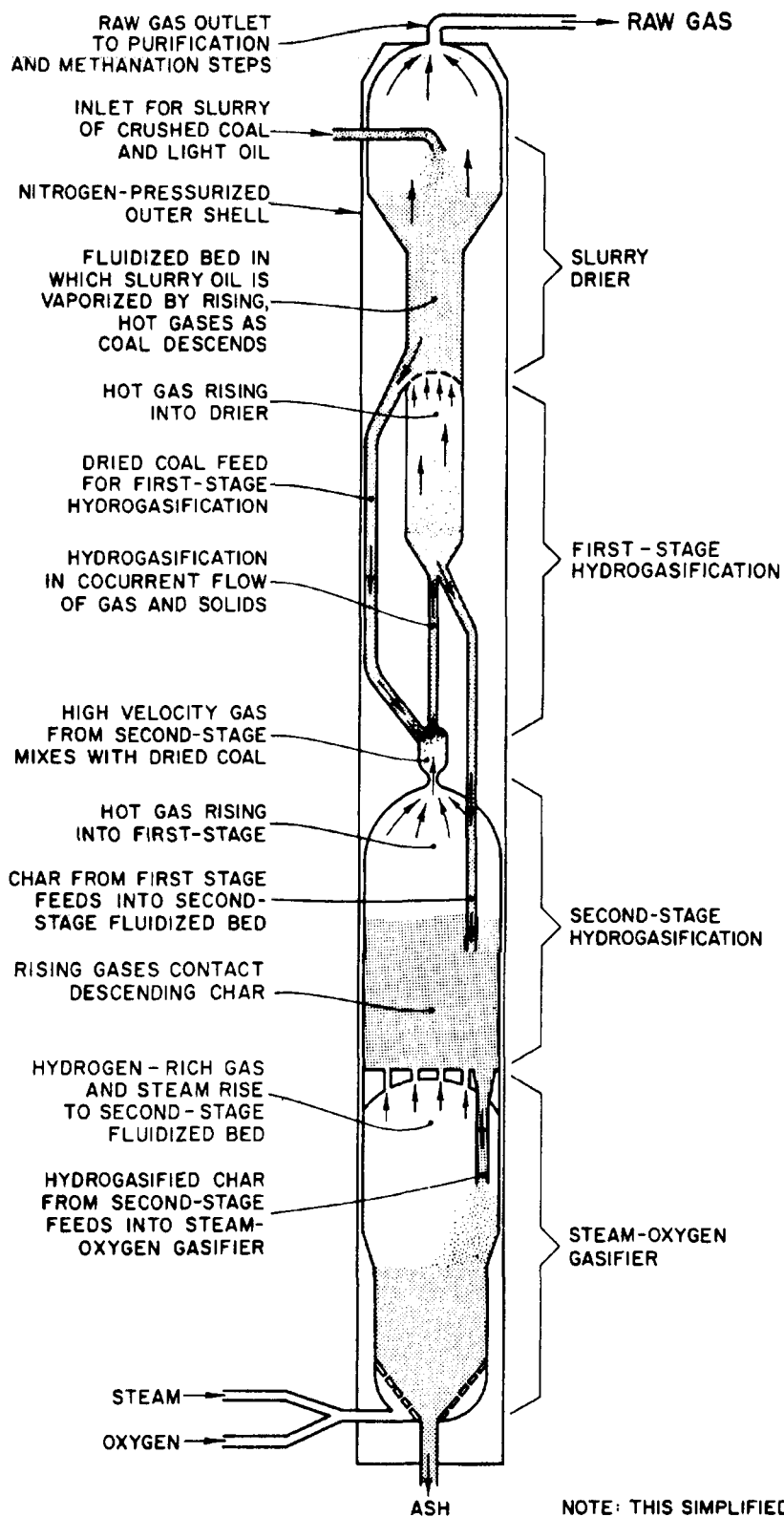
* Product gas does not include water added from water sprays.

† Product gas does not include oil or water used for slurring coal.



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Figure 2. Lurgi pressure gasifier.



NOTE: THIS SIMPLIFIED SKETCH
IS NOT DRAWN TO SCALE

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Figure 3. Hygas gasifier with steam/O₂ gasification.

TABLE 2. FREE ENERGIES OF FORMATION OF ARSENIC-CONTAINING COMPOUNDS, kcal/mole

Basis: Elements in Their Standard State at Temperature of Interest				
Compound	Temperature			
	600 K	800 K	1000 K	1200 K
As ₂ (g)	+ 28.93	+ 21.48	+ 14.23	+ 7.18
As ₄ (g)	+ 10.0	+ 3.0	- 4.1	- 11.2
FeAsS *	- 30.6	- 27.46	- 24.20	- 20.94
FeAs ₂ *(loellingate)	- 14.61	- 16.03	- 17.45	- 18.87
FeAs *	- 9.24	- 10.92	- 12.60	- 14.28
Fe ₂ As *	- 9.90	- 11.50	- 14.10	- 16.70
As ₂ S ₃ *(high orpiment)	- 33.26	- 21.38	- 9.50	- 2.38
As ₂ S ₃ *(low orpiment)	- 33.24	- 21.32	- 9.40	- 2.52
As ₂ S ₂ *(low realgar)	- 23.50	- 15.30	- 7.10	- 1.10
AsH ₃ (g)	+ 17.88	+ 19.52	+ 21.50	+ 23.50
As ₂ O ₃ (g)	- 116.8	- 111.5	- 106.0	- 100.6
As ₂ O ₃ (s)	- 119.0	- 106.8	- 94.8	- 82.3
As ₂ O ₃ (l)	- 119.5	- 110.2	- 101.1	- 92.0
FeS	- 28.7	- 26.2	- 23.75	- 21.8

* Barton⁹

deduced by Duck and Himus as arsenopyrite.⁵ Under gasification conditions when temperatures exceed 820 K, arsenopyrite begins to decompose into pyrrhotite (FeS) and metallic arsenic.



At temperatures greater than 1,025 K, the decomposition proceeds rapidly. This decomposition has been observed in laboratory studies by many investigators including Zhuchkov,⁶ Zviadze et al.,⁷ and Lukesh.⁸ This observation is not totally consistent with thermodynamic data on the iron-arsenic-sulfur system measured by Barton⁹ but is within the experimental error

associated with these measurements. Barton's data, along with other available thermodynamic data, are given in Table 2.

Once arsenopyrite decomposes into pyrrhotite and metallic arsenic, the metallic arsenic can theoretically vaporize as As₄ from the coal. However, this does not—apparently—occur. The trace element data from the Hygas process indicate that arsenic loss from the coal does not occur until the coal reaches the SOG stage of the reactor where the temperature ranges from 1,170 to 1,280 K.¹⁰ Therefore, either the arsenopyrite is embedded in the coal-ash matrix and volatilization is diffusion controlled, or the arsenopyrite is so highly dispersed that formation of As₄ is limited and volatilization occurs by means of As₂ or As, which have lower vapor

pressures.

Assuming elemental arsenic volatilization does not occur until temperatures in excess of 1,170 K are reached, the volatilized elemental arsenic must travel through the gasifier. At these conditions, the stable forms for arsenic are As_4 , AsH_3 (arsine), and As_2 . The question that arises is: How fast will elemental arsenic react with available hydrogen to form AsH_3 ? The normal preparation of AsH_3 is by reaction of AlAs or Na_3As with water¹¹ or from a mixture of NaBH_4 and AsCl_3 in water at pH 8 to pH 10 and 5° to 40° C.¹² No data are reported on the production of AsH_3 from arsenic and H_2 because this route would provide extremely small yields of AsH_3 at temperatures where the kinetics would be favorable.

To estimate the rate at which arsine is produced from elemental arsenic and hydrogen, the gas phase arsine decomposition kinetics studied by Kedyarkin and Zorin¹³ were combined with the free energy of formation of arsine from As_4 and H_2 using the law of microscopic reversibility to derive an expression for the forward reaction of:

$$\frac{d[\text{AsH}_3]}{dt} = 5.22 \times 10^7 \exp(-54,610/RT) [\text{As}_4]^{1/4} [\text{H}_2]^{3/2} \quad (2)$$

Concentrations are in atmospheres and time is in seconds. Based on this equation, equilibrium control occurs when temperatures are greater than 900 K.

Because of the rapid cooldown of the product gases in the lower temperature zones of the Hygas and Lurgi reactors, the arsine-arsenic-hydrogen reaction is assumed to be frozen at an equilibrium temperature of 900 K. In the Koppers-Totzek process, the reaction is assumed to be frozen at 1,800 K because of rapid cooldown of the gases with the water sprays. However, if quench of the Koppers-Totzek gases is not instantaneous, small amounts of arsine may be formed.*

The predicted distribution of elemental arsenic and arsine in the raw product gases from these three processes is shown in Table 3 for three different arsenic levels. Based upon data

*This effect would be more pronounced in Texaco or Shell gasifiers, which operate in a mode similar to a Koppers-Totzek gasifier but at higher pressure.

from the Hygas pilot plant, 50 percent of the arsenic in the feed coal is assumed to be volatilized in the Hygas and Lurgi processes, whereas 100 percent is expected to be volatilized in the Koppers-Totzek process because of the high-temperature, single-stage operating mode. It is evident that operation at moderate temperatures, high pressures, and high arsenic concentrations increases the amount of arsine. Operation at high temperatures and low pressures favors the formation of elemental arsenic with negligible amounts of arsine formation.

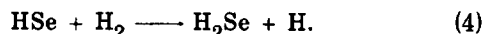
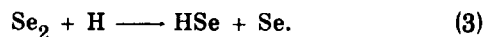
Verification of these predictions is not yet possible; the search for the presence of arsine in operating coal gasification plants is not known to have been performed. As discussed later, experimental investigation of the amount of arsine formation should be of considerable importance.

Selenium Chemistry —

Similar to arsenic, selenium may be initially present in coals as selenopyrite, FeSeS . Selenium concentrations in U.S. coals range from a minimum of 0.45 ppm to a maximum of 7.7 ppm, with an average of about 2.25 ppm. In moderate temperature gasification processes such as Hygas and Lurgi, between 30 percent and 70 percent of the selenium is volatilized from the coal. Based on evidence from the Hygas pilot plant, most of this gasification occurs in the hottest section of the gasifier.¹⁰ In the high-temperature Koppers-Totzek process, no information on percent selenium loss is available, but quantitative volatilization is expected.

The mechanism for volatilization of selenium from the coal is postulated as either decomposition of FeSeS to FeS and Se(g) or reaction of H_2 with FeSeS to produce H_2Se and FeS . This approach, lacking kinetic data, assumes initial FeSeS decomposes, liberating $\text{Se}_2(\text{g})$. Then the Se_2 can react with H_2 to form H_2Se , which is the thermodynamically preferred form.

Estimation of the kinetics of forming H_2Se from Se_2 and H_2 was based on the following mechanism:



Reaction 4 is the reverse mechanism for the initial step of H_2Se decomposition, which has been determined to decompose according to the following rate expression:¹⁴

TABLE 3. PREDICTED ARSENIC DISTRIBUTION IN GASIFIER RAW PRODUCT GAS

Process	<u>HYGAS</u>	<u>Lurgi</u>	<u>Koppers-Totzek</u>
Equilibrium Temp., K	900	900	1800
H ₂ Partial Pressure, atm	12.05	4.43	0.62
Wet Raw Gas Production, g-mol/g-coal	0.0969	0.1165	0.0778
Estimated Arsenic Volatilization, %	50	50	100
At Maximum Arsenic Concentration in Feed Coal (93 ppm)			
	mol fraction		
AsH ₃	4.79 X 10 ⁻⁷	2.86 X 10 ⁻⁷	1.64 X 10 ⁻¹⁴
As ₄	1.48 X 10 ⁻⁶	1.26 X 10 ⁻⁶	4.20 X 10 ⁻¹⁰
As ₂	4.96 X 10 ⁻⁹	9.00 X 10 ⁻⁹	7.98 X 10 ⁻⁶
At Average Arsenic Concentration in Feed Coal (14 ppm)			
AsH ₃	2.79 X 10 ⁻⁷	1.71 X 10 ⁻⁷	2.47 X 10 ⁻¹⁵
As ₄	1.71 X 10 ⁻⁷	1.56 X 10 ⁻⁷	9.56 X 10 ⁻¹²
As ₂	1.77 X 10 ⁻⁹	3.20 X 10 ⁻⁹	1.20 X 10 ⁻⁶
At Minimum Arsenic Concentration in Feed Coal (0.5 ppm)			
AsH ₃	3.40 X 10 ⁻⁸	2.78 X 10 ⁻⁸	1.76 X 10 ⁻¹⁶
As ₄	3.54 X 10 ⁻¹¹	1.13 X 10 ⁻¹⁰	4.88 X 10 ⁻¹⁴
As ₂	2.48 X 10 ⁻¹¹	8.74 X 10 ⁻¹¹	4.29 X 10 ⁻⁸

$$\frac{-d[H_2Se]}{dt} = 8.8 \times 10^{13} \exp(-1500/RT)[H_2Se][H]. \quad (5)$$

Concentrations are in moles per liter and the units of time are seconds.

Assuming microscopic reversibility, the forward rate of Reaction 4 is given by:

$$\frac{-d[HSe]}{dt} = 2.4 \times 10^{14} \exp(-26,792/RT)[HSe][H_2]. \quad (6)$$

The forward reaction given by Equation 3 can be estimated using available correlations for abstraction reactions.¹⁵ The rate of reaction of Se₂ with H is given approximately by:

$$\frac{-d[Se_2]}{dt} = 10^{13} \exp(-8118/RT)[Se_2][H]. \quad (7)$$

Assuming the concentration of atomic hydrogen at these conditions is always in equilibrium with the amount of H₂ present, Equation 7 can be written as:

$$\frac{-d[Se_2]}{dt} = 1.11 \times 10^{16} \exp(-61,612/RT)[Se_2][H_2]^{1/2}. \quad (8)$$

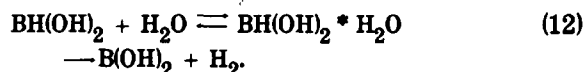
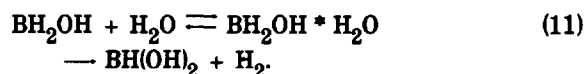
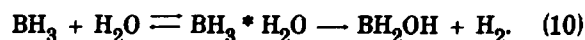
At temperature less than 2,000 K, Reaction 4 is much faster than Reaction 3, indicating that Reaction 3 is rate controlling. If the expression is correct, equilibrium control occurs at temperatures greater than 900 K. Assuming 900 K equilibrium control in the Hygas and Lurgi processes and 1,800 K in the Koppers-Totzek process, the selenium present in the raw product gas is almost exclusively H₂Se.

Boron Chemistry—

Boron is present in coal at concentrations between 2 and 224 ppm, with an average of 67 ppm. Evidence suggests that most of the boron is chelated.¹⁶ Environmental assessment data from the Hygas and Lurgi processes indicate that about 50 percent of this boron is volatilized during gasification. In the Koppers-Totzek process, quantitative volatilization is anticipated.

Chelated boron, when treated with hydrogen at high temperatures, produces BH₃. However, B(OH)₃ is the thermodynamically preferred form in coal gasification environments based on data in Table 4.

Hydrolysis of the borane produced should occur. The hydrolysis of diborane B₂H₆ to boric acid and hydrogen has been used for quantitative analysis of diborane in gas mixtures. The mechanism suggested for this reaction is given by:¹⁸



The rate-controlling step is believed to be the initial attack of H₂O on BH₃. The kinetics of this reaction have been deduced to be:

$$\frac{d[BH_2OH]}{dt} = 1.9 \times 10^5 \exp(-6000/RT)[BH_3][H_2O], \quad (13)$$

where concentrations are given in moles per

TABLE 4. FREE ENERGIES OF FORMATION¹⁷ OF BORON-CONTAINING COMPOUNDS; COMPOUNDS, kcal/mole

Compound	Temperature			
	600 K	900 K	1200 K	1800 K
BH ₃ (g)	28.06	30.33	32.95	38.64
B ₂ H ₆ (g)	35.50	50.13	65.02	94.67
BH ₃ CO(g)	-16.01	-8.206	0.8710	21.87
B(OH) ₃ (g)	-205.6	-118.7	-171.5	-136.8
B(g)	111.5	100.7	90.0	68.88

liter and time is expressed in seconds. Therefore, rapid attainment of equilibrium is assured at all temperatures in a gasification process with quantitative production of $B(OH)_3$.

Lead Chemistry—

Lead in coal is generally believed to exist initially as PbS , with an average lead concentration of 39.2 ppm. Environmental assessment data on lead losses from coal during gasification indicate conflicting results. Minimal loss of lead is reported in Lurgi operations and Hygas pilot-plant operations. However, in Hygas PDU studies, between 30 percent and 60 percent of the lead contained in the coal was volatilized. This disparity is because of the single-stage high-temperature conditions used in the PDU studies. At these temperatures, the vapor pressures of many lead-containing compounds are appreciable, leading to loss from the feed coal. The free energies of formation for a number of lead species at 600 K, 1,200 K, and 1,800 K are shown in Table 5. At 1,200 K in a coal gasification environment, the vapor pressure of PbS is the largest of the lead-containing compounds at 8.83×10^{-1} atm. If this vapor pressure were achieved in the Hygas PDU studies, quantitative loss of the lead from the coal would occur. However, in an integrated Hygas process and in

the Lurgi process, the product gas from the hotter sections of the gasifier is eventually cooled down to temperatures of 600 K by the raw feed coal. At this temperature, the vapor pressures of lead-containing compounds are significantly reduced. The anticipated concentration of gaseous lead compounds in the raw product gas from the Lurgi and Hygas processes is shown in Table 6. This loss represents parts-per-trillion levels of equivalent lead in the feed coal.

The Koppers-Totzek process, which operates at 1,800 K, is expected to volatilize all the lead present in the feed coal but, again, these will be solidified during quench by the water sprays. The only difference postulated between the Koppers-Totzek and the Hygas and Lurgi processes is that the volatilized lead will be Pb and PbS rather than $PbCl_2$.

Mercury Chemistry

The average concentration of mercury in coal is 0.2 ppm. The range of concentrations is 0.02 ppm to 1.60 ppm. At the high temperatures employed in coal gasifiers, quantitative loss from the coal is expected. Thermodynamic calculations have been used to estimate the probable chemical form of mercury in a coal gasification environment, because the initial form and kinet-

TABLE 5. FREE ENERGIES OF FORMATION OF LEAD-CONTAINING COMPOUNDS,¹⁷
kcal/mole

	Temperature		
	600 K	1200 K	1800 K
PbS (g)	10.00	0.29	-9.423
PbS (s)	-22.23	-12.89	-3.556
$PbCO_3$ (s)	-126.07	-91.73	-57.40
$PbCl_2$ (s)	-64.86	-51.18	-37.50
$PbCl_2$ (g)	-48.24	-50.62	-52.96
PbO (g)	6.634	-0.82	-8.266
PbO (s)	-37.94	-24.06	-10.17
Pb (g)	31.10	17.93	4.768

TABLE 6. LEAD CONCENTRATIONS IN COAL GASIFICATION RAW PRODUCT GASES

	<u>Lurgi</u>	<u>HYGAS</u>
	g-mol/g-mol	product gas
PbS	8.13×10^{-14}	2.05×10^{-14}
PbCl ₂	1.11×10^{-11}	2.46×10^{-11}
PbO	2.81×10^{-25}	7.65×10^{-26}
Pb	6.94×10^{-16}	1.42×10^{-16}
Total	1.11×10^{-11}	2.46×10^{-11}

ics of transforming mercury from one form to another are not known. Mercury species included in the calculations were Hg(g), HgS(g), HgH(g), HgCl₂(g) and HgF₂(g). The thermodynamically preferred form in the presence of the gas is Hg(g).

Based on this assumption, the quantity of mercury in the raw gasifier product gas from the Hygas, Lurgi, and Koppers-Totzek processes is shown in Table 7. Mercury concentrations assumed in the feed coal were 0.02, 0.2, and 1.6 ppm.

EFFECT OF GAS PROCESSING ON TRACE ELEMENT DISPOSITION

The Purification System

Estimates of the quantities and chemical forms of the trace elements in the gasifier raw product gas permit projections on the final

disposition of these compounds in downstream processes. A typical gas-processing scheme for a coal gasification plant to produce substitute natural gas (SNG) is shown in Figure 4.

The first step is a cooling of the raw product gas to about 300 K using waste heat recovery, air cooling, and, finally, water cooling. Equilibrium between gas and liquids is usually assumed. In this system excess steam; condensible impurities such as oil and tar; and soluble impurities such as phenol, ammonia, hydrochloric acid, and thiocyanate are removed at pressure.

The product gases then enter a selective H₂S acid-gas removal section where 99 percent of the H₂S and part of the CO₂ are removed. Regeneration of the solvent in this system produces an acid-gas stream containing about 15 percent H₂S, with the balance primarily CO₂.

After H₂S removal, the remainder of the CO₂ is removed in a second acid-gas removal section. The product gas, now free of acid gas and oil, is

TABLE 7. MERCURY CONCENTRATIONS IN RAW GASIFIER PRODUCT GASES

Mercury in Feed Coal, ppm	Process		
	<u>HYGAS</u>	<u>Lurgi</u>	<u>Koppers-Totzek</u>
	g-mol/g-mol raw product gas		
0.02	1.03×10^{-9}	8.55×10^{-10}	1.28×10^{-9}
0.2	1.03×10^{-8}	8.55×10^{-9}	1.28×10^{-8}
1.6	8.23×10^{-8}	6.84×10^{-8}	1.03×10^{-7}

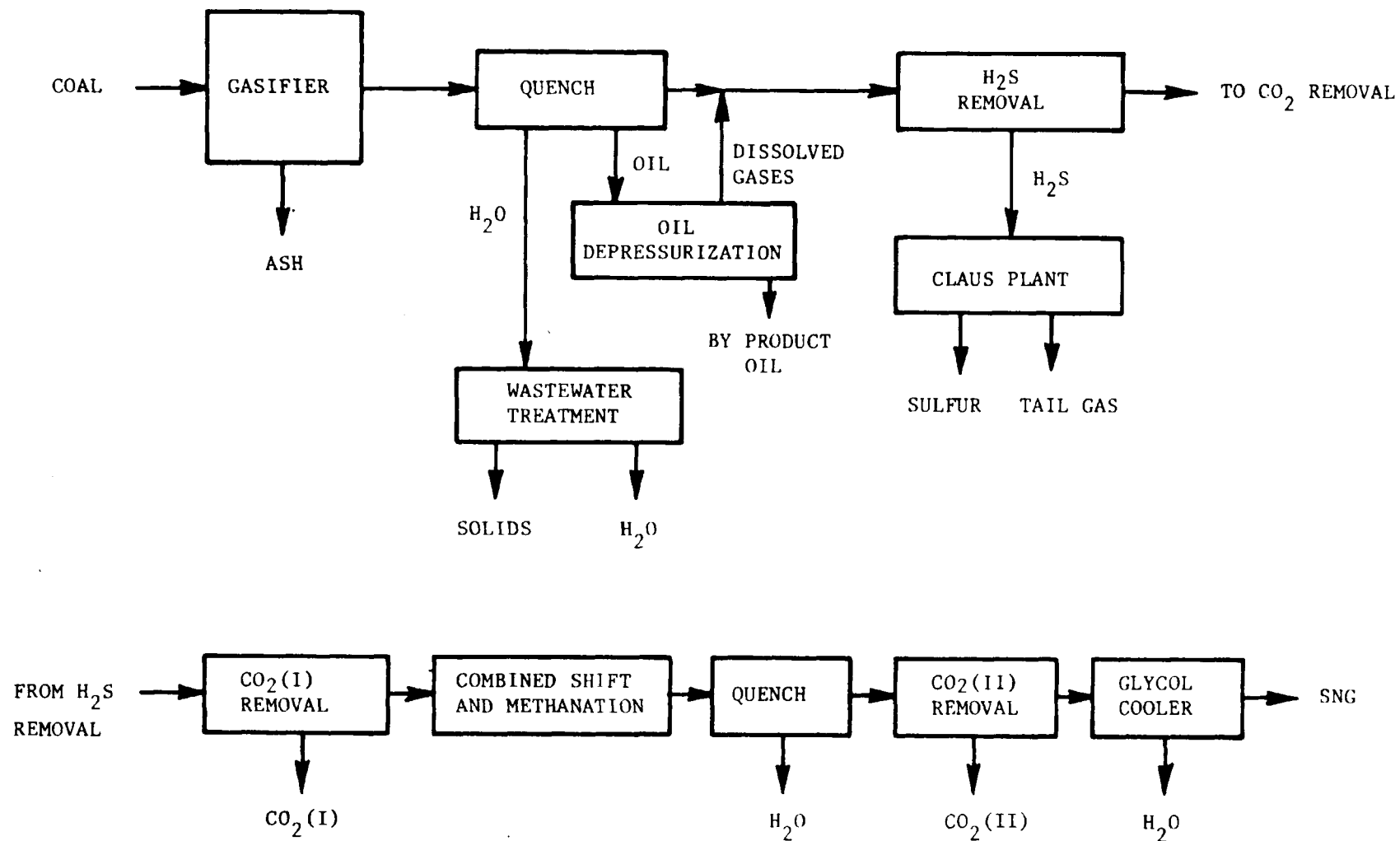


Figure 4. Typical gas producing configuration for producing SNG.

heated to temperatures greater than 500 K and enters a catalytic processing section where a combination of the water gas shift reaction and methanation reaction occurs producing a gas containing only CH₄, CO₂, and H₂O, with residual amounts of H₂ and CO. The water is removed by cooling and the CO₂ is removed in a final acid-gas removal section. Moisture in the product SNG is then removed by a glycol cooler, and the SNG is sent to the pipeline for distribution.

Effects in Quench

Assuming a coal feed with average concentrations of As, Pb, B, Se, and Hg, the chemical form and estimated quantities of these elements in the raw gasifier product gas for the Lurgi,

Hygas, and Koppers-Totzek processes are shown in Table 8. Quenching the gases from these processes should quantitatively remove the As₄, As₂, B(OH)₃, PbS, PbCl₂, PbO, and Pb because of vapor pressure or solubility considerations.

The elemental arsenic will exist as suspended solids, probably condensed on coal fines from the gasifier, in the excess condensate. The lead compounds will also be present as suspended solids because the presence of dissolved H₂S in the water will suppress the solubility of these compounds. These materials will, therefore, be removed from the process with the other suspended solids in the excess condensate, as it is purified for recycle.

The boric acid will dissolve in the excess condensate and report to the sour water treatment

TABLE 8. FORM AND DISTRIBUTION OF SELECT TRACE ELEMENTS
IN RAW GASIFIER PRODUCT GAS

Process	Lurgi	HYGAS	Koppers-Totzek
Operating Pressure, atm	20	80	2
	g-mol/g-mol raw product gas		
AsH ₃	1.71 X 10 ⁻⁷	2.79 X 10 ⁻⁷	2.47 X 10 ⁻¹⁵
As ₄	1.56 X 10 ⁻⁷	1.71 X 10 ⁻⁷	9.56 X 10 ⁻¹²
As ₂	3.20 X 10 ⁻⁹	1.77 X 10 ⁻⁹	1.20 X 10 ⁻⁶
H ₂ Se	1.36 X 10 ⁻⁷	1.13 X 10 ⁻⁷	3.68 X 10 ⁻⁷
B(OH) ₃	4.88 X 10 ⁻⁵	2.43 X 10 ⁻⁵	7.92 X 10 ⁻⁵
PbS	8.13 X 10 ⁻¹⁴	2.05 X 10 ⁻¹⁴	7.62 X 10 ⁻⁷
PbCl ₂	1.11 X 10 ⁻¹¹	2.46 X 10 ⁻¹¹	1.30 X 10 ⁻¹²
PbO	2.81 X 10 ⁻²⁵	7.65 X 10 ⁻²⁶	2.31 X 10 ⁻⁹
Pb	6.94 X 10 ⁻¹⁶	1.42 X 10 ⁻¹⁶	1.67 X 10 ⁻⁶
Hg	8.55 X 10 ⁻⁹	1.03 X 10 ⁻⁸	1.28 X 10 ⁻⁸

section of the plant. The boron content in the sour water stream is computed to be 34 ppm for the Hygas process, 63 ppm for the Lurgi process, and 590 ppm for the Koppers-Totzek process. These values compare favorably with experimental values obtained in a survey analysis of potential toxic/inhibitory elements to biological oxidation of a Hygas pilot-plant sour water.¹⁹ The boric acid will be removed from the water in the system that removes other soluble salts.

The amount of arsine in the quenched raw product gas is expected to be unaffected by the quench system. Arsine solubility in water is negligible. The solubility of AsH_3 in H_2O at 300 K and atmosphere partial pressure is 1.787×10^{-4} g-mol/g-mol H_2O . Therefore, the fraction of AsH_3 that may dissolve in the condensate derived from quenching the raw product gases is 1.03 percent for the Hygas process, 0.31 percent for the Lurgi process, and 0.004 percent for the Koppers-Totzek process. The resultant concentrations of arsine in the excess condensates will be on the order of 1 ppb, several orders of magnitude below current environmental standards, even before water treatment for recycle.

In the Hygas and Lurgi processes, a significant quantity of aromatic oil is also recovered during quench. The fraction of AsH_3 that may dissolve in this oil is estimated at 4.10 percent for the Hygas process and 0.31 percent for the Lurgi process. However, depressurization of this oil will liberate most of the AsH_3 . These liberated gases, because of their quantity, will be recompressed and returned to the quenched raw product gas.

Hydrogen selenide removal in the quench system is also expected to be negligible. The solubility of H_2Se in water is slightly less than that of H_2S . The Henry's constant for H_2Se in water is 963.76 atm at 300 K.²⁰ Therefore, the predicted concentrations of H_2Se in the excess condensate are 0.07 ppm for the Hygas process, 0.02 ppm for the Lurgi process, and 0.002 ppm for the Koppers-Totzek process. These values are also well below proposed environmental standards for discharge, even before treatment.

In the Hygas and Lurgi processes, about 7 percent and 0.6 percent of the H_2Se will initially be dissolved in the product oil. However, as with AsH_3 , depressurization will flash the H_2Se . The H_2Se will, therefore, be returned to the

quenched raw product gas.

The quench system will not remove much of the mercury in the raw product gas. After condensation of steam and oil from the product gases, the partial pressure of Hg in all these processes is below its vapor pressure of 3.4×10^{-6} atm at 300 K. To estimate the solubility of mercury in the excess condensate, it is assumed that its solubility was proportional to its partial pressure with a value of 0.25 mg/L at 3.4×10^{-6} atm, which is the solubility of metallic mercury in water at 300 K. Based on this assumption, the amount of Hg removed from the raw product gas by the excess condensate is 4 percent for the Hygas process, 1.1 percent for the Lurgi process, and 0.01 percent for the Koppers-Totzek process. The resultant concentration of Hg in this condensate is 0.011 ppmw for the Hygas process, 0.0023 ppmw for the Lurgi process, and 0.0002 ppmw for the Koppers-Totzek process.

Solubility of mercury in the condensable oil fractions of the Hygas and Lurgi processes is not known. Because of the recompression of flashed gases from this oil, it is assumed to be negligible.

In summary, the compounds under consideration that remain in the product gas after quench are AsH_3 , H_2Se , and Hg. The projected amounts remaining are shown in Table 9.

Effects During Sulfur Removal

The next process these gases encounter in the typical gas processing scheme is the selective H_2S removal system. For high-pressure processes such as Hygas and Lurgi, a physical-type solvent would probably be used because of lower costs. For low-pressure processes such as Koppers-Totzek, a chemical-type solvent would be used. However, the Koppers-Totzek system might also use a physical solvent, if the gas is to be compressed for delivery, and the chemical system might, on occasion, be used with the other gasifiers. The analysis below is based on the most likely acid-gas removal system to be used. Also, for completeness, an analysis is performed on the use of a chemical acid-gas removal system with a high-pressure process.

In the physical solvent systems, solubility data on these species are unavailable; however, nearly quantitative removal of AsH_3 and H_2Se is expected. This assumption is based on the

TABLE 9. FORM AND DISTRIBUTION OF SELECT TRACE ELEMENTS
IN QUENCHED GASIFIER PRODUCT GAS

	Process		
	Lurgi	HYGAS	Koppers-Totzek
Operating Pressure, atm	20	80	2
	—— g-mol/g-mol quenched product gas ——		
AsH ₃	3.19×10^{-7}	4.81×10^{-7}	2.68×10^{-15}
H ₂ Se	2.50×10^{-7}	1.85×10^{-7}	4.00×10^{-7}
Hg	1.58×10^{-8}	1.72×10^{-8}	1.38×10^{-8}

lower vapor pressures of AsH₃ and H₂Se relative to H₂S; this indicates AsH₃ and H₂Se should be more soluble in the solvent than H₂S. The removal of mercury in physical solvent systems is more difficult to predict because solubility of Hg in solvents is not given by Raoult's law. However, these physical solvent systems operate at temperatures where a significant part of the Hg may condense. The Selexol process operates at temperatures around 280 K. The vapor pressure of Hg at this temperature is $\sim 6 \times 10^{-7}$ atm with 56 percent condensation of Hg. Condensation of up to 99 percent of the mercury in the Lurgi-Rectisol quenched gas stream may occur at operating temperatures of 230 K.

In the Benfield process, which is a chemical-type solvent system that might be used with the Koppers-Totzek process, the normal operating temperature is 390 K. The removal of arsine predicted from its solubility in water is negligible. Removal of mercury is also negligible because of the high temperature and low partial pressure of Hg ($\sim 2.36 \times 10^{-8}$ atm). However, quantitative removal of H₂Se is expected. The pK_a of H₂Se is 4. The pK_a of H₂S is 7. Therefore, dissociation of H₂Se into H⁺ and HSe⁻ in a chemical-type solvent is greater than that of H₂S.

Similarly, if the Benfield process were used in a Hygas plant, hydrogen selenide would be nearly quantitatively removed. Arsine and mercury removal will be slightly larger than that predicted in the Koppers-Totzek process because of higher partial pressures for these com-

pounds.

The resulting distribution of arsine, hydrogen selenide, and mercury for these processes is shown in Table 10. This distribution is based on the assumption that the H₂S selective removal system is designed to produce an H₂S-rich acid-gas stream containing 15 percent H₂S.

The H₂S-rich acid-gas stream is then assumed to go to a Claus process for production of elemental sulfur. Although minimal process problems are anticipated because of the presence of these trace constituents, contamination of the byproduct elemental sulfur may occur. The typical levels of selenium and arsenic in industrial grade sulfur are less than 2 ppm and less than 0.25 ppm, respectively. The arsine and hydrogen selenide in the feed should convert to arsenious oxide and elemental selenium in the combustion zone of the Claus plant. These forms will precipitate with the elemental sulfur. Based on the predicted concentrations of these elements in the H₂S-rich acid-gas, the concentrations of arsenic and selenium in the product sulfur will range from 0 to 280 ppm by weight and 113 to 348 ppm by weight, respectively. The presence of elemental sulfur and H₂S in the combustion and catalytic zones of the plant should convert the mercury to HgS if minimal H₂ is present. The anticipated range of the mercury content of the product sulfur is 0.006 to 20 ppm.

This contamination could render the product sulfur unfit for many industrial applications. However, most sulfur is used for sulfuric acid production for fertilizer. Sulfuric acid manufac-

TABLE 10. PROJECTED ARSINE, HYDROGEN SELENIDE, AND MERCURY LEVELS,
IN H₂S-FREE PRODUCT-GAS STREAM, H₂S-RICH
ACID-GAS STREAM, AND PRODUCT SULFUR

<u>Gasification Process</u>	<u>Lurgi</u>	<u>HYGAS</u>	<u>Koppers-Totzek</u>	<u>HYGAS</u>
<u>Acid-Gas Process</u>	<u>Rectisol</u>	<u>Selexol</u>	<u>Benfield</u>	<u>Benfield</u>
<u>H₂S-Free Product Gas, ppmv</u>				
AsH ₃	< 0.003	< 0.005	Neg	0.49
H ₂ Se	< 0.002	< 0.002	< 0.004	< 0.002
Hg	0.00016	0.0078	0.014	0.017
<u>H₂S-Rich Acid-Gas, ppmv</u>				
AsH ₃	10.38	17.97	Neg	0.37
H ₂ Se	6.47	8.79	19.36	8.79
Hg	0.489	0.387	0.00014	0.00014
<u>Product Sulfur, ppmw</u>				
As	162	280	Neg	5.8
Se	106	144	318	144
Hg	20.4	16.15	0.006	2.24

*Neg = negligible

turers do have means of accommodating these contaminants in new, properly designed plants; an older plant might not be able to use this material, reducing its byproduct value. The proper solution, of course, is to manufacture byproduct acid, rather than elemental sulfur, at the gasification plant. This option not only recovers the initial sulfur byproduct value but produces a more valuable byproduct than elemental sulfur.

The predicted concentrations of AsH_3 and H_2Se in the H_2S -free product-gas streams from the Lurgi and Hygas processes are conservatively based on only 99 percent removal for these compounds in the H_2S selective removal step. Likewise, only 99 percent removal of H_2Se is assumed for the Koppers-Totzek process. More realistically, more than 99.9 percent removal should be expected.

Effects During Initial CO_2 Removal

These H_2S -free product gases then enter the CO_2 removal process, which is similar to the H_2S removal process except higher solvent-to-gas ratios are used. In this step, the residual AsH_3 and H_2Se will be removed and be discharged with the CO_2 vent-gas stream from the plants. In the Hygas and Lurgi processes, using Selexol and Rectisol respectively, additional mercury is removed because the CO_2 removal decreases the quantity of gas and, therefore, increases the partial pressure of mercury in the gas stream. The reduction in gas quantity is ~25 percent; therefore, ~25 percent of the mercury in H_2S -free gas will also be removed to the CO_2 vent-gas stream in each process. Minor removal of mercury is expected in the Koppers-Totzek and Hygas processes using a Benfield acid-gas removal system.

Based on these assumptions, the concentrations of arsine, hydrogen selenide, and mercury in the $\text{H}_2\text{S}/\text{CO}_2$ -free product gas streams and the CO_2 vent-gas stream are shown in Table 11. The range of the predicted concentrations of these components in the CO_2 vent gas is 0 to $47 \mu\text{g}/\text{m}^3$ for hydrogen selenide, and 0 to $79 \mu\text{g}/\text{m}^3$ for the mercury. The concentration of H_2Se in the CO_2 vent-gas stream from any of the process schemes is below the multimedia environmental goal-minimum acute toxicity effluent (MEG-MATE) value of $200 \mu\text{g}/\text{m}^3$. The predicted mercury concentration for the Lurgi and Koppers-Totzek processes is below its MATE value of 50

$\mu\text{g}/\text{m}^3$. The predicted mercury concentration for both variations of the Hygas process is slightly above this value at $69 \mu\text{g}/\text{m}^3$ and $79 \mu\text{g}/\text{m}^3$.

A major question area lies in the projected arsine levels in the CO_2 vent-gas stream. The MEG-MATE value for arsine is $2 \mu\text{g}/\text{m}^3$. Note, however, the current MEG-MATE values have some interesting conflicts between arsenic and other hazardous materials. Hydrogen selenide, mentioned above, has a hazard potential rating of 30, while AsH_3 has a hazard potential of only 25. Yet, the MATE value of H_2Se is 100 times greater than that for AsH_3 .

The projected level of arsine in the CO_2 vent-gas stream for the Lurgi and Hygas processes ranges from $33 \mu\text{g}/\text{m}^3$ to $212 \mu\text{g}/\text{m}^3$. It must be emphasized that these levels are engineering estimates and contain large uncertainties. The Selexol and Rectisol processes are probably capable of removing 99.9 percent of the arsine; the resulting concentrations in the CO_2 vent-gas stream would then be the same magnitude as the MATE. The value of $212 \mu\text{g}/\text{m}^3$ represents projections of arsine in the CO_2 vent-gas stream from using the Benfield process; this value is based on arsine solubility in water, but gas solubility in the Benfield solution is known to be suppressed. All these values should be experimentally derived if possible.

Effects in Later Processes

After the CO_2 removal process, only mercury and arsine remain in the product-gas stream. It is assumed that the combined catalytic water-gas shift-methanation process does not alter the amount of mercury in the product gas from this step. Note, however, that the mercury might well be absorbed within the pores of this catalyst. The arsine present in the case where a Benfield process is used with the Hygas process is expected to decompose into elemental arsenic and hydrogen under these catalytic gas-processing conditions. This is caused by the rapid reduction in the hydrogen partial pressure because of methane formation. The elemental arsenic should be removed from the gas when it is quenched. The resulting concentrations of mercury, elemental arsenic, and arsine after methanation are shown in Table 12.

Next, the CO_2 produced in the methanation step is removed. Because the partial pressure of mercury is increased through the production of

TABLE 11. PROJECTED CONCENTRATIONS OF ARSINE, HYDROGEN SELENIDE,
AND MERCURY IN THE H₂S/CO₂-FREE PRODUCT-GAS
AND CO₂ VENT-GAS STREAMS

<u>Gasification Process</u>	<u>Lurgi</u>	<u>HYGAS</u>	<u>Koppers-Totzek</u>	<u>HYGAS</u>
<u>Acid-Gas Process</u>	<u>Rectisol</u>	<u>Selexol</u>	<u>Benfield</u>	<u>Benfield</u>
	H ₂ S/CO ₂ -Free Product-Gas Stream, ppmv			
AsH ₃	Neg *	Neg	Neg	0.694
H ₂ Se	Neg	Neg	Neg	Neg
Hg	0.00016	0.0078	0.015	0.021
	CO ₂ Vent Gas Stream, ppmv			
AsH ₃	<0.009**	<0.014**	Neg	0.0631
H ₂ Se	<0.007**	<0.005**	<0.001	<0.005
Hg	0.00016	0.0078	Neg	0.0090

* Neg = negligible

**Predictions based on conservative 99% removal in the first stage of acid gas removal. Actual concentrations are expected to be an order of magnitude lower.

**TABLE 12. PROJECTED ARSINE, ARSENIC, AND MERCURY CONCENTRATIONS IN
RAW METHANATION PRODUCT-GAS STREAM, QUENCHED METHANATION
PRODUCT-GAS STREAM, AND PRODUCT SNG**

<u>Gasification Process</u>	<u>Lurgi</u>	<u>HYGAS</u>	<u>Koppers-Totzek</u>	<u>HYGAS</u>
<u>Acid-Gas Process</u>	<u>Rectisol</u>	<u>Selexol</u>	<u>Benfield</u>	<u>Benfield</u>
Raw Methanation Product Gas, ppmv				
AsH ₃	Neg*	Neg	Neg	Neg
As ₄	Neg	Neg	Neg	0.266
Hg	0.00032	0.0120	0.0234	0.0322
Quenched Methanation Product Gas, ppmv				
AsH ₃	Neg	Neg	Neg	Neg
As ₄	Neg	Neg	Neg	Neg
Hg	0.00032	0.0120	0.0234	0.0322
Product SNG, ppmv				
AsH ₃	Neg	Neg	Neg	Neg
As ₄	Neg	Neg	Neg	Neg
Hg	0.00032	0.0045	0.0045	0.0045
*Neg = negligible				

methane and removal of CO₂, condensation can once again occur in the low-temperature acid-gas removal processes. The concentration of mercury in this vent-gas stream is predicted to be about the same as for the previous CO₂-removal step.

This product SNG will then be compressed in the Lurgi and Koppers-Totzek processes to 70 atm.* Then, in all processes, the compressed gases will be treated in glycol coolers at ~274 K to reduce the dew point of the gases. This should reduce the amount of mercury in SNG from the Koppers-Totzek and Hygas processes to 0.0045 ppm (40 µg/m³) or less.

Direct combustion of this gas in an industrial process or use in the home should pose no health hazards because of the mercury content. A stack-gas concentration of about 4 µg/m³ will result from combustion of this gas compared to the MATE value of 50 µg/m³. In the home, the primary nonvented appliance is the gas range. The average annual cooking load is 10.2 million Btu per customer, which results in an annual mercury discharge into the home of 0.01 g. Assuming the average home contains 425 m³ of air with one-half air turnover daily, the average concentration of mercury in the home would be 0.13 µg/m³. Typical concentrations of mercury inside residences is 0.07 µg/m³. The mercury concentrations are 0.1 to 0.2 µg/m³ 3 to 6 mo after an interior repaint of a house.²¹ Thus, the use of SNG from coal gasification plants should not pose any health effects problems because of mercury content. Additionally, some attenuation of the mercury levels in the SNG because of information of HgS in the pipeline is expected, as well as dilution of the SNG by natural gas.

REVIEW BY ELEMENT

The theoretical analysis performed on the disposition of arsenic, selenium, boron, lead, and mercury indicates many areas where further research efforts and environmental assessment work could be most useful in designing coal gasification facilities.

*Note that if the Koppers-Totzek gas had been compressed prior to acid-gas removal, a different H₂S/CO₂-removal process might be economically preferred, with different disposition of these trace inorganics.

Arsenic

The projected mass flow rates of arsenic in the various inlet and outlet streams of the gasification processes are shown in Table 13 and Figure 5. These projections, of course, depend on the postulated occurrence of AsH₃ in the raw gasifier product gas. The presence of arsine and its concentration should be investigated further. The solubility of arsine, if present in acid-gas removal processes, requires study. Finally, if arsine is present, differing sulfur management schemes in coal gasification processes should be investigated. In the worst case, projected air emissions of arsenic from a full-scale coal gasification plant, including boiler, are 6 kg/day compared to 37 kg/day for a coal-fired power plant delivering the same energy.

Boron

The projected mass flow rate of boron in coal gasification processes is shown in Table 14. Boric acid, B(OH)₃, is projected to be the major route for removal from the feed coal. The boric acid, if produced, will be recovered in the dissolved-solids recovery section of wastewater treatment. No problems are anticipated because of its presence.

Lead

Volatile lead components should only exist in raw product gases from high-temperature gasification processes such as the Koppers-Totzek process. This is shown in Table 15. These lead-containing components, however, will precipitate during quench of the raw gasifier product gases and be recovered with other suspended solids in the condensate.

Mercury

The projected mass flow rate of mercury in the analyzed gasification processes is shown in Table 16 and Figure 6. As can be seen, mercury disposition depends upon the gas processing scheme used. These projections, however, are based on estimates of solubility and condensation, and the estimates need to be verified. In this analysis, the projected emissions of mercury from most of the various gas discharge streams are below current MEG-MATE values. Total mercury emissions from the process in-

TABLE 13. PROJECTED ARSENIC DISPOSITION (14 ppm IN FEED COAL)

<u>Process</u>	<u>Lurgi</u>	<u>HYGAS</u>	<u>Koppers-Totzek</u>	<u>HYGAS</u>
<u>Acid-Gas Removal</u>	<u>Rectisol</u>	<u>Selexol</u>	<u>Benfield</u>	<u>Benfield</u>
	kg/day			
<u>Input Stream</u>				
Coal Feed	257.96	225.37	257.96	225.37
<u>Output Stream</u>				
Discharge Ash	128.98	112.68	Neg	112.68
Solids from Wastewater Treatment	100.06	79.94	257.96	79.94
Product Sulfur	28.73	32.41	Neg	0.67
Sulfur Recovery Tail Gas	Neg*	Neg	Neg	Neg
CO ₂ Vent Gas (I)	< 0.275	< 0.321	Neg	1.34
Methanation Quench	Neg	Neg	Neg	31.27
CO ₂ Vent Gas (II)	Neg	Neg	Neg	Neg
Glycol Cooler Recovery	Neg	Neg	Neg	Neg
Product SNG	Neg	Neg	Neg	Neg

* Neg = negligible

cluding the boiler house are estimated to be between 1.5 and 2.2 kg/day for a full-scale facility. A coal-fired power plant producing the same amount of energy would emit ~5 kg/day of mercury using the same coal.

Selenium

The projected selenium disposition in typical coal gasification processes is shown in Table 17

and Figure 7. The projected selenium disposition is controlled by the fate of H₂Se in the gas-processing section of the plants. If H₂Se is present as predicted, the major dispositions will be with the discharge ash and either the product elemental sulfur or product sulfuric acid from which it can be removed. Formation of H₂Se in gasification processes should be checked, as well as its solubility in various processing liquids. In these calculations, maximum gas-phase

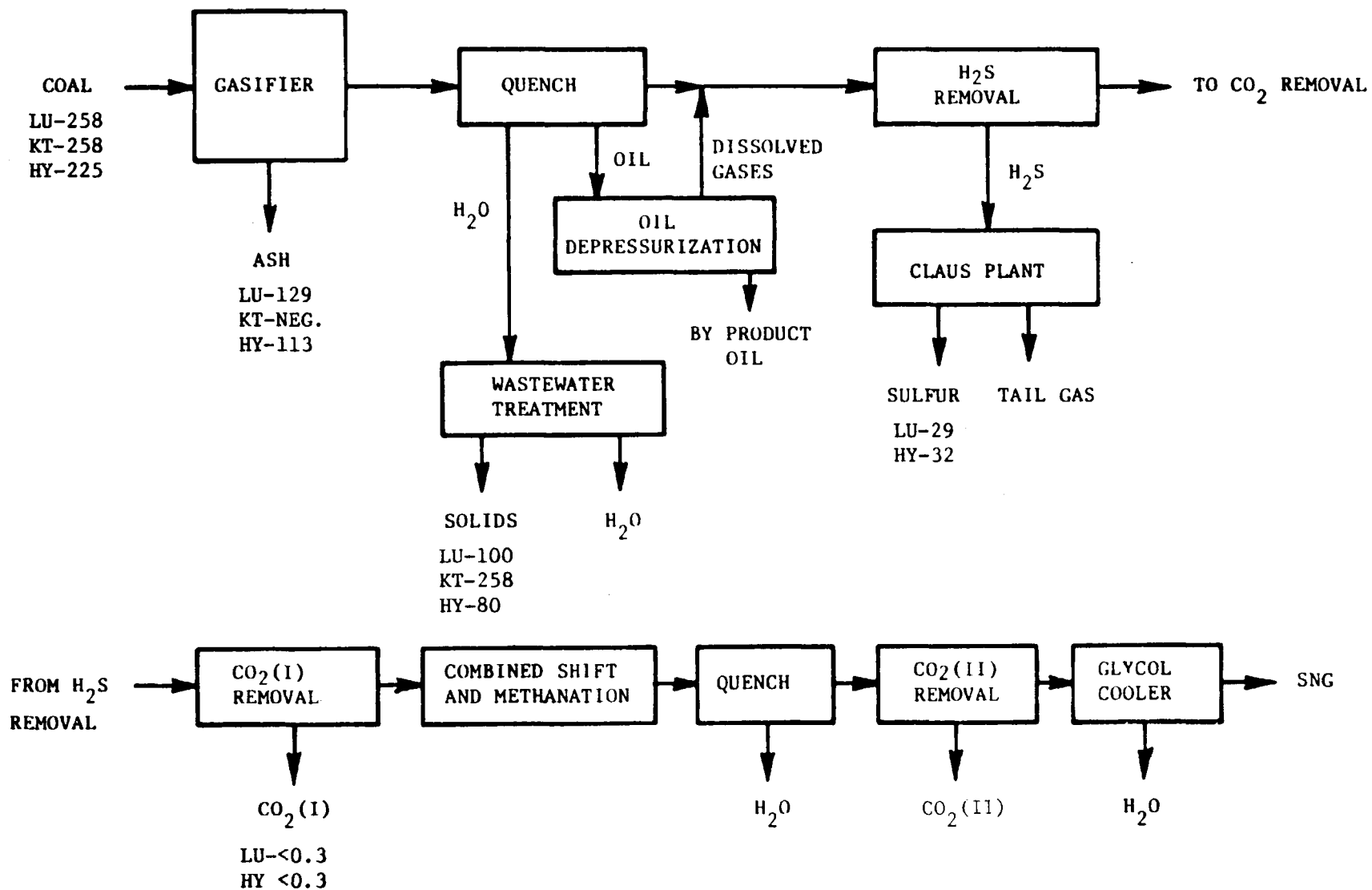


Figure 5. Projected arsenic disposition (kg/day) in 250×10^6 SCF/day coal gasification plants.
(14 ppm in coal)

TABLE 14. PROJECTED BORON DISPOSITION (10.2 ppm IN COAL)

<u>Process</u>	<u>Lurgi</u>	<u>HYGAS</u>	<u>Koppers-Totzek</u>
	<u>kg/day</u>		
<u>Input Streams</u>			
Coal Feed	188.3	164.5	188.3
<u>Output Streams</u>			
Discharge Ash	94.1	82.2	Neg
Solids from Wastewater Treatment	94.1	82.2	188.3
Product Sulfur	Neg*	Neg	Neg
Sulfur Recovery Tail Gas	Neg	Neg	Neg
CO ₂ Vent Gas (I)	Neg	Neg	Neg
Methanation Quench	Neg	Neg	Neg
CO ₂ Vent Gas (II)	Neg	Neg	Neg
Glycol Cooler Recovery	Neg	Neg	Neg
Product SNG	Neg	Neg	Neg
* Neg = negligible			

emissions of selenium in a full-scale process are estimated at 6.6 kg/day. These emissions are primarily due to the boiler house. A coal-fired power plant delivering the same energy is estimated to emit 25 kg/day of selenium into the atmosphere.

It is emphasized that the analysis presented is based primarily on theoretical projections and engineering assumptions. This analysis should provide insight into a better understanding of the factors important in determining the

formation and disposition of some of these constituents. Further experimental investigations are desirable to increase this understanding.

ACKNOWLEDGMENTS

The financial support of the U.S. Environmental Protection Agency (Contract No. 68-02-2648) in performing this work is gratefully acknowledged.

TABLE 15. PROJECTED LEAD DISPOSITION (35 ppm IN COAL)

<u>Process</u>	<u>Lurgi</u>	<u>HYGAS</u>	<u>Koppers-Totzek</u>
	kg/day		
<u>Input Streams</u>			
Coal Feed	641.2	560.0	641.2
<u>Output Streams</u>			
Ash Discharge	641.2	560.0	Neg
Solids from Wastewater Treatment	0.005	0.008	641.2
Product Sulfur	Neg*	Neg	Neg
Sulfur Recovery Tail Gas	Neg	Neg	Neg
CO ₂ Vent Gas (I)	Neg	Neg	Neg
Methanation Quench	Neg	Neg	Neg
CO ₂ Vent Gas (II)	Neg	Neg	Neg
Glycol Cooler Recovery	Neg	Neg	Neg
Product SNG	Neg	Neg	Neg
* Neg = negligible			

TABLE 16. PROJECTED MERCURY DISPOSITION (0.2 ppm IN COAL)

<u>Process</u>	<u>Lurgi</u>	<u>HYGAS</u>	<u>HYGAS</u>	<u>Koppers-Totzek</u>
<u>Acid-Gas Removal</u>	<u>Rectisol</u>	<u>Selexol</u>	<u>Benfield</u>	<u>Benfield</u>
	kg/day			
<u>Input Streams</u>				
Coal Feed	3.672	3.213	3.213	3.672
<u>Output Streams</u>				
Discharge Ash	Neg*	Neg	Neg	Neg
Solids from Wastewater Treatment	Neg	Neg	Neg	Neg
Product Sulfur	3.635	1.854	0.257	0.0007
Sulfur Recovery Tail Gas	Neg	Neg	Neg	Neg
CO ₂ Vent Gas (I)	0.0092	0.3397	0.514	0.0015
Methanation Quench	Neg	Neg	Neg	Neg
CO ₂ Vent Gas (II)	0.0173	0.543	0.424	0.0015
Glycol Cooler Recovery	Neg	0.202	1.743	3.394
Product SNG	0.0097	0.275	0.275	0.275
* Neg = negligible				

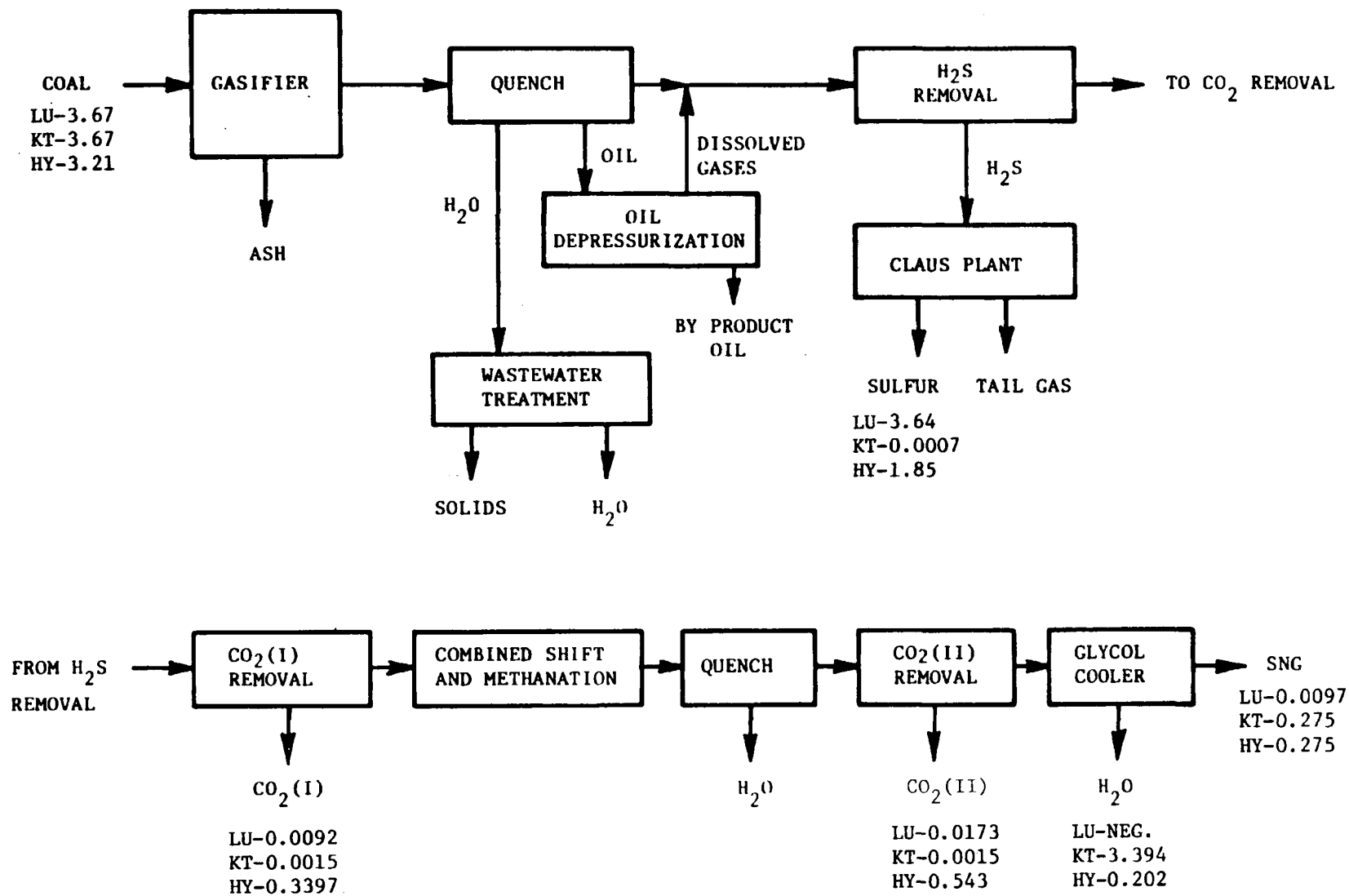


Figure 6. Projected mercury disposition (kg/day) in 250×10^6 SCF/day coal gasification plants.
(0.2 ppm in coal)

TABLE 17. PROJECTED SELENIUM DISPOSITION (2.08 ppm IN COAL).

<u>Process</u>	<u>Lurgi</u>	<u>HYGAS</u>	<u>Koppers-Totzek</u>
	kg/day		
<u>Input Streams</u>			
Coal Feed	38.3	33.5	38.3
<u>Output Streams</u>			
Discharge Ash	19.1	16.7	Neg
Solids From Wastewater Treatment	Neg*	Neg	Neg
Product Sulfur	19.1	16.7	38.0
Sulfur Recovery Tail Gas	Neg	Neg	Neg
CO ₂ Vent Gas (I)	< 0.2	< 0.1	< 0.4
Methanation Quench	Neg	Neg	Neg
CO ₂ Vent Gas (II)	Neg	Neg	Neg
Glycol Cooler Recovery	Neg	Neg	Neg
Product SNG	Neg	Neg	Neg

* Neg = negligible

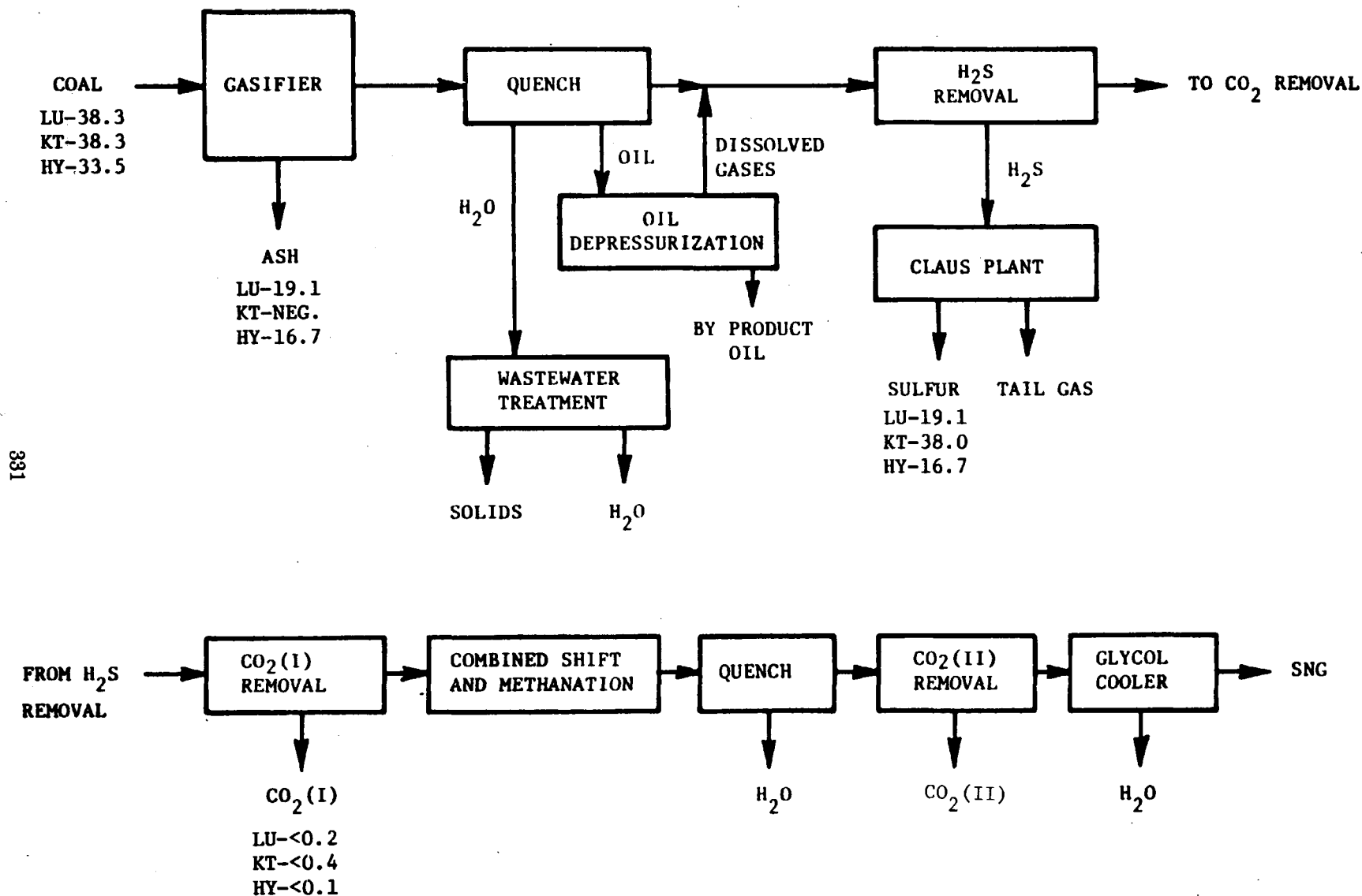


Figure 7. Projected selenium disposition (kg/day) in 250×10^6 SCF/day coal gasification plants.
(2.08 ppm in coal)

REFERENCES

1. Institute of Gas Technology. *Initial Environmental Test Plan for Source Assessment of Coal Gasification*. EPA Contract Number 68-02-1307, Report No. EPA 600/2-76-259.
2. Bodle, W. W., and Vyas, D. C. *Clean Fuels from Coal Symposium II Papers*. Institute of Gas Technology. June 23-27, 1975. p. 30-31.
3. Woodall Duckman, Ltd. *Trials of American Coals in a Lurgi Gasifier at Westfield Scotland*. U.S. Department of Interior. Report RI 15. November 1974.
4. Institute of Gas Technology. *Pipeline Gas From Coal-Hydrogenation*. U.S. Department of Energy. Report FE-2134. February 1978.
5. Duck, N. W., and Himus, G. W. On Arsenic in Coal and Its Mode of Occurrence. *Fuel* 30:267-271. 1951.
6. Zhuchkov, I. A., et al. Behavior of Arsenopyrite During Roasting in an Inert Gas Atmosphere. *Zh Prikl Khim* 40(12):2703-2710. 1967.
7. Zviadadze, G. N., and Rtskhiladze, V. G. Kinetics and Mechanism of the Thermal Decomposition of Arsenopyrite FeAsS. *Soobshch Akad Nauk Gruz SSR* 32(1):125-132. 1963.
8. Lukesh, J. S. Thermal Decomposition of Arsenopyrite. *Am Mineral* 25:539-542. 1940.
9. Barton, P. B., Jr. Thermochemical Study of the System Fe-As-S. *Geochim Cosmochim Acta* 33(7):941-951. 1969.
10. Institute of Gas Technology. *Environmental Assessment of the Hygas Process*. Chicago, Ill. U.S. Department of Energy. Contract Number EX-76-C-2433, Report No. FE-2433-16. February 1978.
11. Fray, D. J. *Inst Min Metall Trans, Sect C* 83:194. 1974.
12. Zaburdyeav, V. S., et al. *Zh Prikl Khim* (Leningrad) 47(7):1459-1463. 1974.
13. Kedyarkin, V. M., and Zorin, A. D. *Tr Khim Khim Tekhnol* 3:161-164. 1965.
14. Dobson, D. C., et al. Photolysis of Hydrogen Selenide. *J Phys Chem* 79(8).
15. Laidler, J. J. *Theory of Chemical Reaction Rates*. New York, McGraw-Hill, 1969. p. 36 ff.
16. Inorganic Constituents of Australian Coals, Part I. Nature and Mode of Occurrence. *J Inst Fuel* 37:422-434. 1964.
17. *JANAF Thermochemical Tables*. The Dow Chemical Co. Midland, Michigan.
18. Weiss, H. G., and Shapiro, L. Mechanism of the Hydrolysis of Diborane in the Vapor Phase. *J Amer Chem Soc* 75:1211-1224. 1953.
19. Luthy, R. G., and Tallon, J. T. *Experimental Analysis of Biological Oxidation Characteristics of Hygas Coal Gasification Wastewater*. Carnegie-Mellon University. Pittsburgh, Pa. NTIS Report Fe-2497-27. 1978.
20. Dubeau, C., et al. Solubility of Hydrogen Selenide Gas in Water. *J Chem Eng Data* 16(1):78-79. 1971.
21. Foote, R. S. Mercury Vapor Concentrations Inside Buildings. *Science* 177:513-514. August 11, 1972.

**Session II: ENVIRONMENTAL ASSESSMENT:
LIQUEFACTION**

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INITIAL SAMPLING OF THE FORT LEWIS SRC PILOT PLANT

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Abstract

During the first phases of the measurement program at the solvent refined coal (SRC) pilot plant at Fort Lewis, Washington, emphasis was primarily directed at determining the quality of the pollutant streams entering the environment. The first measurements were directed at obtaining information relative to the operation of the wastewater treatment facility. Because the pilot plant is not a miniature version of a commercial facility, it was also necessary to obtain samples from streams feeding the wastewater treatment facility. Liquid, gaseous, and solid streams that could affect the environment were sampled and analyzed according to the U.S. Environmental Protection Agency's (EPA) Level 1 and Level 2 procedures.

Coal conversion processes are highly complex systems consisting of a wide variety of inter-related components. Level 1 sampling has shown that certain streams have no significant environmental impact. These data result in fewer streams requiring sampling for the Level 2 analysis. A detailed evaluation of the data resulting from the Level 2 sampling and analysis will indicate the streams and/or specific pollutants that require the attention of a Level 3 methodology.

INTRODUCTION

A number of different processes are under development for producing synthetic fuels from coal. One of these technologies is the solvent refined coal (SRC) system. The process was originally developed by Spencer Chemical Company for the U. S. Department of Interior, Office of Coal Research. Gulf Oil subsequently acquired Spencer Chemical Company and is continuing development under the Pittsburgh and Midway Coal Mining Company.¹ A pilot plant was constructed at Fort Lewis, Washington, which has the capability of converting 45 metric tons of coal per day to the SRC products.

The SRC pilot plant at Fort Lewis, Washing-

ton has the capability to operate either in the SRC-I or the SRC-II mode. In the SRC-I configuration the facility produces a solid product with a sulfur content of less than 1 percent and an ash content of 0.2 percent or less.² When the facility is in the SRC-II operating configuration, it produces a liquid product.

Solid, liquid, and gaseous products and by-products enter the environment as a result of the liquefaction process. The initial sampling of the various streams at the SRC pilot plant at Fort Lewis was designed to obtain preliminary environmental assessment data, identify the potential problem areas, and establish priorities for further considering the streams. The direct streams from a pilot-plant facility to the environment are not the same as those from a commercial operation. To obtain information related to some of the pollution problems that may be associated with a commercial operation, it was necessary to sample the products and all streams that fed the waste treatment components.

Wherever possible, sampling and analysis procedures were followed in accordance with the U.S. Environmental Protection Agency's (EPA) Level 1 and Level 2 procedures.^{3,4,5} Samples were obtained for physical, chemical, and biological testing. In accordance with the philosophy of the phased approach, all streams were surveyed using sampling and analytical methods that permit priority ranking of the streams relative to their containment of potentially toxic materials.

Two field sampling and measurement operations have been performed to obtain samples from the SRC pilot plant at Fort Lewis. The first field operation occurred in March 1978 and the second in February 1979. During both of these field sample-gathering operations, the pilot plant at Fort Lewis was in the SRC-II mode. In March of 1978 the products were sampled, and samples and data were obtained from various locations throughout the wastewater treatment plant. During the February 1979 sampling operations samples and data

were obtained for the products, the source coal, liquid streams, gaseous emissions, and the surrounding atmosphere. Preliminary analysis and evaluation of these data are presented in this paper.

SRC PILOT PLANT AND OPERATION

The SRC pilot plant at Fort Lewis, Washington, was constructed on the military base near Tacoma, Washington, which began operating in October of 1974. Figure 1 shows a block diagram of the SRC system.⁶ In the coal preparation and handling area raw coal is unloaded, crushed, and stored in piles. The coal is sized, pulverized, and mixed with a recycled hydrocarbon solvent. The resulting coal/solvent slurry is mixed with a hydrogen-rich gas and preheated. The preheated mixture enters the hydrogenation zone, which operates at 425° C to 480° C and 6.9 MPa to 13.8 MPa, with about a 30-min holding time. The coal is liquefied by reacting with hydrogen. The liquefied product contains some undissolved material, primarily mineral matter and undissolved coal. The excess hydrogen and gases produced in the reaction are separated from the slurry of undissolved solids and coal solution. The gaseous stream passes through a cleanup system to remove H₂S and CO₂ and is then recycled to the reaction zone. Fresh hydrogen from the hydrogen production area is added to this recycled gas stream. The slurry of solids and coal solution is cooled; the solids are separated from the coal solution, stored, and used for hydrogen generation. The coal solution is further separated into a light oil fraction, a wash solvent fraction, the process solvent, and the solvent-refined coal. The SRC is solidified by cooling. The gasification system will gasify either the residue or a mixture of residue and coal.⁷

A diagram of the plant system is shown in Figure 2. Each area in Figure 2 is numerically designated as follows:

- 01 Coal preparation and slurry mixing,
- 02 Preheating, dissolving, and pressure letdown,
- 03 Mineral separation: very little use for SRC-II,
- 04 Fractionation and solvent recovery,
- 05 Gas recovery and recompression,
- 081 Sandvik belt-vacuum bottoms solidification,

- 082 Solid product storage area, and
- 091 Wastewater treatment area.

Figure 2 also shows the locations from which solid, liquid, gaseous, and atmospheric samples were obtained. These will be discussed later in the paper. An aerial view of the SRC plant at Fort Lewis, Washington, is shown in Figure 3.

Operational constraints of a pilot plant limit the time when samples and data can be obtained. A number of parameters within the pilot plant can be changed, which may result in changes in the constituents of various streams within the system. Operational temperature and pressure and the rate and amount of hydrogen introduced into the process are often changed. The type of coal is also changed. Even if gross parameters of the coal are similar, the presence or absence of trace elements may vary the constituents of potential pollutant streams. Sudden shutdown or recycling procedures will change the equilibrium of the system. A change in the mode of operation of the plant from the SRC-I to the SRC-II or order will change the constituents in the various streams. Considerable differences in the temperature and pressure of the process as well as the amount of hydrogen injected into the system exist between the two modes of operation. Comparable data can be obtained only if operational parameters are similar and the operation is stabilized.

During both March 1978 and February 1979 sampling operations, the SRC plant at Fort Lewis was in the SRC-II mode. Because the plant was operating in the SRC-II mode, data resulting from the sampling operation may indicate some of the conditions that can be expected in demonstration or commercial facility.

Typical Pacific Northwest winter conditions prevailed during the February 1979 field operation. The temperature ranged from -0.6° C (31° F) to 5.6° C (42° F) with some rainfall nearly every day. Conditions included complete cloud cover approximately 85 percent of the time. On the night of February 11, 1979, a severe windstorm damaged power lines and shut down the plant for nearly 2 days.

SAMPLING RATIONALE

The phased approach, developed by the Process Measurements Branch (PMB) of EPA requires three separate levels of sampling and analytical effort. The first level, Level 1, utilizes

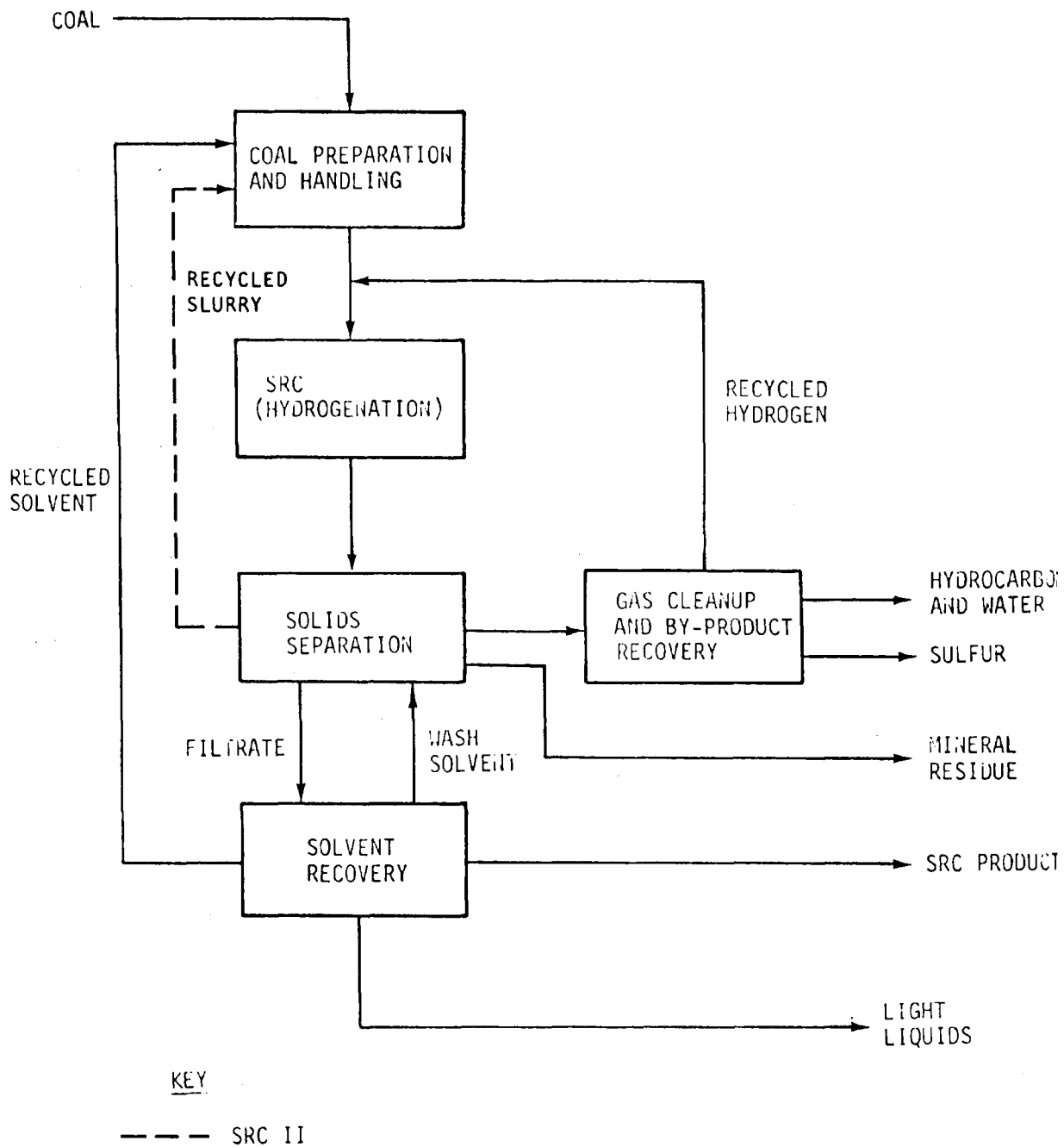


Figure 1. Solvent refined coal system.⁶

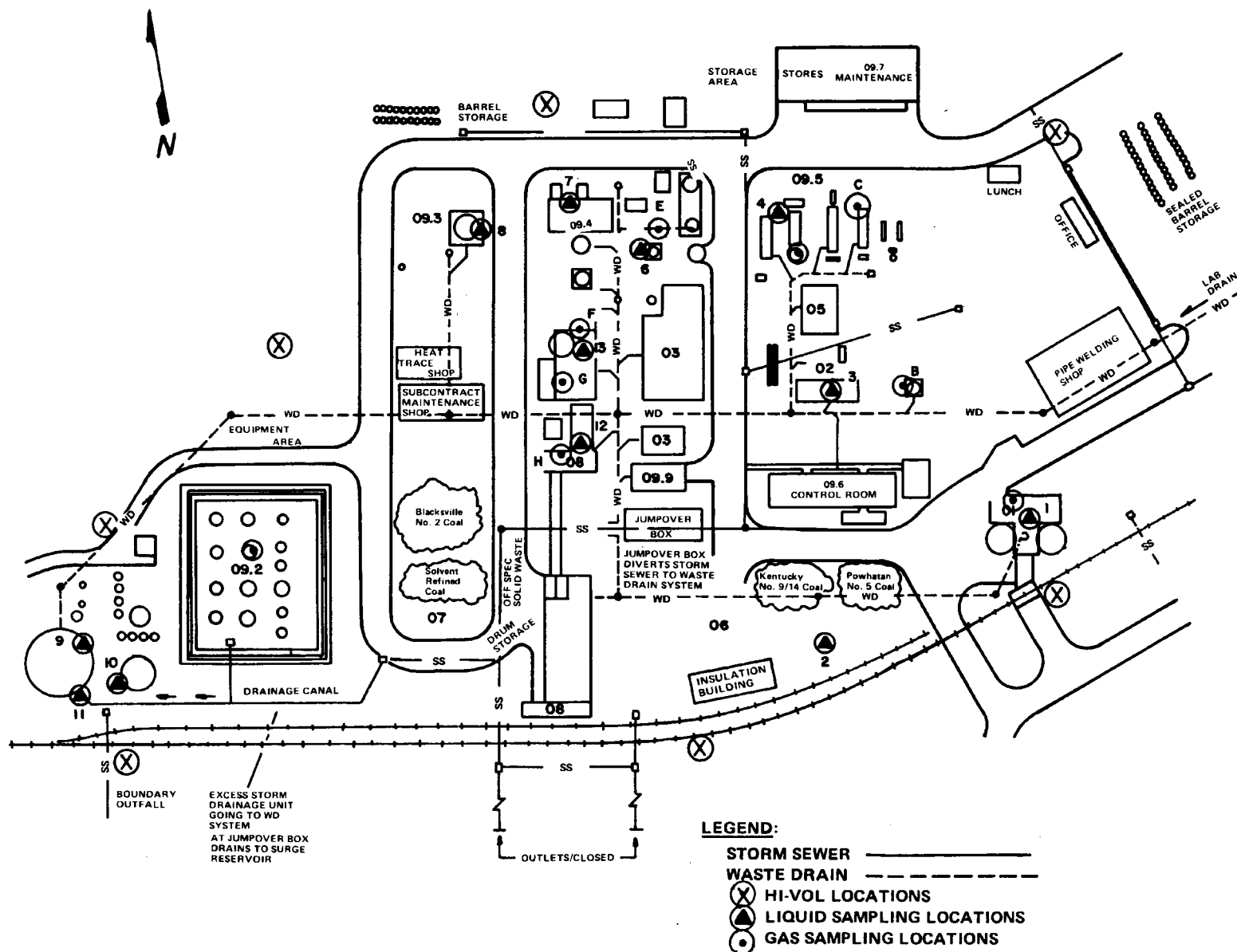


Figure 2. SRC plant and sampling locations.

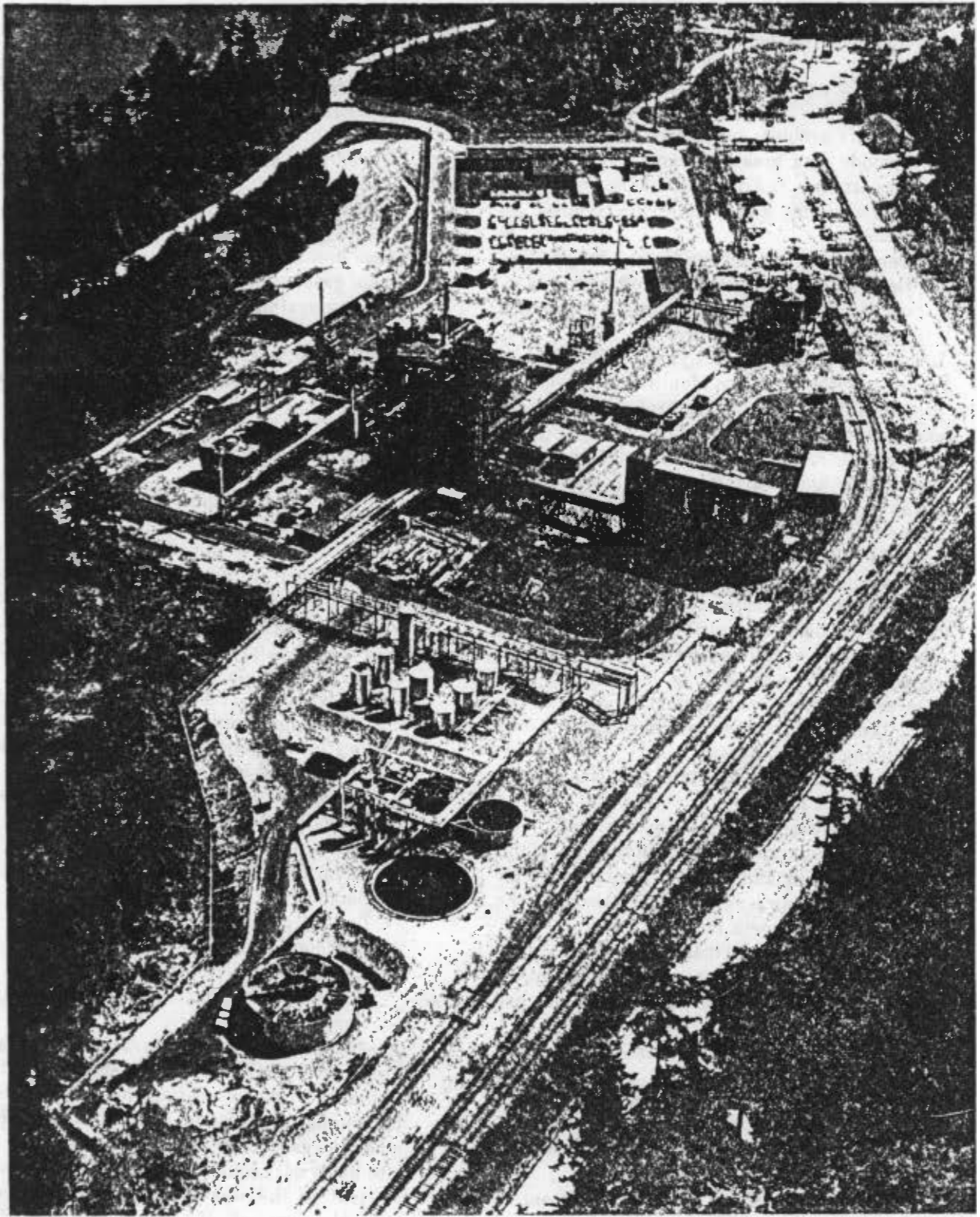


Figure 3. Aerial view of the SRC plant at Fort Lewis, Washington.

quantitative sampling and analysis procedures that yield final analytical results accurate to within a factor of 3 of the sample.³ Level 1 is designed to:

- Provide preliminary environmental assessment data,
- Identify problem areas, and
- Provide data to order priorities for the various streams and/or components.

Level 2 sampling and analysis procedures are designed to:

- Confirm and expand the Level 1 results, and
- Determine exact quantities of organic or inorganic constituents that could provide a health or ecological problem.

Level 3 sampling and analysis are directed at monitoring the problems identified in Level 1 to provide information for control device design and development.³

The basic rationales of the Level 1 and Level 2 sampling and analysis procedures were followed in planning Phase 1 (March 1978) and Phase II (February 1979) sample acquisition and analysis tasks. Phase I sampling was designed to provide preliminary environmental assessment data on the wastewater treatment facility of the SRC plant and of the SRC-II products. The Phase II sampling and analysis were designed to confirm the results obtained in Phase I on the wastewater treatment facility and the SRC-II products and to perform complete Level 1 sampling and analysis on:

- All streams flowing into the wastewater treatment facility,
- All emissions to the atmosphere, and
- The atmosphere surrounding the SRC plant.

Level 2 sampling and analysis were planned for all liquid streams leading to and through the wastewater treatment facility.

Figure 4 is a general diagram of streams that were scheduled to be sampled. Sampling point locations with respect to plant operations are shown in Figure 2, where:

- Numbered locations represent the liquid sampling locations,
- Lettered locations represent the gaseous sample locations, and
- (X) represents location of atmospheric samples.

The following factors limited the extent to which the Level 1 and Level 2 procedures could be followed:

- All electrical equipment had to be equipped with explosion-proof motors and connections to operate inside the plant area.
- No holes could be made in any pipe or stack.
- Safety regulations prevented obtaining flare exhaust samples.
- High-volume samplers did not exist in the area that were equipped with sorbent modules.
- Certain components of the plant failed to operate normally.

These limitations mainly restricted the acquisition of gaseous samples. The source assessment sampling system (SASS) train was not allowed to operate on the premises. In most locations it would have been impossible to operate the SASS train because of the design of the instrument.

SAMPLING OPERATION

In March of 1978, samples were acquired from locations throughout the wastewater treatment system at the SRC pilot plant at Fort Lewis. A block diagram of the wastewater treatment system showing locations of sample acquisition is shown in Figure 5. All samples were 1 gal (3.79 L) grab samples taken during the same day of plant operation. Liquid samples were preserved with acid and stored in ice during holding and shipping to the Hittman Associates laboratory for analysis. Solid samples were placed in polyethylene bags for shipment.

A more complex field sampling operation was required for Phase II in February 1979. The operation was designed to acquire:

- Level 1 and Level 2 liquid chemical samples,
- Samples for bioassay analyses,
- Level 1 gas samples,
- Surrounding atmospheric air samples,
- Coal and product samples, and
- Samples throughout 5 days of plant operation.

A schedule of the samples acquired from the Fort Lewis SRC pilot plant is shown in Table 1. Table 1 also shows location, method, and reason for sample acquisition. This table does not include the gaseous or atmospheric samples or on-site analysis. Liquid samples of the inflow and effluent of the wastewater treatment facility were also sent to Gulf South Research Institute.

Liquid samples were collected in 5 gal

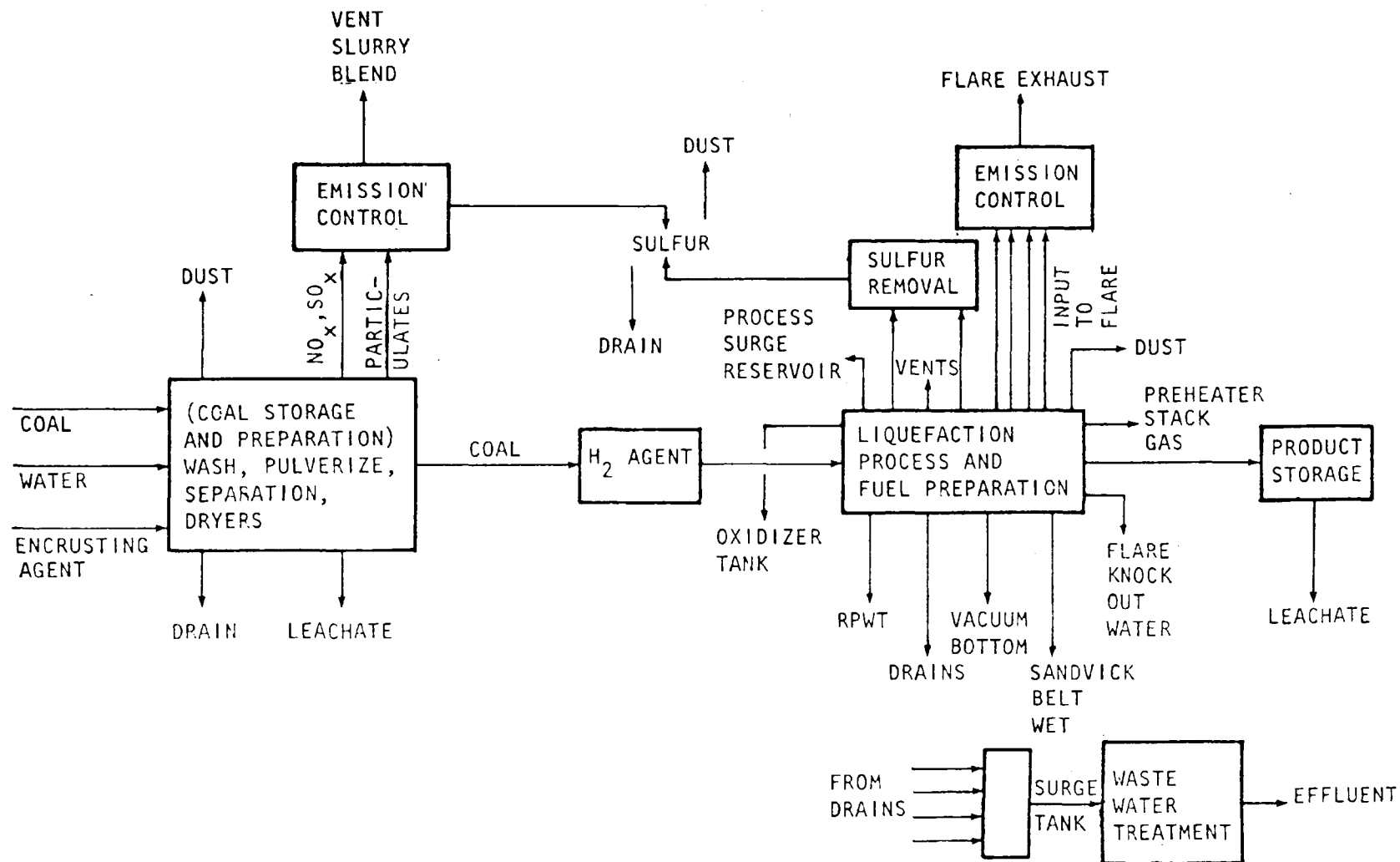
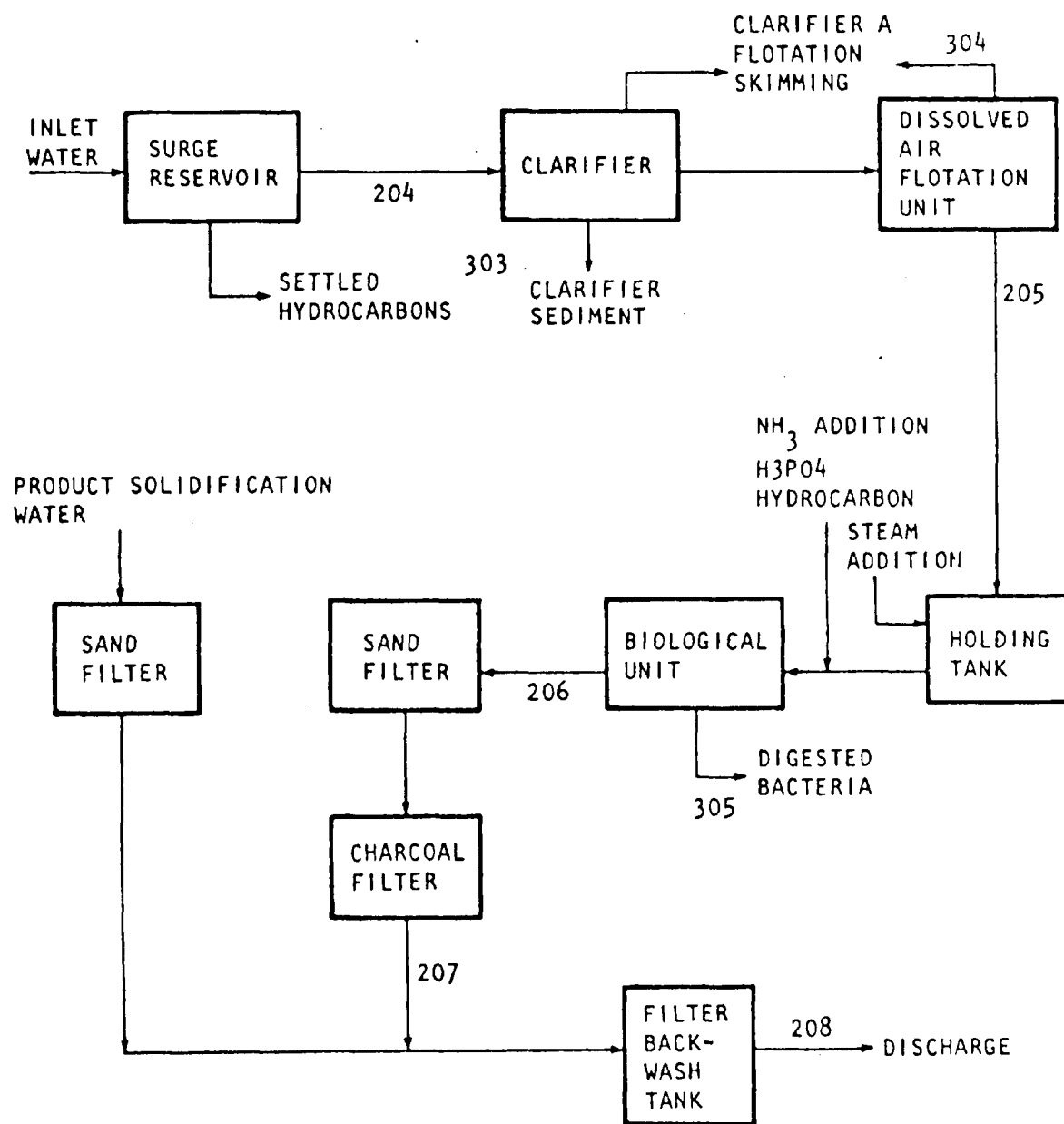


Figure 4. Pollutant streams at SRC system, Fort Lewis, Washington.



NOTE: 200s = liquid samples
300s = solid samples

Figure 5. Overall flow schematic of the SRC pilot plant wastewater system.

**TABLE 1. SAMPLE SHIPMENTS TO INDIVIDUAL LABORATORIES FOR ENVIRONMENTAL
SOURCE TESTS FOR THE SRC SAMPLES COLLECTED FEBRUARY 11
THROUGH FEBRUARY 17 AT FORT LEWIS, WASHINGTON**

Sample Identification	Sampling Meth- od	1st Day (2/11/79)			2nd Day (2/12/79)			3rd Day (2/15/79)		4th Day (2/16/79)		5th Day (2/17/79)													
		HAI	TRW	COM	AMEPA	HAI	LIT	COM	UC	HAI	TRW	AM	HAI	UW	HAI	TRW	AM								
		Shovel	Tap	Dipper	Wet Chemistry+	Trace Element	Original	Leachate	Trace Element	Bioassay	Wet Chemistry+	Trace Element	Bioassay	Trace Element	Original	Trace Element	Wet Chemistry+	Trace Element	Original	Trace Element	Wet Chemistry+	Original	VOM	Trace Element	
1 CPA Coal Preparation Area	•	•	•		•		•					•	•		•	•	•	•		•	•		•	•	•
2 CSPL Coal Storage Pile Leachate	•	•	•		•		•					•	•		•					•	•		•	•	•
3 DSAD Dissolve & Separation Area Drain	•	•	•		•		•					•	•		•		•	•	•	•		•	•	•	
4 SRAD Sulfur Recovery Area Drain	•								•	•	•	•	•		•		•	•	•	•		•	•	•	
6 RPWT Recycle Process Water Tank	•								•	•	•	•	•		•		•	•	•	•		•	•	•	
7 BB Boiler Blowdown	•	•	•		•		•					•	•		•					•	•		•	•	•
8 CW Cooling Water	•	•	•		•		•					•	•		•					•	•		•	•	•
9 WWTP1 Wastewater Treat. Plant Inf.	•	•	•		•		•					•	•		•		•	•	•	•		•	•	•	
10 WWTP2 Wastewater Treat. Plant Eff.	•	•	•		•		•					•	•		•		•	•	•	•		•	•	•	
11 VBSD Vacuum Bottoms Storage Drain	•	•	•		•		•					•	•		•					•	•		•	•	•
12 SBCW Sandvik Belt Cooling Water	•	•	•		•		•					•	•		•		•	•	•	•		•	•	•	
13 SFAD Solvent Fractionation Area Drain	•	•	•		•		•					•	•				•	•	•		•	•		•	•
Naphtha	•		•				•																		
Middle Distillate	•		•				•	•																	
Heavy Distillate	•		•				•	•																	
Recycle Slurry	•		•				•	•																	
Pulverized & Dried Coal	•		•				•	•	•																
Vacuum Bottoms	•		•				•	•	•																
Raw Coal	•		•	•				•	•																
1st QC Sample									•		•			•											
2nd QC Sample									•		•			•											

+ Includes 3 separate bottles for oil and grease, TOC, COD, Phenolics, Alkalinity, Acidity, TDS, TSS and Hardness.
* Also shipped a 1 gallon unextracted RPWT to TRW.
** Number five was to be the sample from the flare knockout drum, which was dry.

(18.93 L) bottles and then split for the various analyses. Ten L of the samples were extracted with methylene chloride for organic analysis. Extractions from each of the liquid streams were then shipped by air to the appropriate analytical laboratory. All liquid samples that were not extracted or sent for trace metal analysis were iced to keep below 4° C. Because atmospheric temperature was generally below 40° F (4.4° C), no difficulty was encountered in sample preservation. Samples were also preserved as shown in Table 2.

Samples of gaseous emissions and atmospheric particulates were obtained from locations shown in Figure 2. Locations indicated in Figure 2 as positions from which gaseous samples were obtained are designated in Table 3, relative to the source of the emissions. A sample of each source was placed in a 10-L, chemically inert mylar container and taken immediately to the laboratory for analysis. With explosion-proof pumps, 50 to 200 L of gas from each source were also passed through impingers. The SASS train was not used because of the stipulated use of explosion-proof equipment within the plant's operating area and the denial of the request for entrance ports to the vent stacks.

Product and solid samples were also acquired for chemical analysis and bioassay. These samples, the method of acquisition, and their disposition are shown in Table 1.

One severe problem was encountered during the second field trip relative to the operation of the wastewater treatment facility. A plug de-

veloped in the line between the aeration tank and the clarifier, which produced a malfunction of the aeration system. Because the wastewater treatment facility was operating beyond the designed capacity, the malfunction reduced the facility's efficiency.

PRELIMINARY SAMPLE ANALYSES

Analysis and preliminary evaluation of data obtained from the samples gathered from the various locations through the wastewater treatment facility indicate that the system was performing adequately when all aspects of the SRC plant and the wastewater treatment facility were operating normally. Table 4 shows the results of a spark source spectrometer analysis for trace elements of the wastewater treatment facility effluent. As a comparison, the Washington State limiting concentrations are also shown. Concentrations of all regulated trace elements were reduced to levels below those required by Washington State.

Figure 6 shows the distribution of organic constituents as a function of location through the wastewater treatment facility. Table 5 shows the percent of total reduction of the organics.

Data from the laboratory of the SRC pilot plant at Fort Lewis indicate that the wastewater treatment facility obtains removals as shown in Table 6. These values, however, may be atypical of results that would be observed in a commercial system for the following reasons:

TABLE 2. SAMPLE PRESERVATION

<u>Samples for Analysis of:</u>	<u>Method of Preservation</u>
Oil to Grease TOC COD	H ₂ SO ₄ to pH of 2 and cool to 4°C
Phenolics	H ₂ PO ₄ to pH of 4.0 g CuSO ₄ /l and cool to 4°C
Trace Elements	HNO ₃ to pH of 2
Organics	CH ₂ Cl ₂ extraction
Volatiles	Cool to 4°C

TABLE 3. GASEOUS SAMPLING LOCATIONS

<u>Location Designation</u>	<u>Gaseous Source</u>
A	Slurry blend tank vent
B	Pre-heater stack gas
C	N ₂ stripper vent
D	Oxidizer tank vent
E	Input to flare
F	Hot well tank vent
G	Process solvent accumulator vent
H	Sandvik belt vent
I	Process liquor tank vent

**TABLE 4. COMPARISON OF TRACE ELEMENT DATA ON TREATED WASTEWATER
WITH REGULATED LIMITATIONS OF WASHINGTON STATE**

<u>Element</u>	<u>Conc. Observed by Washington State (mg/l)</u>	<u>Spark Source Analysis (mg/l)</u>
Sodium (ppm)	25-50	5.9
Potassium	2-10	1.4
Nickel	0.05-0.10	0.04
Iron	0.1-0.5	0.31
Zinc	0.5	0.4
Bromine (ppb)	40-60	13
Selenium	0.2-2	B
Chromium	0.0-4	1
Thorium	0.04	B
Rubidium	0.8-5.0	3
Antimony	0.5-3.0	B
Arsenic	2-4	1

B = Below detection limit.

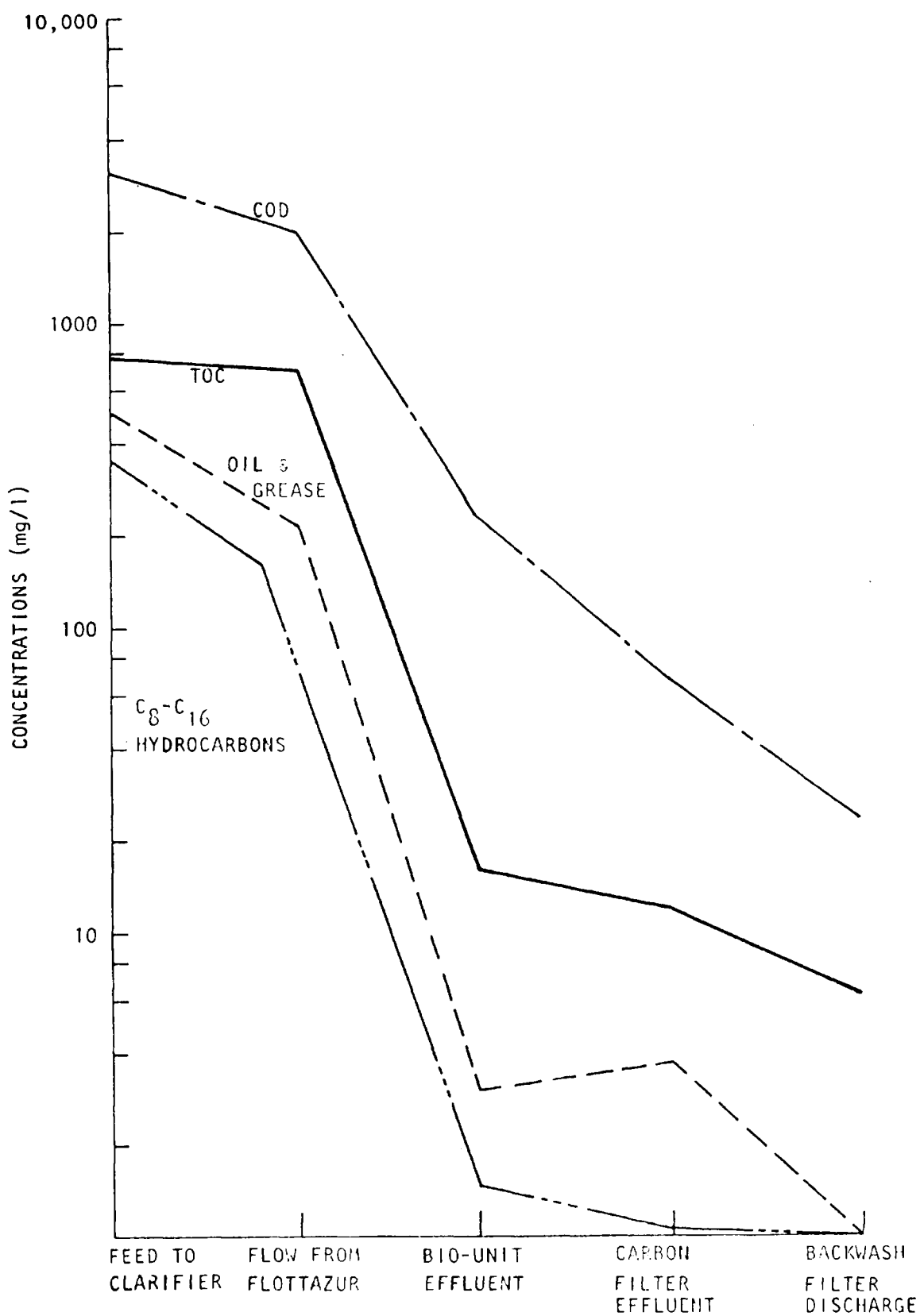


Figure 6. Effects of the wastewater treatment process on organics.

**TABLE 5. PERCENT REDUCTION IN ORGANICS BY THE
SRC WASTEWATER TREATMENT FACILITY**

Oil and grease	99%
COD	89%
TOC	98%
C ₈ -C ₁₆ hydrocarbons	99%

- The process water is only about 1 percent of the total feed to the wastewater treatment system. The actual COD of the foul process water has been reported to range from 25,000 to 43,600.⁹
- Phenols have not been recovered from the wastewater at the SRC-II pilot plant, as would be the case in a commercial system. Results of the Level 1 organic analysis indicate that phenols represent about 30 percent of the total organics. Phenols are readily biodegradable at concentrations from 500 to 1,000 mg/L,^{9 10 11} and the high concentrations of phenols relative to the more refrac-

tory classes of organic compounds detected in the Level 1 analysis explain the high degree of biodegradability.

Although the level of organics was too low following biological treatment to require a Level 1 analysis, results of the infrared analysis indicate that the following classes of hydrocarbons were still present:

- Aromatics, including substituted benzenes, naphthalenes, and other polynuclear hydrocarbons;
- Compound classes with C=O and C-O stretches representing aldehydes, acids, and esters;

**TABLE 6. RANGES OF WASTEWATER PARAMETERS AT
THE FORT LEWIS PILOT PLANT⁸**

	Surge Reservoir	Clarifier Effluent	Flottazur Flotation Unit	Bio-Unit Effluent	Plant Effluent
pH	5.0-9.0	6.2-6.8	6.2-6.8	6.2-7.4	6.2-7.4
BOD, mg/l	-	-	135-350	10-110	4-23
COD, mg/l	1,000-9,600	650-5,000	500-4,000	20-250	5-75
TSS, mg/l	90-400	50-300	30-200	20-300	0-20
Phenol, mg/l	30-1,500	25-1,100	10-1,000	0.1-1.0	0.0-0.4
Extractable oil, mg/l	10-250	6-150	4-30	0-4	0-3

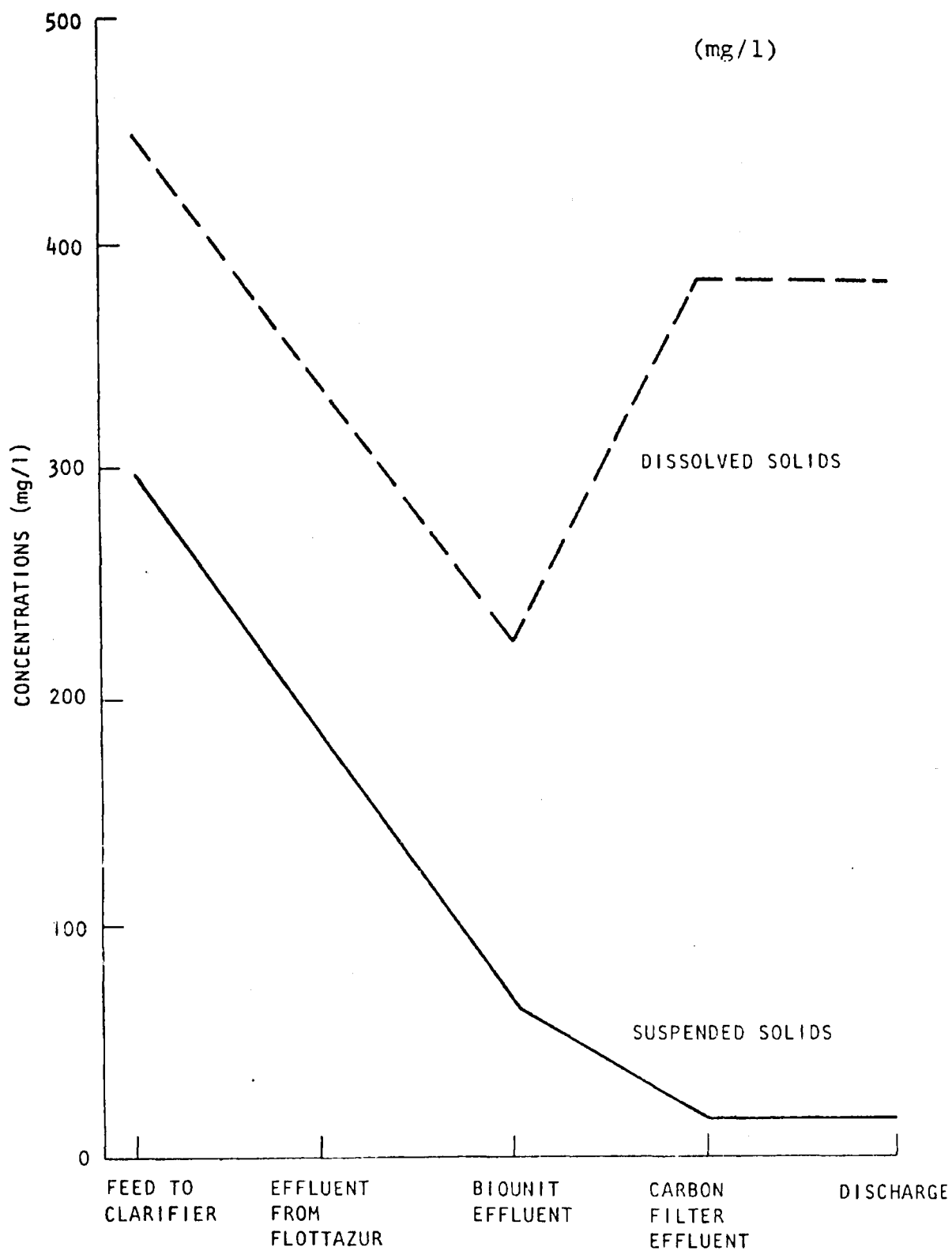


Figure 7. Distribution of dissolved and suspended solids in the wastewater treatment system.

TABLE 7. SUMMARY OF THE SAM/IA MODEL FOR THE EQUALIZED FEED TO THE WASTEWATER TREATMENT SYSTEM AND THE CARBON FILTER EFFLUENT

Effluent Stream Potential Degree of Hazard	Feed to Clarifier	Carbon Filter Effluent
• Health-based MATE	6.49	2.23
• No. of MATEs exceeded	3/31 (10%)	0.24 (0%)
• Ecological-based MATE	15,224	1,528
• No. of MATEs exceeded	7/18 (39%)	5/15 (33%)
Potential Toxic Unit Discharge Rate (1/sec)		
• Health-based MATE	32.77	11.25
• Ecological-based MATE	7.67×10^4	7710.86

- Aliphatic hydrocarbons of aliphatic substitution on ring compounds;
- Compounds with C=N stretch including amines; and
- Phenols.

The results of the analysis of the wastewater for suspended and dissolved solids are illustrated in Figure 7. While the results indicate 98 percent suspended solids removal in the wastewater treatment system, the results for dissolved solids do not show a consistent trend. Net reduction in the treatment system was found to be approximately 14 percent. The suspended solids results agree with available plant data, which indicate that suspended solids levels average 15 mg/L in the biounit effluent and 5.5 mg/L in the carbon filter effluent. Overflow from the backwash filter was found to contain 10 mg/L of suspended solids, well within the Washington State effluent limitations of 50 mg/L.

The SAM/IA model was applied to the feed to the clarifier and the carbon filter effluent, which represent the equalized feed to the treatment system and the treated wastewater, respectively. The results of the SAM/IA application yield an "effluent stream potential degree of hazard" based on comparison of the stream components to the ecologically and health-based MATEs, and a "potential toxic unit discharge rate" based upon the flow rate of the stream, thereby allow-

ing the relative hazard of various streams to be compared on a flow-rate basis. Table 7 summarizes the results of the SAM/IA.

During the second phase of the field sampling program a mobile laboratory was established in a covered truck at the SRC plant. This laboratory was established to obtain on-the-spot measurements of pH, conductivity, ammonium, nitrate, chloride, sulfide, and cyanide. All of these immediate onsite measurements were made by ion probes. Table 8 shows the results of these measurements. A great deal of variability is evident in the data. Extreme care was taken, and multiple measurement acquired, in the attempt to obtain readings as accurate as possible. However, interference often made the degree of accuracy less than desired. Particular attention should be given to the recycle process water tank because of its high concentrations of cyanide, chlorides, sulfides, and ammonium.

Analysis of the samples from the SRC pilot plant for trace elements is being performed by both spark source spectroscopy and plasma jet spectroscopy. The plasma jet has the advantage of excellent quantified results but is limited to only those elements for which the computer has been programmed. At the present time, only metals are spectrographically determined and quantified for the computer. Table 9 shows the concentration of each of the metals for each of the sampling locations.

TABLE 8. METALS IN SRC WASTE STREAMS (PLASMA JET SPECTROGRAPHIC ANALYSIS)

Metals	#1 CPAD	#2 CSPL	#3 DSAD	#7 BB	#8 CW	#9 WWTPI	#10 WWTPE	#11 VBSD	#12 SBCWD	#13 SFAD	Detection Limit
Aluminum	0.47	99.1	0.25	L	L	2.11	L	212	L	0.23	0.15
Barium	0.029	0.066	0.080	0.010	0.014	0.019	0.028	0.050	0.085	0.28	0.001
Boron	0.043	1.15	0.078	0.094	0.049	1.02	0.12	1.21	0.051	0.044	0.01
Calcium	12.8	245	4.07	0.37	30.9	15.3	17.3	235	11.9	3.43	0.01
Copper	0.016	1.40	0.029	L	L	0.053	L	2.40	0.023	0.039	0.015
Iron	1.45	1850	0.35	0.52	2.18	4.90	0.079	2700	0.23	0.52	0.030
Magnesium	3.66	30.4	0.29	0.057	10.4	4.76	4.26	156	3.76	0.70	0.001
Manganese	0.020	6.75	0.014	0.007	0.041	0.031	0.007	11.7	0.005	0.014	0.003
Phosphorus	16.8	22.0	1.34	41.1	6.66	5.16	L	254	L	3.90	0.4
Potassium	3.62	3.44	0.40	1.98	8.70	30.0	1.37	2.51	1.02	0.59	0.01
Silicon	27.6	30.1	4.82	18.8	30.9	17.3	12.4	45.0	11.7	8.12	0.08
Sodium	78.3	140	11.8	170	16.7	71.7	19.1	113	5.90	20.0	0.2
Strontium	0.063	2.63	0.016	0.005	0.17	0.11	-	1.65	0.058	0.014	0.001
Titanium	0.011	0.11	0.007	L	L	0.017	0.014	0.080	L	0.008	0.006
Zinc	0.77	8.75	0.32	L	3.11	0.38	L	5.10	0.041	0.18	0.015

L = Below detection limit

**TABLE 9. PARTICULATE MEASURED BY HIGH VOLUMES
AT THE SRC PILOT PLANT**

<u>Location Indicator</u>	<u>Location</u>	<u>2-12-79 (stormy) $\mu\text{g}/\text{m}^3$</u>	<u>2-15-79 $\mu\text{g}/\text{m}^3$</u>
A	Ground level 04 area	116.0	54.3
B	E side - 5' north of guard shack	21.2	31.6
C	W side - 300' north of generator	30.0	47.8
D	200' SW of flare tower	18.0	19.8
E	75' SW of 091 shack	9.1	23.3
F	Outside fence - 091 area	21.5	26.4
G	Outside fence - south 082 area	23.4	22.7
H	Outside fence - south 01 area	20.2	26.0

Location of the eight high-volume air samplers is shown in Figure 8. Numbers next to the location numbers are the measured concentration of particles in micrograms per cubic meters of air passing through the instrument. Values are the mean of two measurements. The first measurements were obtained February 12, 1979. That evening a severe windstorm damaged power lines and shut down the plant. This storm resulted in the shutdown of the high-volume samplers after approximately 18 hr of operation. A 24-hr operation of the high-volume samplers was obtained February 15 and 16, 1979. Comparison of the data obtained from these two periods of field measurement, shown in Table 10, indicates similarities. During the stormy period, the high-volume sampler near the center of the SRC pilot plant recorded more than twice the concentration of particulates. A definite plume structure toward the northeast is indicated from the mean data plotted on Figure 8.

Analysis by liquid chromatography of the middle and heavy distillates, which are the products of the SRC-II facility, is shown in Figures 9 and 10.

CONCLUSION

Evaluation of the data analyzed at this time indicates rough establishment of priorities

for the wastewater streams associated with an SRC-II pilot plant operation. The most potentially toxic waste stream is the recycle process water tank. Establishment of initial priorities for the wastewater stream is shown in Table 11.

One important fact is demonstrated by preliminary analysis of the samples obtained from the SRC pilot plant: that large variations in chemical concentrations, and perhaps even their existence, occur during minor shifts in operating conditions. Thus, a single grab sample reveals very little about the chemicals or concentrations that can exist in a waste stream from an SRC plant. In order to evaluate changes in wastewater constituents, detailed information is required on operating conditions and changes in coal type, feed rate, temperature, pressure, and other physical parameters.

Extrapolation of data to different operating conditions or to other modes of operation is meaningless at this time. A complete set of nearly identical samples must be obtained and analyzed under the SRC-I mode of operation.

Ordering priorities for the wastewater stream for the SRC-II mode appears to indicate that the following should be evaluated under EPA's Level 3 criteria:

- Recycle process water,
- Sulfur area drain,
- Wastewater treatment plant inflow, and
- Wastewater treatment plant effluent.

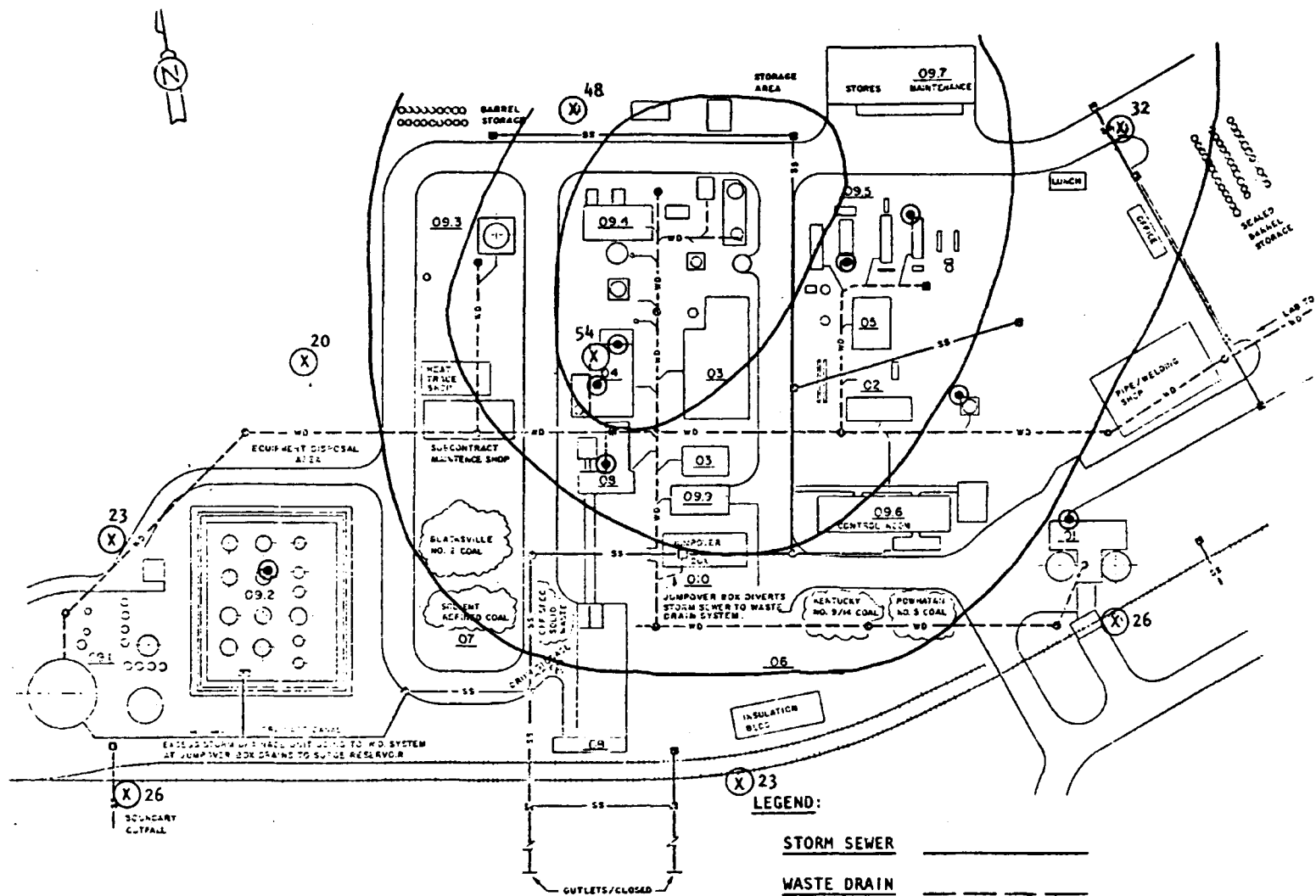


Figure 8. High-volume locations and 24-hr values.

TABLE 10. EMISSION FROM VENT AT THE SRC PILOT PLANT

Sample Site #	Date Taken	pH	NO ₃ ⁻ (mg/l)	Cl ⁻ (mg/l)	Field Analysis		NH ₃ (mg/l)	Conductivity (μmho/cm)
					HS ⁻ (mg/l)	CN ⁻ (mg/l)		
1	2/11	9.65	1.93	74.0	<0.1	0.09	0.1	298
Coal Process Area Drain	2/12	11.80	2.83	35.0	0.5	0.80	0.1	3550
	2/15	10.30	2.20	100.0	1.0	1.50	0.2	793
	2/16							
	2/17	8.20	0.55	6.0	1.0	0.50	0.1	260
2	2/11	2.45		<1.0	<0.1	<0.09	0.1	5900
Coal Storage Area Drain	2/12							
	2/15	1.85	<0.10	<1.0	<0.1	<0.10	0.1	18900
	2/16	1.95	<0.10	27.0	<1.0	<0.10	0.1	11800
	2/17	1.90	<0.10	2.0	<1.0	<0.10	0.1	8400
3	2/11	7.80	2.33	<1.0	<1.0	0.09	0.4	101
Dissolver/ Separator Area Drain	2/12	8.60	0.67	<1.0	0.3	0.10	0.1	99
	2/15	7.25	0.54	23.0	<0.1	<0.10	0.5	146
	2/16	10.70	0.30	52.0	<1.0	<0.50	0.1	3550
	2/17	9.35	1.76	2600.0	<1.0	0.50	0.4	2150
4	2/11							
Sulfur Recovery Area Drain	2/12	9.60	<0.10	730.0	8.0	9.30	5.0	281
	2/15	9.30	<0.10	>100000.0	<0.1	570.00	27.0	13900
	2/16	8.60	<0.10	38300.0	1.1	1700.00	6.4	16500
	2/17	8.25	<0.10	>100000.0	26.0	93.00	14.0	7450
6	2/11							
Recycle Process Water Tank	2/12	9.05	21.20	>100000.0	2200.0	1400.00	8840.0	143000
	2/15	8.90	6.51	>100000.0	800.0	672.00	300.0	10600
	2/16	9.00	<0.10	>100000.0	16700.0	5700.00	3200.0	130000
	2/17	8.85	<0.10	>100000.0	817.0	1300.00	1200.0	100000
7	2/11	11.55	<0.10	7.2	<0.1	0.13	0.1	1670
Boiler Blowdown	2/12							
	2/15	11.60	4.88	115.0	1.0	1.30	1.6	3080
	2/16							
	2/17	11.40	0.09	2300.0	<1.0	0.20	0.5	2350
8	2/11	6.25	2.29	34.0	<0.1	0.09	0.2	469
Cooling Tower Basin	2/12							
	2/15	6.55	1.30	12.0	0.1	<0.10	0.1	3080
	2/16							
	2/17	7.10	0.87	33.0	<1.0	0.10	0.4	257
9	2/11	8.80		55.0	1.9	8.83	100.0	1200
Wastewater Treatment Plant Influent	2/12	8.60	<0.10	755.0	2.1	3.00	6.0	281
	2/15	7.80	1.39	8600.0	0.6	0.60	<0.1	3080
	2/16		0.03	2430.0	<1.0	18.00	10.2	5900
	2/17	7.50	<0.10	193.0	<1.0	0.80	0.5	328
10	2/11	7.20	<0.10	5.6	<0.1	0.16	11.5	316
Wastewater Treatment Plant Effluent	2/12	7.10	0.33	12.0	<0.1	0.30	15.0	257
	2/15	7.25	0.27	148.0	0.2	<0.10	10.5	257
	2/16	7.05	0.01	11300.0	<1.0	6.00	7.9	1900
	2/17	7.90	<0.01	580.0	<1.0	0.40	11.0	228
11	2/11	2.50		<1.0	<0.1	<0.09	0.3	6950
Drain from Blacktop Area	2/12							
	2/15	2.30	<0.10	<1.0	<0.1	<0.10	0.1	12970
	2/16							
	2/17	2.50	0.50	<1.0	<0.1	<0.10	<0.1	3900
12	2/11	7.05	0.92	12.0	<0.1	0.11	0.6	128
Sandvick Belt Cooling Water	2/12	7.15	0.60	<1.0	<0.1	<0.10	<0.1	151
	2/15	7.50	0.47	<1.0	<0.1	<0.10	0.2	163
	2/16	7.05	0.27	4100.0	<0.1	1.00	4.3	144
	2/17	7.40	0.75	12.0	<0.1	0.20	0.2	157
13	2/11	8.60	1.49	15.0	<0.1	2.18	5.6	193
Solvent Fractionation Area Drain	2/12	6.85	<0.10	180.0	2.3	8.20		104
	2/15	7.45	<0.10	340.0	9.0	<0.10	6.0	151
	2/16	7.25	<0.10	275.0	<1.0	2.40	4.0	107
	2/17	6.85	0.58	933.0	<1.0	0.70	0.5	146

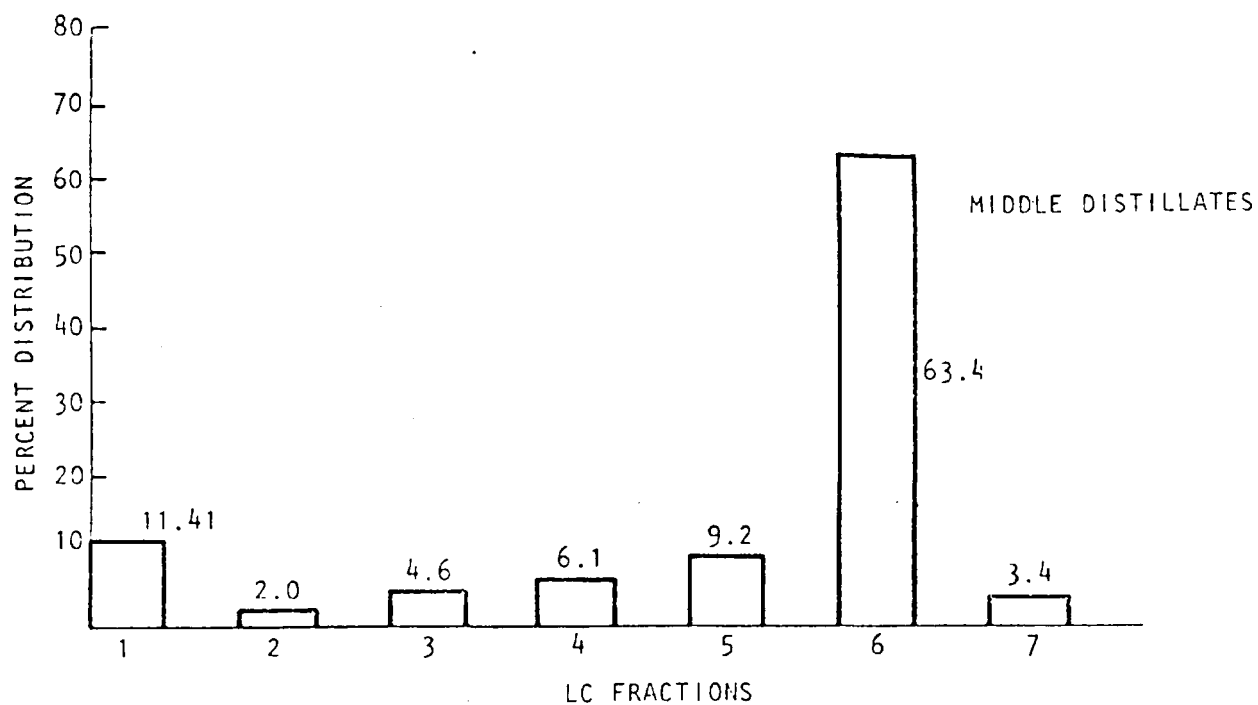


Figure 9. Relative distribution of total organics in seven LC fractions.

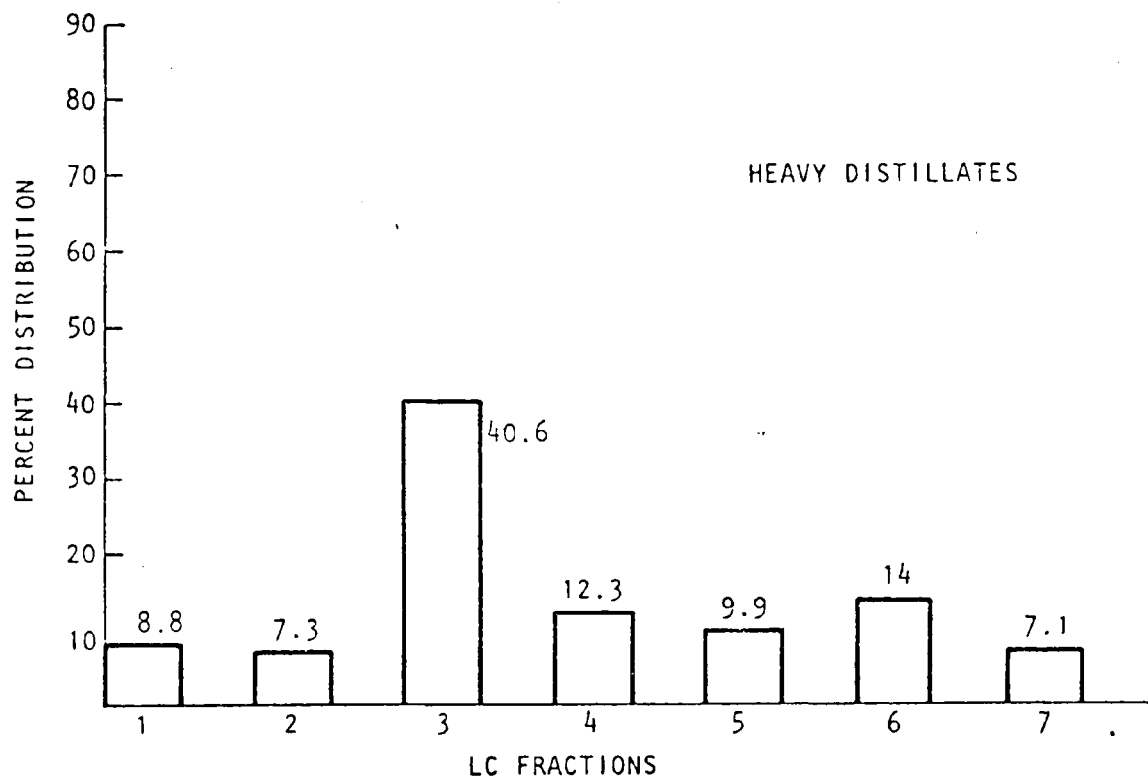


Figure 10. Relative distribution of total organics in seven LC fractions.

**TABLE 11. ESTABLISHING PRIORITIES FOR WASTEWATER STREAMS
FROM SRC PILOT PLANT**

Order	Stream
1	Recycle process water tank
2	Sulfur recovery area drain
3	Wastewater treatment plant inflow
4	Wastewater treatment plant effluent
5	Coal storage area drain
6	Drain from general surfaced area
7	Coal preparation area drain
8	Dissolver/separator area drain
9	Solvent fractionation area drain
10	Boiler blowdown
11	Sandvik belt water
12	Cooling water

In addition, the flare knockout drum water was not sampled because of operational difficulties and should be evaluated for potential toxic substances.

ACKNOWLEDGMENTS

Information for this paper was compiled from work performed by Hittman Associates, Inc., under EPA Contract Number 68-02-2162. This work has been guided and supported by EPA's Fuel Process Branch of the Industrial Environmental Research Laboratory at Research Triangle Park, N.C.

REFERENCES

1. *Coal Liquefaction* (quarterly report). U.S. Energy Research and Development Administration. Washington, D.C. ERDA 76-33-4. October-December 1975.
2. Koralek, C.S., and S. S. Patel. *Environmental Assessment Data Base for Coal Liquefaction Technology, Volume I, Systems for 14 Liquefaction Processes*. U.S. Environmental Protection Agency. EPA-600/7-78-184a. September 1978.
3. Lentzen, D. E., D. E. Wagoner, E. D. Estes, and W. F. Gutkneck. *IERL-RTP Procedure Manual: Level 1 Environmental Assessment Draft*. (second edition). U.S. Environmental Protection Agency. EPA-600/7-78-201. January 1979.
4. Duke, K. M., M. E. Davis, and A. J. Dennis. *IERL-RTP, Procedure Manual: Level 1 Environmental Assessment Biological Tests for Pilot Studies*. U.S. Environmental Protection Agency. EPA-600/7-77-043. April 1977.
5. Harris, J. C., and D. L. Levin. *EPA/IERL-RTP Interim Procedures for Level 2 Sampling and Analysis of Organic Materials*. U.S. Environmental Protection Agency. EPA-600/7-78-016. February 1978.
6. Ferretti, E. J. Coal Liquefaction Gains Prominence. *Coal Mining and Processing*. 13(2). February 1976.
7. Schmid, B. K. Status of the SRC Project. *Chemical Engineering Progress*. 71(4). April 1, 1975.

8. *Solvent Refined Coal (SRC) Process—Development of a Process for Producing an Ashless, Low-Sulfur Fuel from Coal*. U.S. Energy Research and Development Administration. Report Number 52. 1977.
9. Goldstein, D. S., and D. Yoring. *Water Conservation and Pollution Control in Coal Conversion Processes*. EPA Industrial Environmental Research Laboratory. Research Triangle Park, N.C. EPA-600/7-77-065. June 1977.
10. Ghassemi, M., et al. *Applicability of Petroleum Refinery Control Technologies to Coal Conversion*. EPA Industrial Environmental Research Laboratory. Research Triangle Park, N.C. EPA-600/7-78-190. October 1978.
11. Manual on Disposal of Refinery Waste. In: *Volume on Liquid Wastes*. American Petroleum Institute, 1969.

ENVIRONMENTAL ASSESSMENT OF SRC-II—AN UPDATE

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Abstract

This paper describes the activities that have been undertaken, as well as future environmental activities that will occur in the succeeding phases of the 6,000 T/D SRC-II Coal Liquefaction Demonstration Project. This plant will be built in the Morgantown, West Virginia area under sponsorship of the U.S. Department of Energy (DOE).

Currently, the phase is characterized by efforts in two main areas:

- 1. Collection of baseline data for incorporation into an environmental impact statement. A brief description of our data-gathering effort is given with special attention to:*
 - Results from the air-monitoring station, especially regarding the ozone attainment/nonattainment status in the area.*
 - Existing levels of PNAs in soils, ambient suspended particulate matter, groundwaters, and surface waters/sediments in the Monongahela River and the various tributaries that traverse the project site.*
 - Expected impact of the project on the existing socioeconomic climate of the region.*
- 2. Identification of the following anticipated major environmental concerns of the project:*
 - Current plans for the onsite disposal of approximately 800 T/D of a potentially hazardous waste.*
 - Industrial hygiene and potential health effects of the plant. A medical surveillance program for plant workers and the status of the toxicology programs for SRC-II (solvent refined coal) products and intermediate streams will be addressed.*
 - Consumptive use of water and its impact*

on the Monongahela River.

- Status of combustion tests on SRC-II product oil and anticipated environmental concerns of its use.*

INTRODUCTION

Increased use of America's coal supplies is not only a goal of the National Energy Policy but also a highly desirable fuel supply alternative for the electric power-generating industry. Unfortunately, conversion from fuel oil to coal is not only expensive but prohibited in certain regions of the country because of existing and proposed environmental regulations. We are all familiar with the U.S. Environmental Protection Agency's (EPA) proposed regulations of 85 percent sulfur removal for the utility industry. The economic consequences of this removal rate are formidable, with estimates ranging around \$800 to \$1,000/ton of SO₂ removed.

The objective of the SRC-II project is to use our coal reserves to provide a liquid fuel that is competitive with petroleum-derived boiler fuel, both environmentally (low sulfur and low ash) and economically. Longer range utilization of SRC-II products could include heating oils, gasoline, and feedstocks for chemical production.

HISTORY

In July of 1978, the U.S. Department of Energy (DOE) entered into a contract with the Pittsburg & Midway Coal Mining Company to undertake a conceptual design of demonstration plant. This plant would have a coal feed rate of 6,000 T/CD and produce the equivalent of 20,000 bbl/d. Table 1 traces part of the historical development of the process that led to this contract.

*Speaker.

**TABLE 1. HISTORICAL DEVELOPMENT OF THE
SRC-II PROCESS**

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- 1965 - Technical feasibility of Solvent Refined Coal is proven by Spencer Chemicals under sponsorship of the Office of Coal Research.**
- 1972 - The Pittsburg & Midway Co. is contracted by DOE to construct a 50 T/D pilot plant at Ft. Lewis, Washington.**
- 1974 - Start-up of pilot plant.**
- 1978 - DOE contracts The Pittsburg & Midway Coal Mining Co. to undertake:**
- Conceptual design of a 6,000 T/CD Demonstration Plant**
 - Marketability and economic assessments**
 - An Environmental Analysis of the plant site including the defining of all air, liquid and solid waste emissions.**
-
-

PROCESS DESCRIPTION

Figure 1 shows the location of the proposed demonstration plant site, approximately 5 mi north of Morgantown and bordering on the west side of the Monongahela River. The location of the meteorological and air quality monitoring station (MAQS), which is actually in Pennsylvania, is indicated by a star on the figure.

Figure 2 shows a schematic flow diagram of the process. The feed, a typical high-sulfur Pittsburgh seam coal, is mixed with a recycle slurry produced by the process. Hydrogen enters the coal-slurry mixture and is pumped through a preheater to the reactor where the coal is dissolved and hydrocracked.

The effluent from the reactor enters a series of vapor-liquid separators. The light process gases containing hydrogen, H_2S , and CO_2 are sent through an acid-gas removal system followed by a cryogenic unit to separate the hydrogen that is recycled to the process. The hydrocarbon gases are refined into a methane, ethane, propane, and mixed C_4 product streams.

The light liquid stream is fractionated into a naphtha product (C_5 -350° F and End Point) and a middle distillate (350° to 600° F). The product slurry is split so that part is recycled to the front end to be mixed with the feed coal. The other portion is sent to vacuum distillation where a heavy distillate is produced and mixed with the middle distillate from the atmospheric tower. These two streams (heavy and middle distillates) comprise the final SRC-II fuel oil product.

The vacuum tower bottoms are sent to a high-pressure slagging gasifier for production of synthesis gas, a mixture of hydrogen and carbon monoxide. Part of this gas is catalytically reacted with steam (water gas shift) to reproduce hydrogen. The other part of the synthesis gas is treated to remove acid gases and is used for plant fuel.

The temperatures in the gasifier are sufficient to liquefy the mineral matter in the feed. This molten ash is cooled and solidified by a water quench and, after appropriate dewatering steps, is sent to the ash disposal area located onsite. Approximately 800 T/CD of slag will be produced by the plant.

BASELINE COLLECTION EFFORT

The main objective of any demonstration plant must be that all aspects of the project are investigated to determine their feasibility for commercialization. These aspects include not only engineering technology, economics, and marketability of products, but also the environmental acceptability of the technology and its products. If a demonstration project does not adequately address all these issues, it has not accomplished its objectives.

Before one can characterize the environmental impacts, it is necessary to undertake extensive environmental baseline monitoring. This, plus the post-operational monitoring, will facilitate scientifically sound conclusions regarding these impacts and provide a firm foundation on which to judge the impacts of a commercial plant.

A brief summary of the baseline collection effort underway at Morgantown is presented in Tables 2 through 7. During establishment of a detailed work plan for this effort, two objectives were of prime concern:

- That sufficient data be collected on the existing environment to comply with the requirements of NEPA documents and permits; and
- To characterize aspects of the environment that the plant might affect so that the post-operational monitoring would logically continue from the baseline data collection effort.

Only at the demonstration phase of any fuel conversion technology development can real environmental issues be quantified and judgments made regarding the environmental acceptability of the process.

RESULTS OF BASELINE DATA COLLECTION

Currently, the data collection effort is approximately 75 percent complete. It is anticipated that all sampling, analyses, and compilation of data will be complete for inclusion in the draft EIS scheduled for January 1, 1980. DOE plans to issue the final EIS in July 1980.

In this section, no attempt will be made to list

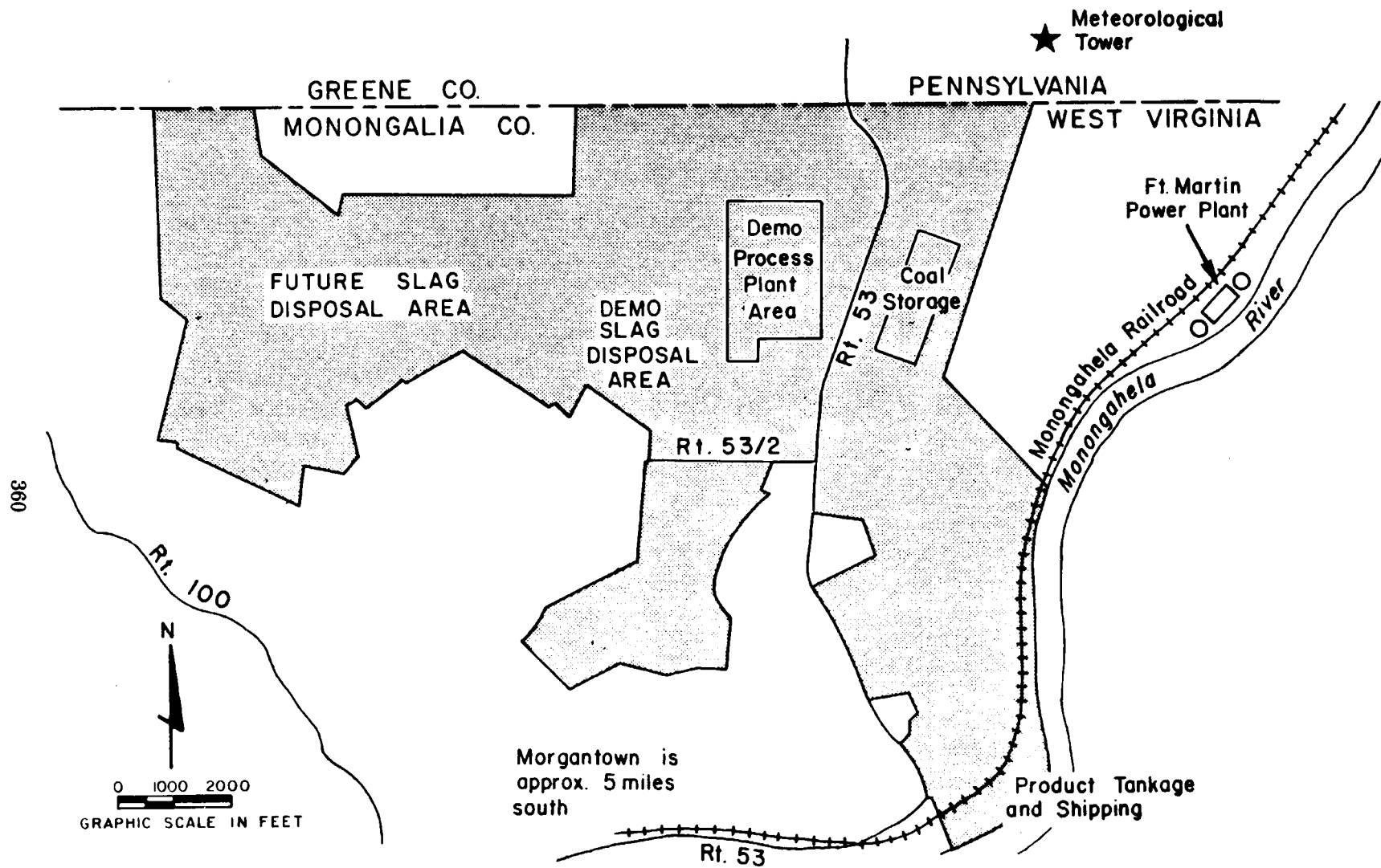


Figure 1. Proposed site for SRC-II demonstration plant.

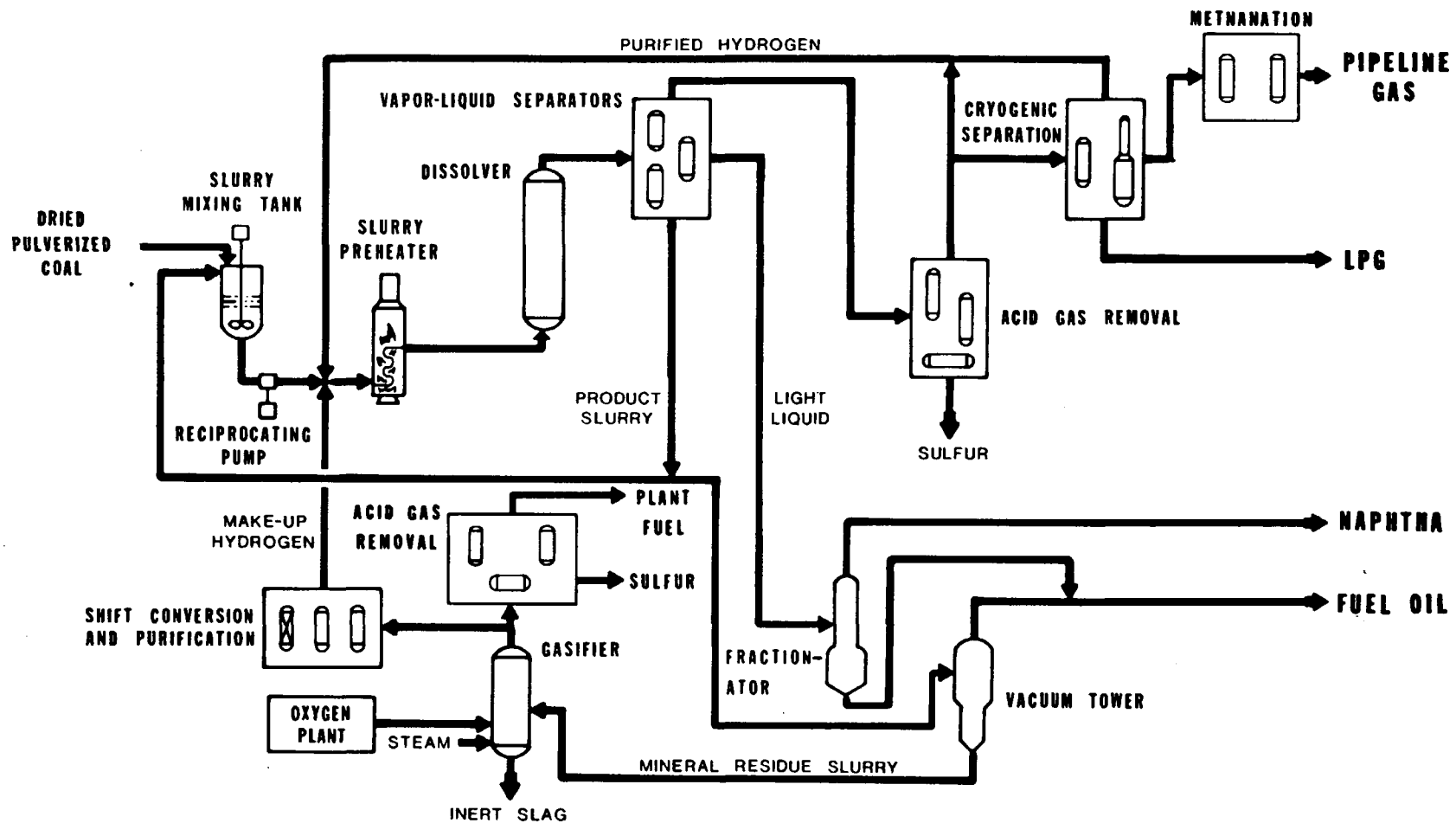


Figure 2. SRC-II process.

TABLE 2.

(1) Collect one-year of meteorological data utilizing the 60-meter meteorological tower located near the Morgantown site.

362 **(2) Collect one-year of air quality data for SO₂, NO_x, O₃, NMHC, CO, total suspended particulates (every third day). On a quarterly (seasonal) basis, analyze collected particulate matter for various trace metals (approximately 70 elements) and trace polynuclear aromatic hydrocarbon (four PNA's have been selected that have been historically used as "indicator" compounds of possible carcinogenic activity.)**

TABLE 3.

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-
- (1) Make quarterly analyses of surface waters near the site: Monongahela River (three stations), Robinson Run (two stations) and Crooked Run (three stations). In addition to the "standard" water quality parameters, e.g., COD, BOD, TSS, pH, dissolved oxygen, TOC, O&G, TDS, etc., trace metals and polynuclear aromatics concentrations are also being determined.**
- (2) The same analyses, except BOD, are being conducted on groundwater samples taken from four existing wells near or on the plant site.**
- (3) A hydrogeology study involving six drill holes will be conducted in the slag disposal and coal storage and preparation areas to determine:**
- Rock identification**
 - Potential seepage rates and pathway identification**
 - Depth to nearest aquifer**
 - Piezometer measurements**
 - Ability of existing clay to prevent seepage from ash disposal**
 - Logs of all holes and cores**
-
-

TABLE 4.

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-
- (1) Seasonal studies to qualitatively analyze the existing plant communities.**
Included in this work is species inventory, plant community identification, construction of vegetation maps, and examination for unique, rare, and proposed special-status plant species.
- (2) Seasonal sampling and observation of existing wildlife at the site via live-trap transects, mist nets, and vehicular and walking transects.**
- (3) Sample aquatic flora and fauna quantitatively and qualitatively at three stations on the Monongahela River and two on Crooked Run. Under investigation will be such groups as fish, macroinvertebrates, zooplankton, and phytoplankton.**
-
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TABLE 5.

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-
- (1) Conduct a study to identify the existing relationship between population, economy, land use, and the demand for public and private utilities, services, and facilities in Morgantown and neighboring communities. A labor availability study will be conducted, as well as an evaluation of the adequacy of the present roads and highways.**
- (2) Conduct a study of the possible presence of cultural resources (historical/ archaeological) within the 2600-acre area.**
-
-

TABLE 6.

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-
- (1) Characterization and mapping of soils present within the project as area boundaries will be conducted. Trace metals and polynuclear aromatics will also be analyzed in the soils and in sediments collected from the Monongahela River (two stations) and at the mouths of Robinson and Crooked Runs.
- (2) A revegetation plan for the solid waste disposal area will be developed to satisfy West Virginia solid waste regulations. Stabilization considerations will include both material and procedural aspects of top soil handling, seedbed preparation, seeding, application of soil amendments, mulching and maintenance.
-
-

TABLE 7.

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- (1) Conduct two noise surveys (one winter and one summer) to establish existing noise levels at established measuring points.**
 - (2) Sampling for ichthyoplankton (fish larvae) will be conducted during spawning times to assess the environmental affects of the raw water intake structure.**
-

in detail all results of the data collection; rather, only issues judged to be environmentally significant will be discussed.

Air

Table 8 summarizes the data collected in the first 3 mo of the program. Of particular note is the fact that the mean nonmethane hydrocarbon (NCHC) value for the 3-mo period is essentially twice the EPA guideline. This is not considered unusual for heavily wooded areas such as the Morgantown site. Sulfur dioxide values average about 7 percent of the National Ambient Air Quality Standard (NAAQS), although few data have been obtained with SE wind direction (i.e., the direction of a major source of SO_2 in the area — an electrical power-generating station).

The maximum 1-hr concentration for ozone was 0.115 ppm, only slightly below the new NAAQS of 0.12 ppm. This level was observed in September (the only month that the instrument operated properly). Of the 595 hourly observations, 16 (2.6 percent) exceeded the old 1-hr NAAQS of 0.08 ppm. We see this as a potential problem in that the theory of photochemical oxidant formation suggests that the highest levels will be observed during the hottest months of the year. Consequently, the exact situation regarding ozone will not be known until summer data are collected. This area of Pennsylvania was previously listed as a nonattainment area. A new designation, if any, has not been published in the *Federal Register*. All other aspects of air quality are well within the NAAQS.

Table 9 shows the data that have been obtained on the background levels of polynuclear aromatics. These analyses are performed at Gulf Science & Technology on the particulate matter collected by high-volume air samples. While no Federal or State standards exist for these materials, the values are judged to be quite low. We envision these analyses to be a very important part of the post-operational monitoring program.

A composite of the particulate material collected on four high-volume filters was analyzed for trace element concentrations using mass spectrographic and atomic absorption techniques. Table 10 shows some of the data resulting from these analyses. Of the elemental

concentrations, silicon, aluminum, copper, calcium, and potassium represented the major constituents. However, the concentrations of these five elements were within the ranges normally observed in the atmosphere. Of the toxic elements, only copper was slightly above normal background levels. Beryllium, chromium, fluorine, lead, molybdenum, and selenium were all within normal ambient ranges while arsenic, cadmium, mercury, nickel, vanadium, and zinc were below normal measured ranges.

West Virginia has no ambient standards for trace elements. EPA has only a standard for lead of $1.5 \mu\text{g}/\text{m}^3$, 3-mo average.

Pennsylvania has ambient standards for the following trace elements:

Element	Allowable Concentration
Lead	$5 \mu\text{g}/\text{m}^3$, 30-day mean
Beryllium	$0.01 \mu\text{g}/\text{m}^3$, 30-day mean
Sulfates	$10 \mu\text{g}/\text{m}^3$, 30-day mean
Fluoride	$5 \mu\text{g}/\text{m}^3$, 24-hr mean

The measured concentrations of lead, beryllium, and fluoride were within these ambient standards, while the sulfate concentrations slightly exceeded the standards.

In terms of expected SO_2 emission from the demonstration plant, Table 11 shows the results of some preliminary dispersion calculations. The table also shows the corresponding PSD allowable increments. There are potentially 12 sources of SO_2 in the plant, but by far the major source is the incinerator on the sulfur recovery system. Current plans are to use a combination of Claus unit and Super-Scot tail gas cleanup unit.

During normal operations, all nonmethane hydrocarbons within the process will be within a completely enclosed system with vapor recovery systems on all storage tanks and vessels. The only source of fugitive emissions will be leakage losses from valves, flanges, etc. If measured according to the EPA's publication, AP-42, "Guideline for Emission Factors," these leakage emissions of total hydrocarbons from the SRC-II Demonstration Plant will be 28 lb per 1,000 barrels of liquid hydrocarbon product. With 16,058 barrels of liquid hydrocarbon products per day and 88.1 MM SCF (million standard cubic feet) per day of gaseous product, fugitive hydrocarbon emissions are estimated to be 450 lb/day, 18.7 lb/hr, or 2.36 g/s. Because some por-

TABLE 8. SUMMARY OF BACKGROUND AIR QUALITY DATA
(PPM)

<u>POLLUTANT</u>	<u>OBSERVED LEVELS</u>	<u>NAAQS</u>
Sulfur Dioxide	3-hr. Max. = 0.044	0.500 (Secondary)
	24-hr. Max. = 0.012	0.140
	3-Month Mean = 0.002	0.030 Annual
Nitrogen Oxides	24-hr. Max. = 0.03	
	3-Month Mean = 0.01	0.05 Annual
Carbon Monoxide	1-hr. Max. = 2.35	35.0
	8-hr. Max. = 1.37	9.0
Ozone	1-hr. Max. = 0.115	0.12
NMHC	3-Month Mean = 0.5	0.24 Guideline
Particulate Matter	24-hr. Max. = 114 $\mu\text{g}/\text{m}^3$	260 $\mu\text{g}/\text{m}^3$
	3-Month Mean = 49 $\mu\text{g}/\text{m}^3$	75 $\mu\text{g}/\text{m}^3$ Annual

TABLE 9. AMBIENT LEVELS OF POLYNUCLEAR AROMATICS

<u>COMPOUND</u>	<u>CONCENTRATION ($\mu\text{g}/\text{m}^3$)</u>
Benz(a)Anthracene	0.000458
Benz(a)Pyrene	0.001044
Benz(e)Pyrene	0.000027
Benz(g, h, i)Perylene	(none found)
Pyrene	0.000516

TABLE 10. TRACE ELEMENTS

<u>ELEMENT</u>	<u>CONCENTRATION ($\mu\text{g}/\text{m}^3$)</u>
Aluminum	1.26
Bromine	0.01
Calcium	0.46
Copper	0.59
Iron	0.30
Lead	0.09
Magnesium	0.25
Manganese	0.02
Mercury	0.0002
Phosphorous	0.16
Potassium	0.39
Silicon	2.06
Sodium	0.11
Sulfate	13.97
Sulfur	0.25
Tin	0.01
Titanium	0.05
Zinc	0.08

tion of the leakage hydrocarbon losses will be methane, leakage losses of nonmethane hydrocarbons will be somewhat less than this amount. The leakage losses for the SRC-II Plant will be less than this amount. The leakage losses for the SRC-II Plant will be less than losses from conventional gas plants and oil refineries.

No specific estimation for benzene release to the atmosphere has been made; however, such releases are expected to be less than releases in petroleum refineries. Analytical results on the SRC-II light oil (naptha) conducted at Gulf Research & Development and at independent laboratories have shown that the benzene content is less than 1.0 percent.

Water

In the area of surface water analyses, quarterly (seasonal) analyses are being made on the Monongahela River at three stations and on the various tributaries that traverse the plant site (i.e., Robinson Run, Crooked Run, and Crafts Run). Table 12 summarizes the summer and fall analyses. Rather than show the com-

TABLE 11. MAXIMUM GROUNDLEVEL SULFUR DIOXIDE CONCENTRATION ESTIMATES
SRC-II DEMONSTRATION PLANT

<u>EMISSION SOURCE</u>	<u>MAXIMUM SO² CONCENTRATIONS (ug/m³)</u>		
	<u>3-HOUR</u>	<u>24-HOUR</u>	<u>ANNUAL</u>
1	9.9	3.9	0.1
2	2.1	0.8	0.0
3	8.4	3.3	0.1
4	1.7	0.7	0.0
5	0.2	0.1	0.0
6	80.3	31.7	0.8
7	1.2	0.5	0.0
8	0.2	0.1	0.0
9	1.0	0.4	0.0
10	2.1	0.8	0.0
11	0.2	0.1	0.0
12	0.6	0.2	0.0
TOTALS	107.9	42.6	1.0
Federal PSD			
Class II Standards	512	91	20

TABLE 12. SUMMARY OF SUMMER AND FALL SURFACE WATER ANALYSES

pH	- exceeds existing and proposed criteria in Robinson and Crafts Run, August and November.
Arsenic	- exceeds existing and proposed criteria in Robinson Run, August.
Lead	- exceeds existing and proposed criteria in Robinson Run, November.
Manganese	- meets or exceeds the proposed criteria in every sample, August and November.
Iron (total)	- exceeds the proposed criteria in many of the tributary samples, August and November.
Phenols	- exceeds proposed criteria in Crooked Run, August.

plete list, the table indicates parameters that currently exceed proposed water quality criteria. Our sampling program has been modified to obtain additional data on these particular parameters and streams.

The polynuclear aromatic analyses of surface water is shown in Table 13. As in the case with ambient air levels of PNAs, we view the continuation of these analyses to be an important part of the post-operational monitoring.

In terms of the effect of the plant on water quality, current engineering design calls for zero discharge of liquid effluents. This is accomplished by (Table 14):

- Recycling of sour water after cleanup,
- Recycling of boiler and cooling tower blowdowns after evaporation,
- Recovery of process sewer water via an oil-water separation,
- Collection and processing of rainwater runoff resulting from a 10-yr 24 hr storm,
- Tertiary treatment of sanitary sewage, and
- Incineration of all sludges and solids obtained by these operations.

In addition, ammonia and tar acid recovery units will be an integral part of the plant design.

Consumptive use of water is a problem that all conversion plants must face. While it is not as severe a problem in the East as in some Western States, when a project consumes approximately 4,000 gal/min of water, there are environmental concerns that must be addressed. The U.S. Army Corps of Engineers has indicated that the Monongahela River can supply sufficient water for the project except during periods of extreme drought (e.g., droughts from the 1930's and 1950's. However, with the completion of Stonewall Jackson Dam, now under construction on the West Fork River, the Corps has indicated that ample water flow should be available not only for the demonstration plant but also for a full-size commercial plant.

Solid Wastes

By far, the largest volume of solid waste generated in the SRC-II demonstration plant will be the gasifier bottoms. This material, which amounts to approximately 800 ton/day, is expected to be very similar to the bottoms from a coal-burning facility. Analytical programs aimed at characterizing this material are underway at Oak Ridge National Laboratory, Battelle

(Pacific Northwest Laboratory), and Gulf's Research Laboratory in Harmarville, Pennsylvania. With no firm analytical data on the hazardous nature (as defined by the Resource Conservation & Recovery Act) of the waste material, current plans call for managing and disposing of the initial material according to the most restrictive regulations. If the analytical results obtained during the initial phase of demonstration plant operation show the material to be "non-hazardous," appropriate changes will be made to the disposal plans.

Health Effect

The overall development of the SRC process has included, in addition to the technical development of the process, various health programs, environmental studies, trace element studies, engineering studies, and product characterization and market development studies. The health programs under the SRC pilot-plant contract include an industrial hygiene monitoring program, an employee hygiene and education program, a medical surveillance program, and a toxicology program. Similar programs are anticipated for the SRC-II demonstration plant.

The principal objectives of the pilot plant health programs are:

- Protecting the workers from exposure to materials that could result in adverse health effects;
- Monitoring the worker environment to measure the extent and nature of exposure, both to safeguard health and to identify needs for additional engineering controls or process modifications; and
- Assessing the toxic characteristics of the SRC materials through extensive bioassay studies.

Process modification and control technology needs identified in the pilot plant can be incorporated in the demonstration plant.

Only limited prior experience is available in the area of hydroliquefaction of coal. Similar technology was practiced in Germany during and prior to World War II with a maximum of 12 plants operated; peak production was about 100,000 bbl/d of distillate products. Little health information was obtained from these operations. Union Carbide operated a 300-ton per day coal liquefaction plant at the Institute of West Virginia, from 1952 to 1956. Elevated levels of

TABLE 13. POLYNUCLEAR AROMATIC CONTENT OF SURFACE WATERS
(PPT)

	<u>Benz(a) Anthracene</u>	<u>Benz(a) Pyrene</u>	<u>Benzo(e) Pyrene</u>	<u>Benzo(g,h, i) Perylene</u>	<u>Pyrene</u>
374 Robinson Run	0.0	0.0 - 0.4	0.0	0.0	2.0
Crooked Run	0.0 - 39.0	0.0 - 3.0	0.0	0.0	43.0
Crafts Run	0.0 - 34.0	0.0 - 7.0	0.0	0.0	24.0
Monongahela River	0.0	0.0 - 0.5	0.0	0.0	11.0 -28.0

TABLE 14. WASTEWATER TREATMENT

-
- (1) Recycling sour water after cleanup.**
 - (2) Recycling boiler and cooling tower blowdowns after evaporation.**
 - (3) Recovery of process sewer water via an oil-water separator.**
 - (4) Collection and processing of the quantity of rainwater runoff equivalent to the 10-year 24-hour flood.**
 - (5) Tertiary treatment of sanitary sewage.**
 - (6) Incineration of all sludges and solids obtained by these operations.**
-

skin cancer were observed in the Institute plant population.¹ Many precautionary measures of the health programs at the SRC pilot plant were designed based on the Institute experience.

Industrial Hygiene Monitoring Program—

A two-phase industrial hygiene program was designed and implemented at the SRC pilot plant. The first phase was an intensive data-gathering effort. Following the data gathering and interpretation, an ongoing monitoring program was begun to document the continuation of the low exposure levels observed during the initial phase and to alert plant personnel to increased exposures from equipment failures or process modifications. Findings of the monitoring program may indicate the need for additional engineering controls of process modifications in the pilot plant or in subsequent plants.

Table 15 summarizes the principal studies under the industrial hygiene monitoring program and reports typical findings during SR-I and SRC-II operation. The results of these studies indicate, in general, low worker exposures. Details of these studies have been reported elsewhere.^{2,3} Monitoring and characterization development work is underway in two areas: the development of accurate and reproducible measurements of particulate polycyclic aromatic hydrocarbons, as benzene solubles;⁴ and quantification of dermal exposure.

Results of the pilot-plant industrial hygiene monitoring program will be directly useful in planning and implementing appropriate programs in the SRC-II demonstration.

Employee Personal Hygiene and Education—

The pilot-plant employee personal hygiene and educational program has two major objectives:

- To inform the employee of the known and potential hazards in the work environment, particularly those associated with exposure to coal-derived materials, and to motivate the employee to use the protective measures available; and
- To provide the employees with protective equipment, clothing, facilities, and techniques needed to minimize the potential hazard.

The employee educational program consists of new employee orientation and continuing education. The new employee orientation consists of an audiovisual slide presentation describing the plant, potential exposures in the plant, and appropriate protection techniques. After the slide presentation, the new employee is given the *SRC Health Protection Manual* and required to read it. Then the employee is taken through the locker room change house area and shown the proper entrances and exits within the area, proper disposition of soiled clothing, and proper storage of clean work clothing and street clothes. Similar training is anticipated for the SRC-II demonstration plant staff.

Each process area employee is issued rubber boots and/or leather safety shoes, work uniforms, underclothing, socks, work coats, hard hats, barrier creme, and skin emollient. Employees working in areas of possible exposure are required to wear the company-supplied clothing, shoes, and appropriate safety equipment.

Pilot-plant employees are required to change into the company-supplied clothing before going into the work area and to remove that clothing, shower, and change to their street clothing before leaving after their shift. To change, facilities are divided into clean areas, dirty areas, and shower areas to minimize contamination of individuals and clothing. These procedures have been discussed in detail elsewhere.^{2,3}

Experience gained in the pilot plant, together with the available results from the toxicology program and estimates of potential exposures from the SRC-II demonstration design effort, will be used to develop appropriate protective clothing and personal hygiene programs for the SRC-II demonstration plant.

Medical Surveillance Program—

Each process-explored employee at the pilot plant is given a detailed preemployment medical examination and an annual followup examination. This is supplemented by a quarterly skin examination by the plant nurse and the referral of observed skin problems to a dermatologist.

The preemployment and annual examinations consist of a medical history, a complete physical examination, a complete blood count, blood chemistries, urinalysis, chest X-rays, and careful examination of the skin for evidence of lesions. Pulmonary function tests are performed

**TABLE 15. SOLVENT-REFINED COAL PILOT-PLANT MAJOR INDUSTRIAL
HYGIENE STUDIES AND TYPICAL RESULTS**

	<u>OPERATION</u>	
	<u>SRC-I</u>	<u>SRC-II</u>
Airborne Organic Vapors, ppm	<0.1	< 0.1
Benzene Vapor, ppm	<<1	<<1
Total Suspended Particulates, mg/m³	~ 0.7	~ 0.6
Asbestos Fibers, fibers/ml	<0.1	*
Hydrogen Sulfide, ppm	Trace	Trace
Sulfur Dioxide, ppm	≤0.04	≤ 0.04
Phenolic Vapors, ppm	<0.008	< 0.008

*** No asbestos used in plant during SRC-II operation.**

by a plant nurse. A detailed description of the program has been previously presented.²

Evaluation of the findings of the medical surveillance program has indicated no discernible changes in the medical profiles of the exposed employees. The only known occupational health problems encountered at the SRC pilot plant are mild transient dermatitis from skin contact with coal-derived materials. Table 16 summarizes medical observations during the period of pilot-plant generation.

The most common medical problem has been eye irritation with 50 to 60 cases, approximately 10 of which involved substantial quantities of coal-derived solvents contacting the employees' eyes. In all cases, these eye irritations responded satisfactorily to first aid treatment consisting of eye irrigation with saline solution. Followup medical examination by an ophthalmologist confirmed the absence of any prolonged or permanent eye damage. The strongly irritating characteristic of the lower boiling fractions of SRC liquids is attributed to their phenolic content.

About 25 cases of transient erythema and multiple cases of mild folliculitis (mechanics' acne) have been observed. These cases have responded well to temporary suspension of exposure.

One employee developed a squamous cell cancer of the lower lip. The employee had previously worked 9 yr in a petroleum refinery and was a cigarette smoker. The Washington State Board of Industrial Insurance Appeals determined that the cancer was not related to his employment in the SRC pilot plant.

The present experience with the SRC pilot-plant employee population has not revealed any of the problems experienced at the Institute plant population, where 60 skin lesions were excised from a group of 359 coal hydrogenation workers during a 5-yr period.¹ The intensive employee health programs, functioning at the SRC pilot plant essentially since startup, seem to account for the major differences between the plants. Similar continuing medical surveillance of process-exposed personnel will be implemented at the SRC-II demonstration plant.

Toxicology Program—

In early 1975, a toxicology program on SRC-I

materials was recommended to ERDA. The proposed work included various acute and subacute tests and chronic skin painting studies. The scope of work was subsequently expanded to include chronic inhalation studies and teratogenic studies. Animal testing at a contract laboratory began early in 1977. This initial program (summarized in Table 17) was, of course, devoted to SRC-I products and process materials. It was terminated in June 1978 because of several problems in the contract toxicology laboratory.⁵ A revised toxicology program that includes studies of SRC-II materials has been proposed. The SRC-II portion of the proposed program is summarized in Table 18. A complementary program has been developed at the Battelle Pacific Northwest Laboratory.

Summary-Health Effects

Extensive industrial hygiene monitoring, employee education and hygiene, medical surveillance, and toxicology programs have been implemented during the development of the SRC process. The level of effort is probably unprecedented for a nonnuclear fuel of commodity process development effort. Results to date have been generally reassuring; measured worker exposures have been low; medical profiles of plant personnel have remained essentially unchanged; preliminary toxicology work has not indicated exceptional toxicity problems.

The worker protection, employee education, industrial hygiene monitoring and medical surveillance programs employed during the pilot-plant program will provide the basis for those activities in the demonstration plant. As additional information on toxicological properties, worker health experience, and demonstration plant worker exposures becomes available, the health programs will be reviewed and modified as needed.

ACKNOWLEDGMENTS

Portions of the work discussed in this paper were conducted by the Pittsburgh & Midway Coal Mining Company and its subcontractors under Contract Number EX-76-C-01-0496 with the U.S. Department of Energy, Division of Coal Conversion and Utilization.

TABLE 16. SOLVENT-REFINED COAL PILOT-PLANT
MEDICAL OBSERVATIONS

<u>DESCRIPTION</u>	<u>NO. OF INCIDENTS</u>	<u>NO. RELATED TO SRC WORK</u>
Eye Irritation	50-60	Most
Erythema	25	25
Foliculitis (mechanics acne)	Multiple	Most
Skin Cancer	1	0

**TABLE 17. SOLVENT-REFINED COAL PROCESS SUMMARY OF
ORIGINAL TOXICOLOGY PROGRAM**

Test Material	Process Solvent	Coal Slurry	Filter Feed	Dry Mineral Residue	Wet Mineral Residue	Light Oil	Wash Solvent	Pulver- ized SRC	Pulver- ized Coal
Acute Oral Range Finding in Rats	X	X	X	C	X	X	X	C	
Acute Dermal Toxicity in Rabbits	X	X	X	C	X	X	X	C	
Guinea Pig Skin Sensitization	X	X	X	X	X	X	X	X	
Eye Irritation in Rabbits	C	C	C	C	C	C	C	C	
Acute Inhalation Range Findings in Rats	C					C	C		
Subacute Dermal Study in Rabbits	X						X	X	
Subacute Inhalation Toxicity in Swiss Mice	C	C	C		C	C	C		
Dermal Teratogenicity in Rats	X		X		X	X	X	X	
Dermal Teratogenicity in Rabbits	P		P		P	P	P	P	
Inhalation Teratogenicity in Rats and Rabbits	P		D	P		X	P	P	P
Two-year Skin Painting in Mice	X	X	X		X	X	X	X	
Two-year Inhalation Carcinogenesis	X			X			X	X	

X = material to be studied

C = study completed

P = pilot study completed

D = study deleted, impractical to aerosolize filter feed

**TABLE 18. REVISED TOXICOLOGY PROGRAM PROPOSAL
SRC-II**

	Task 1					Task 2		Task 3			Task 4			Task 5
	Acute Studies					Dermal Studies		Reproductive Toxicology			Inhalation			Muta- genicity
Materials	Oral LD50	Dermal LD50	Eye Irrit.	Guinea Pig Sens.	Aspir. Hazard	90-Day* Rabbit	18-Mo.* Mouse	Teratology		Dermal Multigen. Rat	Inhal. LC50	90-Day* Rat	2-Year Rat	In Vitro
								Dermal* Rat/Rabbit	Inhal.* Rat/Rabbit					
Coal Slurry	X	X	X	X		X	X	X		X				X
Stripper Tower Bottoms	X	X	X	X				X						X
Product Fuel Oil	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Vacuum Bottoms	X	X	X	X			X	X						X

X = Material to be studied
* = Pilot study necessary

REFERENCES

1. Section, R. J., M.D. *Archives of Environmental Health*. 1:208. 1960.
2. *Solvent Refined Coal (SRC) Process: Health Programs, Research and Development* (Report No. 53, Interim Report No. 24, Volume III, Part 4.) Industrial Hygiene, Clinical and Toxicological Programs. FE/496-T15. January 1978.
3. *Solvent Refined Coal (SRC) Process: Health Programs, Research and Development* (Report No. 53, Interim Report No. 28, Volume III, Part 4.) Industrial Hygiene, Clinical, and Toxicological Programs. FE/496-T19. April 1979.
4. Jackson, J. O., and J. A. Cupps. *Carcinogenesis: Polynuclear Aromatic Hydrocarbons* (Volume 3). New York, Raven Press, 1978. p. 183-191.
5. Schmalzer, D. K. *SRC Pilot Plant: Health Programs and Observations*. (Electric Power Research Institute Advisory Workshop on Carcenogenic Effects of Coal Conversion. Pacific Grove. September 26, 1978.)

ENVIRONMENTAL ASSESSMENT REPORT: SOLVENT-REFINED COAL

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Abstract

Environmental assessments reports (EARs) have been developed by the U.S. Environmental Protection Agency (EPA) to provide assistance in meeting commitments to preserve environmental quality. EARs are applicable both to emerging coal gasification and liquefaction systems. This paper addresses the environmental assessment of coal liquefaction via solvent refined coal (SRC).

An overview of the hypothetical SRC system considered is made. Potential sources of air emissions, water effluents, and solid waste discharges are identified. Applicable control alternatives for the discharges are discussed. Based on utilization of these controls, a summarized version of the multimedia environmental goals (MEGs) and source analysis models (SAMs) applied to SRC system discharges is presented, highlighting existing areas of environmental concern. Research needs for subsequent environmental assessments of SRC also are noted.

INTRODUCTION

As part of its goal of maintaining the nation's environment, the U.S. Environmental Protection Agency's (EPA) Industrial Environmental Research Laboratory at the Research Triangle Park (IERL/RTP), N.C., is directing an effort to evaluate the environmental aspects of emerging coal conversion technologies. Hittman Associates, Inc. (HAI), a prime contractor to IERL/RTP, is responsible for environmental analysis of coal liquefaction systems. Environmental assessment reports (EARs) were developed to provide best available environmental assessment data on specified coal conversion systems in a standardized format, thereby facilitating utilization by EPA personnel and other researchers in the field. This paper discusses a draft EAR prepared by HAI addressing solvent refined coal (SRC) liquefaction systems.

SRC systems convert high-sulfur coal and ash

coal into clean-burning gaseous, liquid, and/or solid fuels by noncatalytic direct hydrogenation. There are two basic system variations: SRC-I, which produces a solid, coal-like primary product of less than 1.0 percent sulfur and 0.2 percent ash by weight; and SRC-II, which produces low-sulfur fuel oil (0.2 to 0.5 percent sulfur by weight) and naphtha as primary products. Both system variations produce significant quantities of gaseous hydrocarbons, which are further processed to yield substitute natural gas (SNG) and liquefied petroleum gas (LPG) products. Some constituents formed during coal hydrogenation may be recovered as byproducts.

ENVIRONMENTAL OVERVIEW OF SRC SYSTEMS

Major inputs to SRC systems consist of coal, water, and air. Major products consist of gaseous and liquid hydrocarbons. Sulfur, ammonia, and phenols are recovered from waste streams as byproducts. The SRC-I and SRC-II systems are defined to consist of the following system operations,¹ which perform specific functions essential to solvent refining:

- Coal pretreatment: preparation of the coal feed to meet system specifications for size and moisture content.
- Coal liquefaction: reaction of feed coal with hydrogen, yielding a three-phase mixture of increased liquid and gaseous hydrocarbon content.
- Separation: includes all necessary phase separations. Gas separation and solids/liquids separation processes are employed in SRC systems.
- Purification and upgrading: a fractionation process is used to separate components of the raw liquid products mixture by distillation, because of differences in boiling points. A hydrotreating process may be optionally employed to upgrade the quality of fractionated product liquids.

In addition, SRC systems require the following auxiliary processes incidental to the functions of

the system operations:¹ coal receiving and storage, water supply, water cooling, steam and power generation, hydrogen generation, oxygen generation, acid-gas removal, hydrogen/hydrocarbon recovery, sulfur recovery, ammonia recovery, phenol recovery, and product/byproduct storage facilities.

Figure 1 is a flow schematic of the SRC-I (solid product) system that shows how the system operations and auxiliary processes transform the major input materials into products and byproducts.¹ Comparison of Figure 1 with Figure 2, the SRC-II (liquid product) system flow diagram, identifies the major differences in the two processing schemes as follows:¹

- The SRC-I feed slurry consists of feed coal mixed with system-derived solvent produced in the fractionation process. SRC-II feed slurry consists of feed coal mixed with product slurry from the gas separation process.
- In the SRC-I system, solids/liquids separation precedes fractionation; in the SRC-II the sequence of these processes is reversed. Solids/liquids separation in SRC-I is most likely to be performed by filtration, producing the filter cake sent to hydrogen generation. In SRC-II, solids/liquids separation is achieved by vacuum distillation, which produces a bottom residue of high mineral matter content to be gasified in the hydrogen generation process.

Waste discharges to air, water, and land media are identified in Figure 3. Discharges specific either to the SRC-I or SRC-II system are noted. Subsequent discussions of discharge characteristics, applicable control technologies, and environmental impact assessment are based on a hypothetical SRC-II commercial-scale facility, although the preliminary results may be considered representative of SRC-I.

Waste Streams to Air

As shown in Figure 3, air emissions are associated with a majority of the processes that make up the SRC systems. In addition to the air emissions sources shown, fugitive emissions, such as vapor leaks from pressurized process equipment, may occur in the SRC systems.¹ Emissions shown in the figure are outlined below.

- Flue gases: flue gases are produced by com-

bustion units (primarily preheaters) during liquefaction, fractionation, solids/liquids separation, hydrotreating, hydrogen generation, and sulfur recovery. Assuming the SNG and LPG products are used as fuel in these units, minimal environmental effects are anticipated.

- Coal dust: coal handling, processing, and storage in coal receiving and storage, and coal preparation result in particulate coal dust entering the atmosphere. Composition of the dust is the same as that of the raw coal.
- Dryer stack gas: to conform to system feed specifications for moisture content, feed coal is dried in the coal pretreatment operation. The stack gas produced by coal drying contains particulate coal and possible volatilized hydrocarbons present in the raw coal.
- Vapors and particulates from cooling: mineral residue resulting from solids/liquids separation (in the SRC-II mode) and SRC product from fractionation (in the SRC-I mode) require cooling. Air cooling of these substances may result in emissions of particulate solids and hydrocarbon vapors. Insufficient data exist to characterize these emissions and estimate environmental effects.
- Drift and evaporation: the cooling tower loses water to the environment as water vapor. Chemical additives used in water cooling may also be present in this emission.
- Boiler stack gas: presumably, coal is fired in the boilers of the steam and power generation auxiliary process. The resulting stack gas contains oxide of sulfur and nitrogen and particulates in the form of fly ash. Utilization of SRC system products is one alternative for reducing these emissions.
- Nitrogen-rich gas: the cryogenic oxygen generation process separates an oxygen-rich gas from ambient air for use in the hydrogen generation process. Other components of the air (mainly nitrogen) are discharged as an air emission.
- Carbon dioxide-rich gas: production of hydrogen by gasification produces a mixture of gases. An acid-gas removal unit separates sulfur gases (primarily hydrogen sulfide) from the gasifier product gas. This stream is sent to sulfur recovery. An additional acid-gas removal stage removes a stream of near-

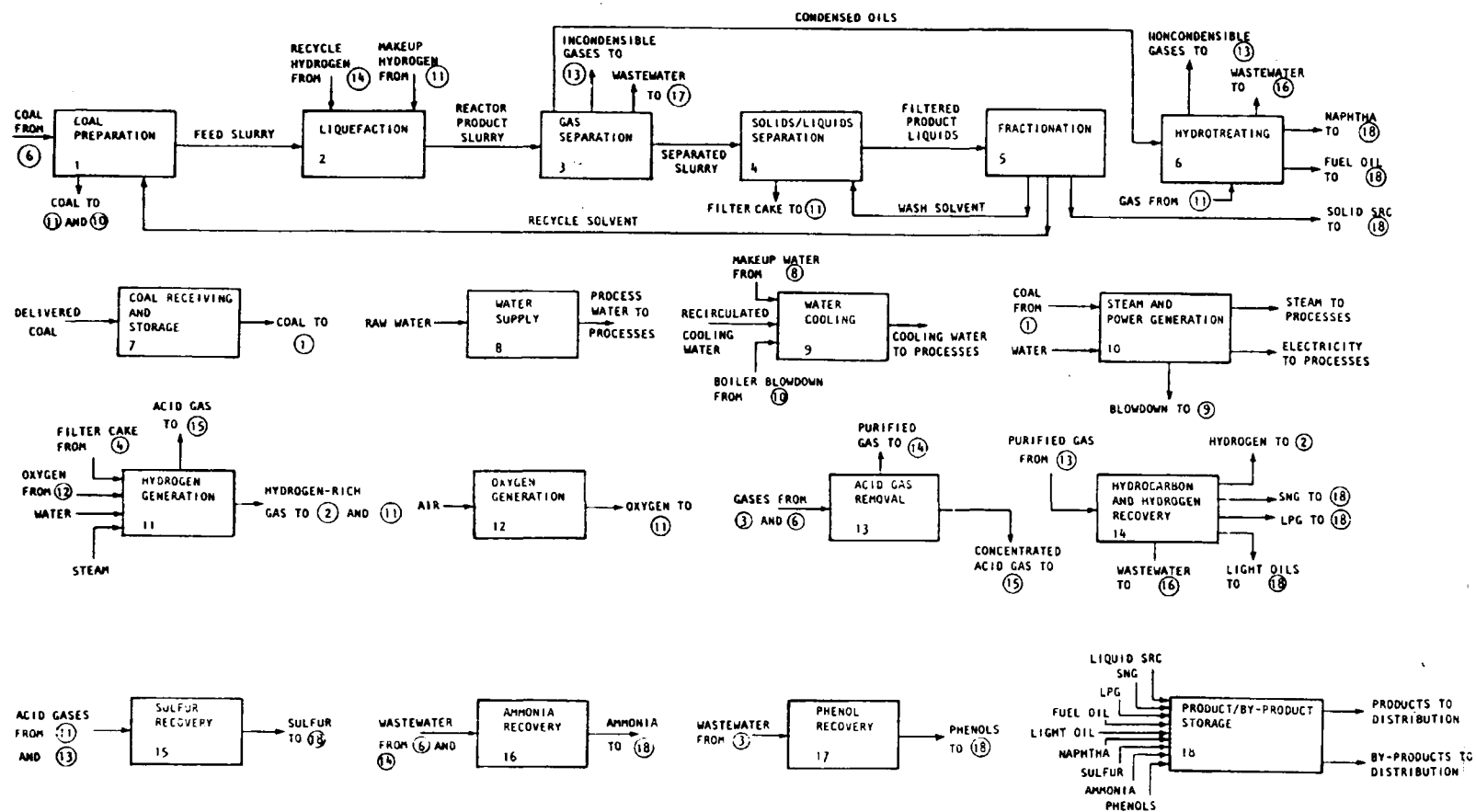


Figure 1. Flow diagram of SRC-I system.

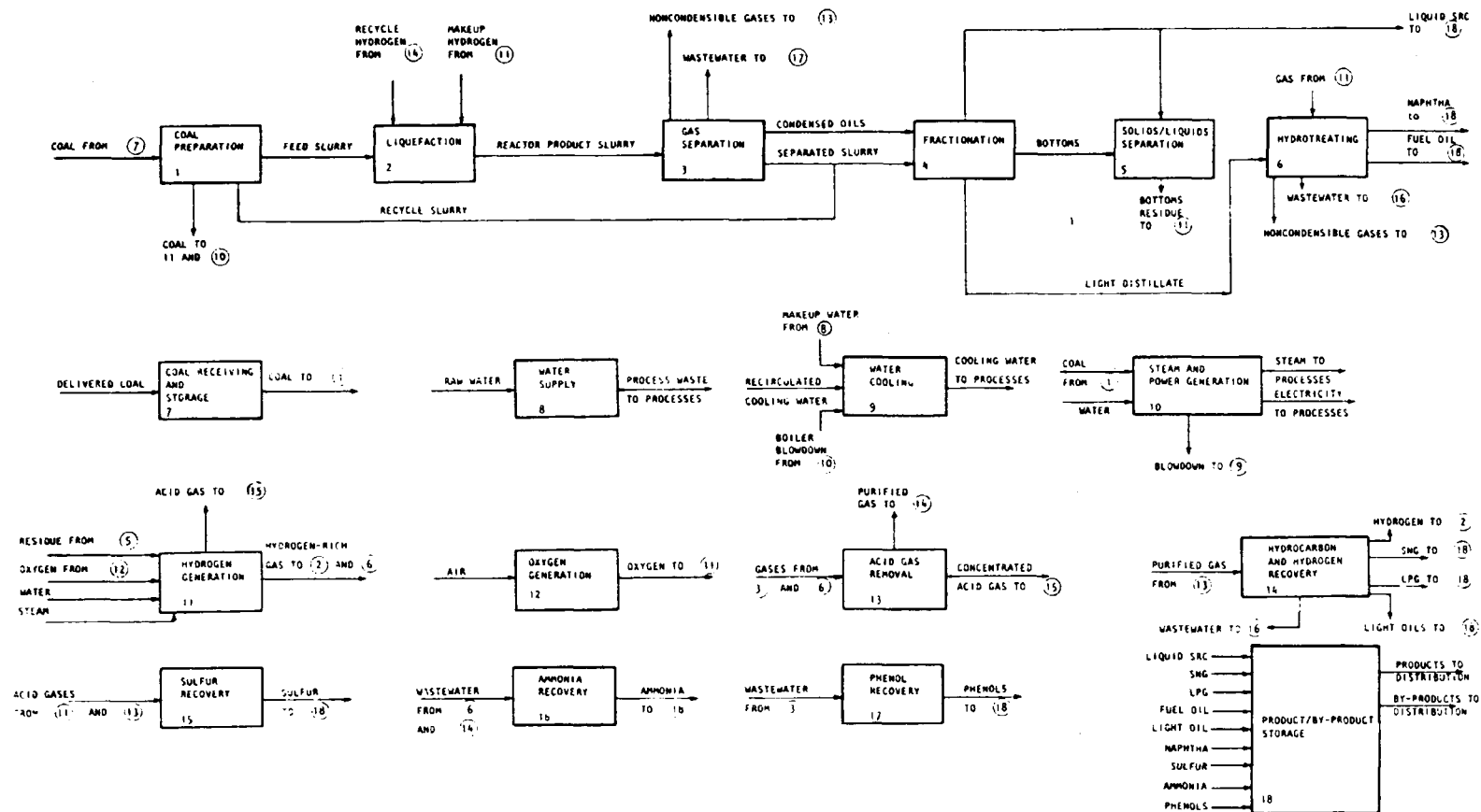


Figure 2. Flow diagram of SRC-II system.

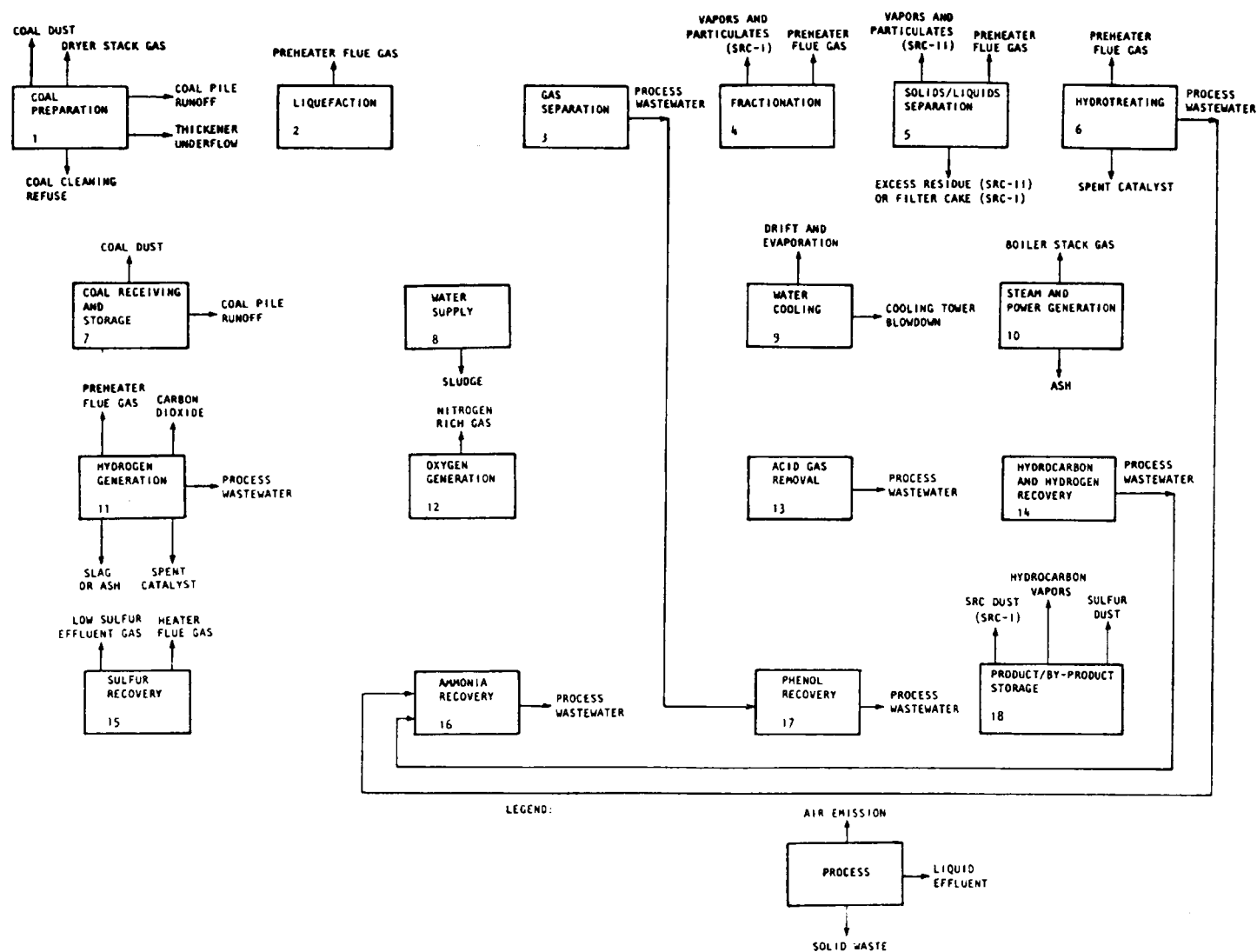


Figure 3. Source of waste discharges in SRC systems.

ly pure carbon dioxide.

- Low-sulfur effluent gas: sulfur-bearing acid gases from hydrogen generation and SRC system operations are treated to convert sulfur gases to elemental sulfur.
- SRC dust (SRC-I mode) and sulfur dust: handling and storage of SRC system solid products and byproduct sulfur result in release of dust to the environment.
- Hydrocarbon vapors: liquid products of SRC systems contain volatile hydrocarbon components. Care must be exercised in handling and storage of these liquids to minimize emissions.

Waste Streams to Water

Sources of wastewater shown in Figure 3 are briefly discussed below.

- Coal pile runoff: precipitation striking the raw coal in coal receiving and storage and coal preparation infiltrates the coal pile. During this contact, leaching of both organic and inorganic constituents of the raw coal occurs. Runoff water is collected for treatment.
- Thickener underflow: wastewater from the coal pretreatment operation is routed to a thickener. Clarified water is recycled to coal preparation. The underflow stream contains a high level of suspended solids and coal-derived organic constituents.
- Cooling tower blowdown: drift and evaporation from the cooling tower result in increased concentrations of dissolved and suspended solids in the process cooling water. A blowdown or "bleed" stream is withdrawn to maintain dissolved and suspended solids concentration within design specifications.
- Process wastewater from hydrogen generation: wastewater from hydrogen generation may contain tars, oils, and ammonia. This stream is directed to the main wastewater treatment facility.
- Process wastewater from acid-gas removal: a purge stream is removed from the amine-based acid-gas removal process to maintain the concentration of amine and to remove spent amines that have formed nonregenerable compounds. This stream is directed to the main wastewater treatment facility.
- Process wastewater from ammonia recovery process: wastewaters from hydrotreat-

ing, hydrogen generation, and hydrogen/hydrocarbon recovery contain significant quantities of ammonia. These wastewaters are combined and input to the ammonia recovery process. The effluent wastewater exiting ammonia recovery contains hydrogen sulfide, phenols, hydrocarbons, and traces of ammonia. This stream is directed to the main wastewater treatment facility.

- Process wastewater from phenol recovery process: the gas separation operation removes gaseous constituents of the liquefaction reactor effluent. Condensation of the gases yields a phenol-rich aqueous phase, which is sent to the phenol recovery process. After phenol recovery the wastewater stream, containing hydrocarbons, ammonia, hydrogen sulfide, and traces of phenol, is combined with other process wastewaters (from hydrogen generation, acid-gas removal, and ammonia recovery) during wastewater treatment.

Waste Streams to the Land

Sources of solid wastes in SRC systems are also shown in Figure 3. Sources and characteristics of solid wastes are described below.

- Coal-cleaning refuse: refuse is a mixture of mineral matter (such as slate and tramp iron), water, and coal. Refuse is recovered during coal sizing and drying.
- Excess residue (SRC-II mode) or filter cake (SRC-I): depending on the method of hydrogen production employed in SRC systems, the possibility exists that excess SRC-II mineral residue of SRC-I filter cake may be produced. These solids consist of mineral matter present in the feed coal and high molecular weight hydrocarbon species.
- Spent catalysts: the hydrotreating operation uses a catalyst to upgrade coal liquids. A catalyst also may be employed in the shift converter of the hydrogen generation process. In order to maintain conversion efficiencies, catalysts must be withdrawn periodically and replaced with fresh ones.
- Ash from steam and power generation: ash is the oxidized mineral matter present in coal fed to the boilers.
- Slag or ash from hydrogen generation: gasification of mineral residue or filter cake to produce hydrogen converts mineral matter

to ash. If a high-temperature gasifier is used, the ash may fuse and be recovered as a slag.

CONTROL TECHNOLOGY FOR SRC SYSTEMS

Environmental impact assessment of waste streams from SRC systems is based on application of the control methods described in this section. Selection of control practices is primarily based on work efforts contributing to preparation of the EAR¹ and a previous report by Rogoshewski et al.²

Control of Emissions to Air

Suggested control alternatives for controlling air emissions from SRC systems are given in Table 1. Final selection of controls for an actual facility should be based on regional, regulatory, economic, and site-specific considerations.¹ Accidental vapor discharges may occur because of leaks caused by mechanical failure of equipment. Accidental release control is best achieved by routing emergency vent gases into a header that directs them to the flare system. Development and implementation of preventive maintenance measures are essential to minimize accidental air emissions because of equipment failure.²

Control of Water Effluents

Table 2 summarizes the preferred control alternatives for treating water effluents from SRC systems. In addition to the discharges shown in the table, accidental leaks may occur, although they can be minimized by good preventive maintenance procedures. In addition, SRC facilities should develop a material spills contingency plan including provisions for spills detection, containment, recovery, and disposal.²

Runoff from coal preparation, receiving, and storage is combined with thickener underflow from coal preparation and sent to a tailings pond. Overflow from the thickener is recycled to the coal-cleaning process.

Cooling tower blowdown is treated to remove dissolved solids. Lime softening, ion exchange, and reverse osmosis are processes used to reduce dissolved solids content. Selection of side-stream treatment should be based on more detailed analysis of regional, economic, regulatory,

and site-specific factors. The treated water is then discharged to receiving waters.

The remaining process wastewater discharges are combined during treatment in the main wastewater treatment facility. Two alternative wastewater treatment schemes, shown in Figure 4, are considered applicable to treatment of the water discharges.

Control of Solid Wastes

Preferred control and disposal alternatives for solid wastes discharged from SRC systems are summarized in Table 3. Most of the solids appear suitable for direct landfilling or minefilling without predisposal treatment. Spent catalysts produced may be returned to the manufacturer for analysis and subsequent regeneration or disposal. Should catalyst regeneration be technically or economically unfeasible, additional research is recommended to determine if predisposal treatment of the catalysts is required. Mineral residue from SRC-II and filter cake from SRC-I are not well-characterized materials. If economically feasible, it is recommended that these materials be gasified to recover available energy. The slag or ash produced by gasification may be disposed of as solid waste.

ASSESSMENT OF ENVIRONMENTAL IMPACTS

This section discusses environmental impacts associated with SRC waste discharges to air, water, and land media.¹ In addition, environmental aspects of handling and utilization of SRC products are addressed.

Impacts on Air

Analysis of existing information indicates that dust emissions from coal receiving and storage and coal preparation, low-sulfur effluent gas from sulfur recovery, boiler flue gas from steam and power generation, and the emission from the flare system should be regarded as those emissions to air of greatest environmental concern. Component pollutants of concern are summarized in Table 4, based on SAM/IA analysis using health-based minimum acute toxicity effluent (MATEs) for evaluation of degree of hazard.¹ Trace element data given in these

**TABLE 1. SUMMARY OF AIR EMISSIONS CONTROL TECHNOLOGY
APPLICABILITY TO SRC SYSTEMS**

Operation/Process	Air Emissions Discharged	Preferred Control Technology Applications
Coal preparation	Coal dust	(1) Spray storage piles with water or polymer. (2) Cyclones and baghouse filters for control of dust due to coal sizing.
	Particulate-laden flue gas from coal dryers	(1) Cyclones and baghouse filters. (2) Wet scrubbers such as venturi.
Liquefaction	Preheater flue gas	(1) None required (fired by SNG).
	Pressure letdown releases	(1) Flaring
Gas separation	Pressure letdown releases	(1) Flaring
Fractionation	Preheater flue gas	(1) None required (fired by SNG).
	Particulate-laden vapors from product cooling (SRC-I)	(1) Cyclone and baghouse filter. (2) Wet scrubbers.
	Pressure letdown releases	(1) Flaring
Solids/liquids separation	Preheater flue gas	(1) None required (fired by SNG).
	Particulate-laden vapors from residue cooling (SRC-II)	(1) Cyclone and baghouse filter. (2) Wet scrubbers.
	Pressure letdown releases	(1) Flaring
Hydrotreating	Preheater flue gas	(1) None required (fired by SNG).
Coal receiving and storage	Pressure letdown releases	(1) Flaring
	Coal dust	(1) Spray storage piles with water or polymer.

(Continued)

TABLE 1 (continued)

Operation/Process	Air Emissions Discharged	Preferred Control Technology Applications
Water supply	None	
Water cooling	Drift and evaporation	(1) No controls available - good design can minimize losses.
Steam and power generation	Boiler flue gas	(1) Sulfur dioxide scrubbing with aqueous magnesium oxide solution.
Hydrogen generation	Carbon dioxide rich gas	(1) None required.
	Preheater flue gas	(1) None required (fired by SNG).
Oxygen generation	Nitrogen rich gas	(1) None required.
Acid gas removal	Pressure letdown releases	(1) Flaring
Sulfur recovery	Flue gas	(1) None required (fired by SNG).
	Low-sulfur effluent gas*	(1) Carbon adsorption. (2) Direct-flame incineration. (3) Secondary sulfur recovery.
Hydrogen/hydrocarbon recovery	Pressure letdown releases	(1) Flaring.
Ammonia recovery	None	
Phenol recovery	None	
Product/by-product storage	SRC dust (SRC-I)	(1) Spray storage piles with water.
	Sulfur dust	(1) Store in enclosed area.
	Hydrocarbon vapors	(1) Spills/leaks prevention.
* A secondary sulfur recovery process may be necessary to meet specified air emission standards.		

**TABLE 2. SUMMARY OF WATER EFFLUENTS CONTROL TECHNOLOGY
APPLICABILITY TO SRC SYSTEMS**

Operation/Process	Water Effluents Discharged	Preferred Control Technology Applications
Coal preparation	Coal pile runoff	(1) Route to tailings pond.
	Thickener underflow	(1) Route to tailings pond.
Liquefaction	None	
Gas separation	None	
Fractionation	None	
Solids/liquids separation	None	
Hydrotreating	None	
Coal receiving and storage	Coal pile runoff	(1) Route to tailings pond.
Water supply	None	
Water cooling	Cooling tower blowdown	(1) Sidestream treatment (electrodialysis, ion exchange or reverse osmosis) permits discharge to receiving waters.
Steam and power generation	None	
Hydrogen generation	Process wastewater	(1) Route to wastewater treatment facility.*
Oxygen generation	None	
Acid gas removal	Process wastewater	(1) Route to wastewater treatment facility.*
Sulfur recovery	None	
Hydrogen/hydrocarbon recovery	None	
Ammonia recovery	Process wastewater	(1) Route to wastewater treatment facility.*

(Continued)

TABLE 2 (continued)

Operation/Process	Water Effluents Discharged	Preferred Control Technology Applications
Phenol recovery	Process wastewater	(1) Route to wastewater treatment facility.*
Product/by-product recovery	None	

* Two alternatives for the wastewater treatment facility are shown in Figure 4

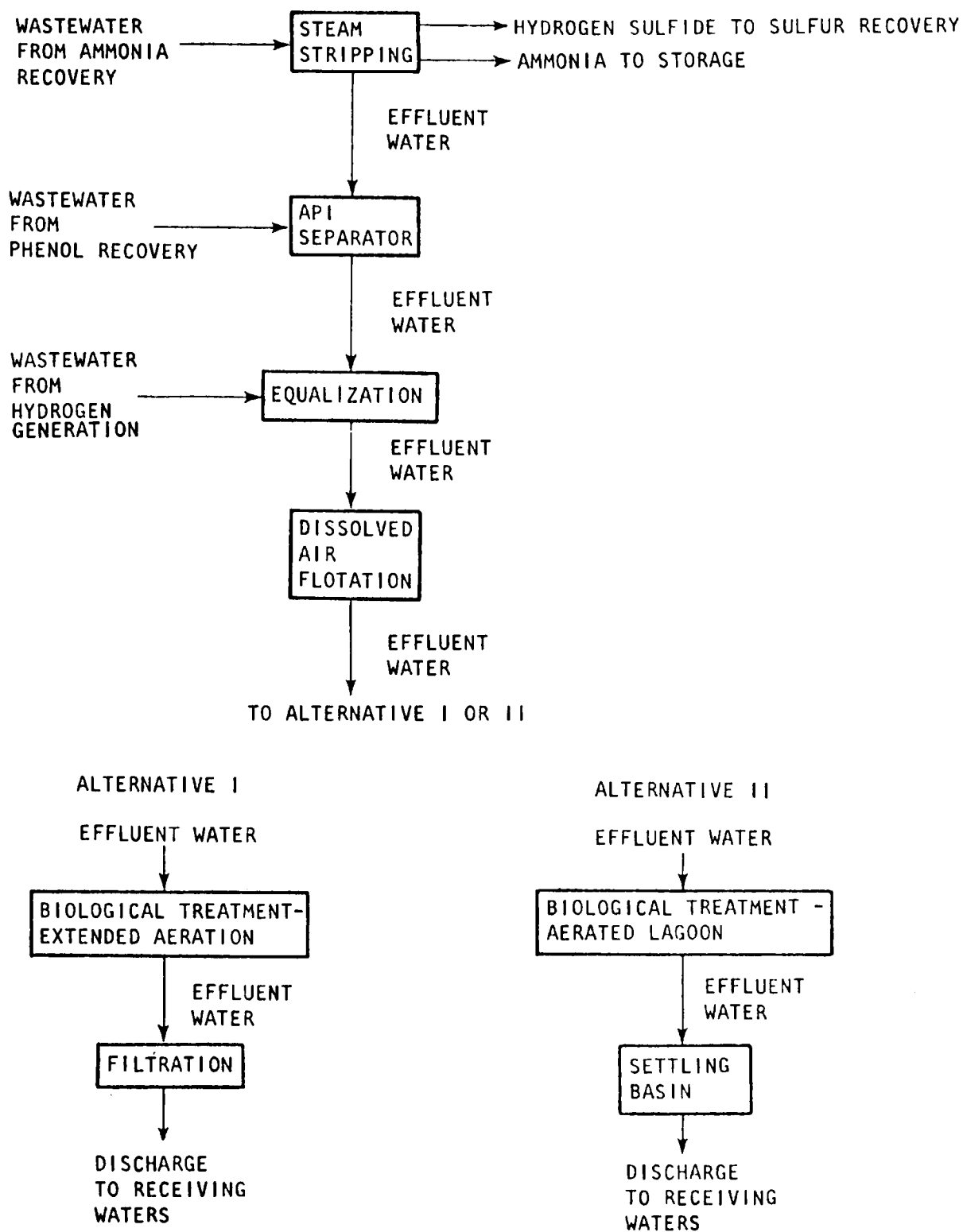


Figure 4. Two wastewater treatment alternatives applicable to SRC systems.

**TABLE 3. SUMMARY OF SOLID WASTES CONTROL TECHNOLOGY
APPLICABILITY TO SRC SYSTEMS**

Operation/Process	Solid Wastes Discharged	Preferred Control Technology Applications
Coal preparation	Refuse	(1) Landfill (2) Dumping (Minefill)
Liquefaction	None	
Gas separation	None	
Fractionation	None	
Solids/liquid separation	Excess residue (SRC-II) or filter cake (SRC-I)	(1) Gasification to recovery energy content followed by disposal (landfill or minefill)
Hydrotreating	Spent catalyst	(1) Return to manufacturer for regeneration
Coal receiving and storage	None	
Water supply	Sludge	(1) Dewatering followed by landfilling
Water cooling	None	
Steam and power generation	Ash	(1) Landfill (2) Dumping (Minefill)
Hydrogen generation	Ash or slag	(1) Landfill (2) Dumping (Minefill)
Oxygen generation	None	
Acid gas removal	None	
Sulfur recovery	None	

(Continued)

TABLE 3 (continued)

Operation/ Process	Solid Wastes Discharged	Preferred Control Technology Applications
Hydrogen/hydrocarbon recovery	None	
Ammonia recovery	None	
Phenol recovery	None	
Product/by-product storage	None	

**TABLE 4. AIR EMISSIONS OF CONCERN* ASSOCIATED
WITH SRC SYSTEMS BASED ON SAM/IA ANALYSIS**

Air Emission	Pollutant	Health-Based MATE ($\mu\text{g}/\text{m}^3$)	Potential Degree of Hazard**
Particulate coal dust***	Aluminum	5200.	2.3×10^{-3} -1.7
	Arsenic	2.0	4.9×10^{-3} -3.6
	Chromium	1.0	1.5×10^{-2} -11.0
	Iron	1000.	1.3×10^{-2} -9.9
	Lithium	22.0	1.4×10^{-3} -1.1
	Silicon	1.0×10^4	2.1×10^{-3} -1.5
Sulfur re- recovery tail gas****	Carbon dioxide	9.0×10^6	87.0
Boiler flue gas	Arsenic	2.0	3.0
	Carbon monoxide	4.0×10^4	1.3
	Chromium	1.0	7.3
	Iron	1000.	3.7
	Nitrogen oxides	9000.	56
	Sulfur dioxide	1.3×10^4	49
Flare system emission	Carbon dioxide	9.0×10^6	20
	Carbon monoxide	4.0×10^4	14

* Based on liquefaction of "average" U.S. coal.

** Degree of hazard = $\frac{\text{Projected air concentration } (\mu\text{g}/\text{m}^3)}{\text{Health based MATE } (\mu\text{g}/\text{m}^3)}$

*** Ranges due to different types of particulate controls employed.

**** Carbon monoxide and ammonia concentrations exceed ecological-based MATE but not health-based MATE.

discussions are projections based on an "average" U.S. coal converted to SRC. Partitioning factors based on analyses of SRC waste materials were used to simulate distribution of trace elements in streams exiting an SRC facility. Results of trace elements' degree of hazard should be viewed as indicative, but not conclusive, of SRC behavior.

Two important conclusions can be drawn from Table 4. First, all emissions cited are associated with existing industries (coal mining, petroleum refining, and steam-electric power generation). Concern with these emissions is not directly attributable to operations or auxiliary processes unique to SRC systems. Second, in

the case of coal dust, application of the more effective recommended control technology (cyclone and baghouse filter) reduces degree of hazard values below one; i.e., below the health-based MATE value.

Impacts on Water

Coal pile runoff and effluent water from the wastewater treatment facility are considered water effluents of concern.¹ Specific pollutants of concern are shown in Table 5. The characteristics of coal pile runoff do result from SRC technology; however, combined wastewater characteristics do result from SRC liquefaction.

TABLE 5. WATER EFFLUENTS OF CONCERN* ASSOCIATED WITH SRC SYSTEMS BASED ON SAM/IA ANALYSIS

Air Emission	Pollutant	Health-Based MATE, ($\mu\text{g}/\text{m}^3$)	Potential Degree of Hazard**
Coal pile runoff	Aluminum	8.0×10^4	9.1
	Calcium	2.4×10^5	1.2
	Chromium	250.	8.0
	Iron	1500.	6000.
	Manganese	250.	272.
	Mercury	10.	1.4
	Nickel	250.	4.3
	Sulfate	1.5×10^4	170.
Combined wastewater	Bismuth	6.1×10^3	5.2
	Cresols	5.	188.
	C ₃ -phenols	5.	18.0
	Naphthols	5.	60.0
	Phenol	5.	78.0
	Xylenol	5.	76.0

* Inorganics based on "average" U.S. coal.

Organics based on characteristics of SRC bio-unit effluent.

** Degree of hazard = $\frac{\text{Projected water concentration } (\mu\text{g}/\text{l})}{\text{Health-based MATE } (\mu\text{g}/\text{l})}$

**TABLE 6. SOLID WASTES OF CONCERN* ASSOCIATED
WITH SRC SYSTEMS BASED ON SAM/IA ANALYSIS**

Air Emission	Pollutant	Health-Based MATE, ($\mu\text{g/g}$)	Potential Degree of Hazard**
SRC-II mineral residue***	Aluminum	1.6×10^4	3.7
	Arsenic	50	1.1
	Barium	1000	1.2
	Beryllium	6	1.2
	Calcium	4.8×10^4	2.2
	Cobalt	150	2.4
	Iron	300	310.
	Lead	50	1.4
	Manganese	50	4.8
	Nickel	45	2.1
	Potassium	6000	3.0
	Selenium	10	2.0
API separator bottoms	Arsenic	50	2.0
	Beryllium	6	80.0
	Cadmium	10	5.0
	Cobalt	150	250.
	Dysprosium	4.6×10^2	350.
	Lead	50	364.
	Mercury		530.
	Nickel	45	51.0
	Selenium	10	260.
Biosludge	Aluminum	1.6×10^4	1.1
	Mercury	5.0×10^1	7.0
	Vanadium	500	1.1

* Based on liquefaction of "average" U.S. coal.

** Degree of hazard = $\frac{\text{Projected pollutant concentration } (\mu\text{g/g})}{\text{Health-based MATE } (\mu\text{g/g})}$

*** Similar characteristics expected for SRC-I filter cake.

Impacts on Land

Solid wastes of environmental concern, based on SAM/IA analysis with the health-based MATEs, are shown in Table 6. API separator bottoms and biosludge from the wastewater treatment system and SRC mineral residues contain component pollutant species that exceed their MATE values. These solids are considered greater risks to the environment than either SRC air emissions or water effluents.¹

The mineral residue or filter cake produced during solids/liquids separation in SRC-II and SRC-I systems respectively contains high molecular weight organic species. It is recommended that all such material be gasified to render it safe for land or mine burial. Energy recovered by gasification of excess residue can be used onsite or sold as additional SNG product.

A review of available analysis data on organics in SRC-II mineral residue indicated no organic species present in concentrations exceeding the land-based health MATE value. Organics associated with SRC mineral residue are shown in Table 7. Organics presently not assigned MATE values are also included in the table.

With reference to the hazardous nature of several SRC solid wastes, the following precautions should be considered prior to disposal:¹

- That the solids, singly or in mixture, should be chemically stabilized.
- That the potential physical/chemical reactions of sludges, singly or in mixture, should be known.
- That the compatibility of the hazardous waste with appropriate liners, sealants, and container materials should be established.
- That the life span of the land disposal site should meet the most stringent State standards (500 yr for the most hazardous wastes).

Toxic Substances in Products

Polynuclear aromatic species detected in analysis of light oil and solid SRC product produced in the SRC-I mode are shown in Table 8. The variety of polynuclear species indicated in the table illustrates the need to exercise care in handling these materials.

SRC Product Utilization

To potential industrial and utility users, the environmental benefits of using synfuels are of primary concern. To date only two large-scale tests have been conducted:⁸

- (1) SRC-I, June 16-24, 1977, Georgia Power Company's Plant Mitchell, Albany, Georgia; and
- (2) SRC-II, September 10-15, 1978, Commonwealth Edison's 74th Street Generating Station, New York.

The SRC-I combustion test used 2,700 mg of SRC-I material from a 3.9-percent sulfur coal. No particular problems were experienced during the 18-day test burn, and the following levels of emission were achieved:

Constituent	Concentration, ppm (vol)
Nitrogen oxides	175-300
Particulates	0.015-0.025
Carbon monoxide	50
Uncombusted hydrocarbons	3
Sulfur trioxide	1

The SRC-II combustion test used about 800 m³ of liquid SRC-II product produced at the pilot plant in Fort Lewis, Washington. Reported levels of emission are shown below:

Constituent	Current EPA requirements*	SRC*
SO _x	0.52	0.43
NO _x	0.30	0.20
Particulates	0.04	0.02

*Units are Kg/GJ.

Data on sulfur dioxide concentrations were not reported.

Based on these data, it appears likely that SRC-II can be utilized in compliance with proposed emissions standards for coal-derived liquids.¹

TABLE 7. ORGANIC SPECIES PRESENT IN SRC-II MINERAL RESIDUE

<u>Organic Constituent</u>	<u>Concentration, $\mu\text{g/g}$</u>	<u>MATE Value, $\mu\text{g/g}$</u>	
		<u>Health-based</u>	<u>Ecological-based</u>
indane	85	6.8×10^5	-----
methylindane	40	6.8×10^5	-----
dimethylindane	25	6.8×10^5	-----
tetralin	110	4.0×10^5	200
6-methyltetralin	50	4.0×10^5	200
naphthalene	1500	1.5×10^5	-----
2-methylnaphthalene	740	6.8×10^5	-----
1-methylnaphthalene	180	6.8×10^5	-----
dimethylnaphthalene	470	6.8×10^5	-----
2-isopolynaphthalene	2	6.8×10^5	-----
1-isopolynaphthalene	1	6.8×10^5	-----
Cy-naphthalene	15	6.8×10^5	-----
cyclohexylbenzene	1	-----	-----
biphenyl	5	3000	-----
acenaphthylene	270	-----	-----
dimethylbiphenyl	61	-----	-----
dibenzofuran	60	-----	-----
xanthene	20	-----	-----
dibenzothiophene	70	-----	-----
methyldibenzylthiophene	8	-----	-----
dimethyldibenzylthiophene	20	-----	-----
thioxanthene	5	-----	-----
fluorene	80	-----	-----
9-methylfluorene	40	-----	-----
1-methylfluorene	50	-----	-----
anthracene/phenanthrene	500	1.7×10^5	-----
methylphenanthrene	100	9.1×10^4	-----
1-methylphenanthrene	50	9.1×10^4	-----
C ₂ -anthracene	10	-----	-----
fluoranthrene	200	2.8×10^5	-----
dihdropyrene	10	-----	-----
pyrene	200	-----	-----

**TABLE 8. POLYNUCLEAR AROMATICS DETECTED IN SRC-I
LIGHT OIL AND SRC SOLID PRODUCTS**

<u>Organic Constituent</u>	<u>Concentration, ppm (wt)</u>		<u>MATE (water-based, µg/l)</u>	
	<u>Light Oil</u>	<u>SRC</u>	<u>Health-based</u>	<u>Ecological-based</u>
0-ethylbenzene	9800	---	6.5×10^6	1.0×10^3
C ₃ -benzene	3900	---	3.3×10^6	1.0×10^3
indane	4300	---	6.8×10^5	-----
methylindane	180-510	---	6.8×10^5	-----
dimethylindane	< 5	---	6.8×10^5	-----
tetralin	330	---	4.0×10^5	200
dimethyltetralin	< 5	---	4.0×10^5	200
6-methyltetralin	110	---	4.0×10^5	200
naphthalene	1630	1	1.5×10^5	-----
2-methylnaphthalene	690	8	6.8×10^5	-----
1-methylnaphthalene	110	5	6.8×10^5	-----
dimethylnaphthalene	10-80	3-6	6.8×10^5	-----
biphenyl	80	2	3000	-----
acenaphthylene	2	8	-----	-----
dimethylbiphenyl	15-21	7-9	-----	-----
dibenzofuran	8	9	-----	-----
xanthene	10	5	-----	-----
dibenzothiophene	3	30	-----	-----
methyldibenzothiophene	-----	4	-----	-----
dimethyldibenzothiophene	5	13	-----	-----
thioxanthene	-----	3	-----	-----
fluorene	15	27	-----	-----
9-methylfluorene	15	11	-----	-----
1-methylfluorene	10	18	-----	-----
anthracene/phenanthrene	25	300	1.75×10^5	-----
methylphenanthrene	6	50	9.1×10^4	-----
1-methylphenanthrene	6	30	9.1×10^4	-----
C ₂ -anthracene	6	1	----- ⁵	-----
fluoranthrene	15	180	2.8×10^5	-----
dihdropyrene	6	1	----- ⁵	-----
pyrene	20	280	6.9×10^5	-----

ADDITIONAL DATA REQUIREMENTS AND RECOMMENDATIONS

Currently, the pilot plants at Fort Lewis, Washington, and Wilsonville, Alabama, are the most advanced SRC facilities in existence. Information obtained during solvent-refining operations at Fort Lewis and Wilsonville is being used to design SRC demonstration plants. In an analogous manner, data from demonstration plants will be used to permit successful commercialization of SRC systems.

The draft EAR is based on the best existing information, namely SRC pilot data, bench-scale data, and conceptual design studies.¹ Just as additional operating data are required to commercialize SRC systems, additional environmental assessment data are necessary to adequately characterize discharges, estimate environmental impacts, and evaluate control technology applicability relevant to SRC systems. Expansion of the existing environmental assessment data base for SRC systems should include the following areas:

- SRC stream characterization: with the purpose of developing representative physical, chemical (inorganic and organic), and biological (with bioassays) characteristics of SRC plant streams, in particular *before* and *after treatment* waste streams. While characterization of waste streams is essential to environmental assessment, better characterized process streams will permit construction of an advanced material balance, ideally permitting one to "track" pollutants through the SRC system to the environment.
- Determination of the variability of waste stream characteristics because of changes in system operating characteristics: an expanded data base on stream characteristics may permit such correlations, possibly suggesting ideal operating conditions for minimized environmental effects.
- Performance evaluations and costs of applicable control technology alternatives.
- Reassessments of environmental impacts based on the expanded data base.

Because of the relative applicability of SRC pilot-plant data, the above efforts would be more beneficial if performed at SRC demonstration facilities.

Environmental assessment methodologies

such as multimedia environmental goals (MEGs) and source analysis models (SAMs) have been developed to provide an organized, consistent approach for evaluating emerging energy technologies such as SRC. Technically, there are many differences between existing SRC pilot facilities and the demonstration and commercial plants of the future. Consequently, operating data on process and waste stream characteristics from the pilot plant are only an indication of commercial or demonstration plant behavior.

However, sampling, analysis, and application of environmental assessment methodologies to pilot-plant data are essential to permit the following prior to emergence of SRC systems into the commercial sector:

- Sampling and analysis techniques may be tried and problem areas identified, thereby permitting refinement of the techniques.
- Sampling and analysis priorities for the demonstration/pilot SRC facilities may be identified based on pilot studies.
- Application of the environmental assessment methodologies to SRC pilot data will allow additional development and evaluation.
- Each of the above activities will accord SRC system personnel with the expertise to confidently assess commercial SRC systems at the time technical progress and economic conditions permit their emergence.

The following recommendations can be made regarding future environmental assessments of SRC systems:

- Efforts to characterize waste streams, process streams, products, and byproducts should be continued at an increased level of effort. In so doing, numerous benefits are derived including expanding the preliminary data base on SRC systems, perfecting sampling and analysis procedures, and developing more sophisticated environmental impact methodologies. Results of these efforts will be invaluable in establishing research needs for environmental characterization of SRC demonstration/commercial facilities.
- Efforts should be undertaken to define suitable sites for commercial SRC facilities. Subsequent to definition, applicable sites should be identified. Information required to perform site-specific environmental impact analyses should be collected for those sites identified as potentially suitable for SRC

facilities, including preconstruction ambient air and water quality monitoring. Initiating expanded background monitoring studies in applicable locations would be useful for environmental assessment and could hasten construction of commercial facilities.

- Candidate control technologies identified as applicable to control of wastes from SRC systems should be tested at SRC pilot and demonstration facilities to the extent technically and economically feasible. Sampling and analysis of discharge streams before and after treatment would greatly expand the environmental assessment data base. Small-scale, slid-mounted control technology units could be placed on flatbed trucks and moved to pilot or demonstration facilities for testing with continuous samples of the plant's waste stream, thereby providing a cost-effective means of performance testing numerous candidate control options.
- Continued efforts should be made to promote cooperation, coordination, and information exchange between the various private and government organizations involved in development and environmental analysis of SRC systems. Preparation and presentation of technical papers at appropriate symposia and meetings is an excellent way to informally stimulate interaction of researchers, leading to more formal interaction during performance of research. The benefits include reduced duplication of environmental

assessment efforts, permitting more efficient use of available research funds.

ACKNOWLEDGMENTS

Information for this paper was compiled from work performed by Hittman Associates, Inc., under EPA Contract Number 68-02-2162. This work has been guided and supported by EPA's Fuel Process Branch of the Industrial Environmental Research Laboratory at Research Triangle Park, N.C., under the direction of W. J. Rhodes, Project Officer.

REFERENCES

1. Information obtained and developed by Hittman Associates, Inc., During Preparation of Draft Document, Environmental Assessment of Solvent Refined Coal (SRC) Systems for Producing Solid and Liquid Fuel From Coal. EPA Contract Number 68-02-2162.
2. Rogoshewski, et al. *Standards of Practice Manual for the Solvent Refined Coal Liquefaction Process*. Hittman Associates, Inc. Research Triangle Park, N.C. EPA 600/7-78-091. 1978.
3. Morris, J. W., and K. J. Shields. *Environmental Impacts of Coal Liquefaction*. (Prepared for National Conference on the Impact of the National Energy Act on Utilities and Industries Due to the Conversion of Coal. December 4-6, 1978.)

COMBUSTION OF LIQUID SYNFUELS

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Abstract

This paper summarizes the available information on the state-of-the-art emission control technology for the use of petroleum-, shale-, and coal-derived liquid fuels in stationary combustion sources. Because the data on combustion of alternative liquid fuels in practical systems are limited, the properties of these fuels are compared to those of petroleum-derived fuels as a basis for postulating the effectiveness of combustion process modifications on emissions from alternative fuels. The formation and control of nitrogen oxides are related to fuel characteristics, particularly the distribution of the fuel-bound nitrogen. The effectiveness of staged combustion techniques is correlated with a defined measurement of volatile nitrogen. The effect of fuel composition on carbon particulate formation is also discussed. Finally, based on promising results for heavy petroleum fuel oils and coal, it is concluded that burner and combustion process design modifications have a high probability of success for alternative fuels.

INTRODUCTION

In the search for energy supplies, the United States is projected to place heavy reliance on coal, which is the most abundant fossil fuel available. Many methods of extracting the energy from coal are being pursued; however, the ultimate decisions on the paths to be followed depend on both economic and environmental considerations. These considerations cover the full range from resource extraction, through processing, to end utilization. On the economic side, it is necessary to include not only capital and operating costs but also the overall energy effi-

ciency of the process. On the environmental side, there are potential impacts in every step, and the overall effect on air, water, and land quality must be assessed. For the purposes of this paper, only the end use processes (i.e., combustion systems) will be considered. The characteristics of the combustion also influence the route that will be chosen. For mobile sources (e.g., automobiles and aircraft), light liquid hydrocarbon fuels probably will be required for a significant period in the future. In this instance, the necessity for a specific fuel type may overcome some of the other potential obstacles (e.g., economics). For stationary sources, the fuel used may not be constrained as significantly by the requirement of a fuel of specific characteristics, and the choice of approach may be wider.

The ways in which coal can be used in an environmentally acceptable manner depend on the type of combustion source. The pollutants that must be controlled include sulfur oxides, nitrogen oxides, carbon monoxide, unburned hydrocarbons, and total particulate. Perhaps the most options exist for utility generation of electric power. One option currently being used is the direct combustion of coal with stack gas cleaning for sulfur oxides and particulate, and combustion modifications for control of nitrogen oxides, carbon monoxide, and unburned hydrocarbons. Improvement of the existing technology is being pursued in a number of U.S. Environmental Protection Agency (EPA) projects. A second option is the conversion of coal into low-sulfur gaseous, liquid, or solid fuels to be utilized in conventional steam boilers or combined cycle plants. The use of liquid fuels in power generation appears to be most applicable to existing plants already burning petroleum-derived heavy fuel oils. The large energy losses currently associated with fuel-cleaning processes ap-

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pear to require use of the advance design combined cycle with integrated gasifier to achieve energy efficiency comparable to the first option. Major unknowns in these designs are the criteria for minimizing nitrogen oxides and other combustion-related pollutants. The third option is the use of fluidized-bed combustion to minimize sulfur oxides and other pollutants. The control of sulfur oxides has been a major consideration in the development of all three technologies;¹ however, other pollutants have been considered less extensively for the latter two options. For other stationary source applications, such as residential and commercial heating, low-sulfur high-Btu fuels will be required, which may include distillate and/or residual fuels derived from coal or shale. The purpose of this paper is to summarize available information on pollutant formation and control during combustion of petroleum-derived liquid fuels as related to synthetic liquids where combustion data are much more limited. The effect of fuel properties on emission control technologies is also discussed.

BACKGROUND

A wide range of subject matter relates directly to combustion of alternate fuels. The topics include pollutant formation mechanisms, applicable emission-control techniques, fuel characteristics, and end use equipment type. Since these areas have been treated in detail for alternate fuels previously,² the background presented is a brief general summary. The most recent information on combustion and emission characteristics is summarized.

Pollutant Formation Mechanisms

The mechanisms of formation of nitrogen oxides (NO_x) have been discussed extensively;^{3,4} however, a brief summary is in order. (Nitric oxide [NO] is the primary form of NO_x found in the flue gas of conventional combustion equipment; the NO_2 that is present is believed to be the product of oxidation of NO after the combustion process is completed.) The mechanisms for formation of NO during combustion are as follows:

- Thermal NO is formed from fixation of atmospheric nitrogen by Zeldovitch reactions,

which have a strong temperature dependence.

- Fuel NO is formed through oxidation of chemically bound nitrogen in the fuel by reactions with a low-temperature dependence but a strong oxygen availability dependence.

There is also experimental evidence⁵ to show that nitrogen species (e.g., NH_3 and HCN) can be synthesized in fuel-rich flames as postulated by Fenimore⁶ and subsequently oxidized to NO as is fuel nitrogen. The other pollutants of concern are SO_x , CO, hydrocarbons, POM, carbon particulate, and metallic particulate. One of the primary incentives for alternate fuels is sulfur removal; therefore, SO_x levels should be low. Since proper system designs for stationary sources can minimize CO and hydrocarbon emissions, no problem is anticipated with alternate fuels. Carbon particulate emissions for heavy liquid fuels pose a potential problem that may be complicated further by the higher carbon-to-hydrogen ratios of many synthetic liquid fuels. Metallic particulate is dependent primarily on the mineral content of the fuel and, therefore, on the extent of coal ash removal during fuel processing. Metal form and particle size distribution also may be affected by the combustion process; however, no detailed information is presently available. Use of alternate fuels in combustion systems will require careful design to minimize these emissions.

Emission-Control Techniques

The basic combustion modification techniques for NO control can be summarized as follows:

- Diluent addition to reduce flame temperature is accomplished through the addition of either water or recycled flue gas to the combustion air.
- Staged combustion is based on operation of burners at a fuel-rich condition with delayed secondary air addition to complete heat release, thereby limiting both peak flame temperatures and primary zone oxygen availability.
- Burner modifications involve changes in fuel and air mixing conditions to promote localized fuel-rich conditions and/or combustion gas recirculation.
- Novel techniques, such as catalytic combus-

tion, may allow NO emissions lower than those achievable for combustion of clean fuels in conventional systems and may be particularly applicable to redesign for maintaining system efficiency.

The first technique controls only thermal NO, whereas the last three also may control fuel NO. The emissions of the products of incomplete combustion (CO, unburned hydrocarbons, and carbon particulate) are subject to increase as NO is decreased past a critical point for fixed system design. However, there is a body of evidence that indicates that these emissions can be controlled if the system is designed or modified with both NO and carbonaceous emissions-control requirements in mind. Since stack measurements are for nitrogen oxides (NO_x), that term will be used in subsequent discussion of control techniques.

Fuel Characteristics

The properties of alternate fuels have been summarized previously,² and only a brief updated discussion is presented below.

Synthetic liquids may be grouped into two general categories: Those synthesized from the products of coal gasification, and those derived directly as liquids by hydrogenation of coal or by retorting of oil shale. The fuels in the first category tend to be clean low-boiling fuels such as alcohols and Fischer-Tropsch liquids. Since these fuels are also essentially free of both nitrogen and sulfur, combustion problems are minimal. The liquids in the second category may be compared to crude petroleum oils because both consist of a wide range of hydrocarbon compounds with boiling points from 300 to over 900 K. In the crude synthetic liquid fuels, the bound nitrogen content is generally quite high (more than 0.5 percent). In addition to this, the nitrogen is distributed more evenly over the range of fuel cuts than it is in crude oil. The most complete information is available on a 2.19-percent nitrogen Paraho shale crude, as shown in Figure 1.⁷ The nitrogen content is above 1.2 percent by weight for all fuel fractions shown here. The sulfur levels are below 1 percent and decrease in the higher boiling fractions. For comparison, a Wilmington, California, crude⁸ that contained 0.65 percent nitrogen yielded only 0.07 percent in the distillate oil product (corresponding in boiling point to the

33-percent volume fractions of the shale crude). The nitrogen and sulfur can be removed to low levels by hydrotreating;⁹ however, it is an expensive process. Where other considerations are paramount (e.g., fuel stability for aircraft uses), severe hydrotreating may be unavoidable. For other applications, it may be possible to achieve NO_x control by combustion modification of fuels with minimum hydrotreating to upgrade the carbon-to-hydrogen ratio for smoke suppression or to modify the nitrogen compounds to more volatile forms without substantial denitrification.

In a recent review of commercialization potential of coal-derived liquid fuel processes,¹⁰ Whitaker summarized the Electric Power Research Institute's view of coal-derived liquids. The discussion dealt with three processes: solvent refined coal (SRC-II), H-Coal, and Exxon Donor Solvent (EDS). While the article indicated that the fuel properties would probably depend both on the process and on the coal feedstock, it did not specify these properties.

DISCUSSION

For all combustion systems (except reciprocating engines, which are not a subject of this paper), the common feature is the use of a burner for initial fuel and air mixing. Although the characteristics of specific systems significantly differ, the combustion zone conditions that lead to minimum emissions are quite similar for two broad classes of fuels (i.e., nitrogen-free and nitrogen-containing). A large body of information has been built up on burner designs for emission control for conventional fuels, much of which should apply directly to systems burning alternate fuels.

The primary emission category that is controllable by combustion technology is NO_x . Control of carbonaceous emission (e.g., CO, hydrocarbon, POM, and carbon particulate) also is affected by combustion technology; however, it may be treated as a second-order effect, except for gas turbines operating at low load. This is not based on establishing priorities for health or environmental effects of the pollutants but rather on the approaches necessary to control all emissions by combustion technology. Many conventional design approaches are currently used that offer the potential for low carbonaceous emissions by employing conditions

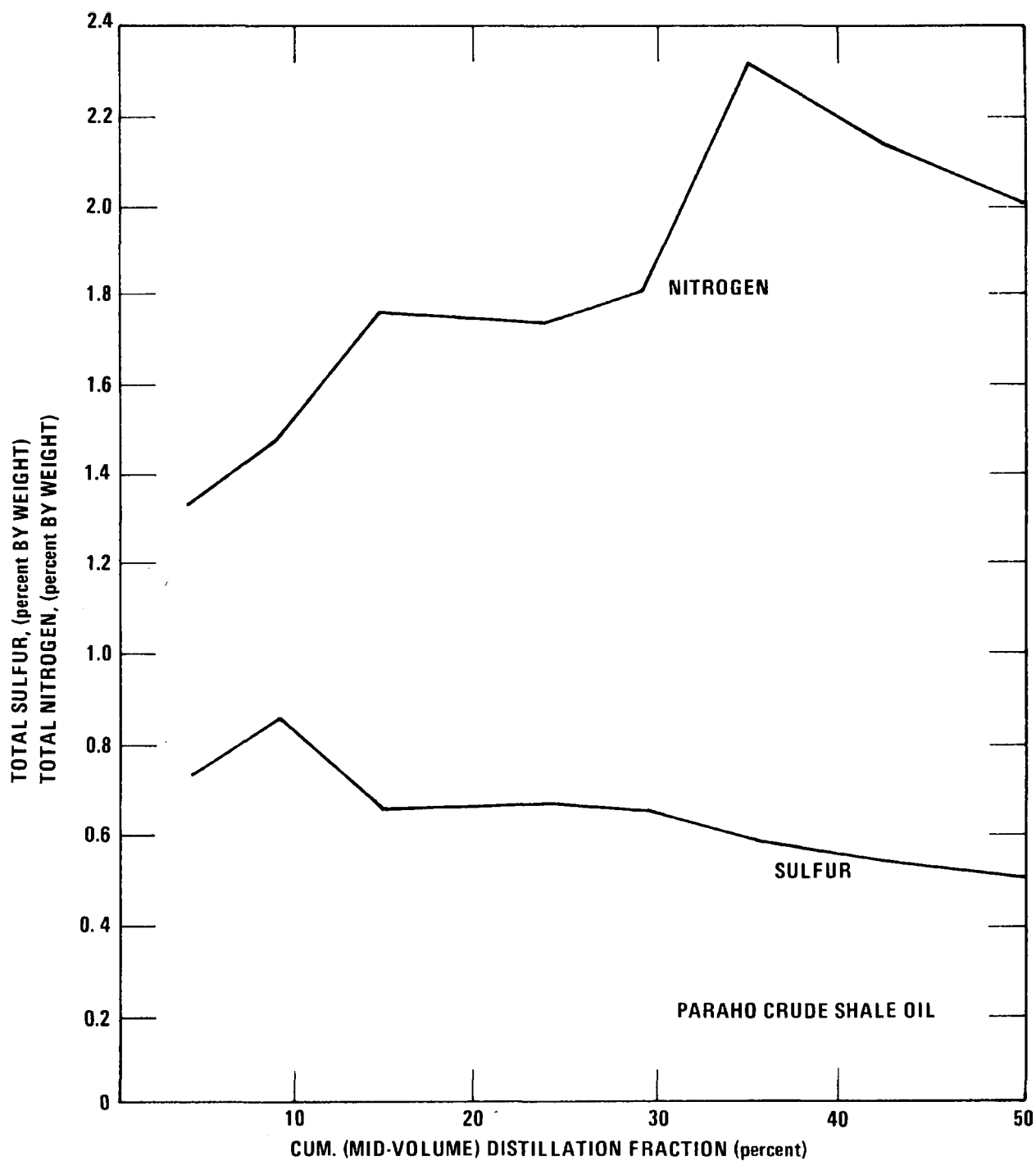


Figure 1. Total weight of nitrogen and sulfur as a function of the cumulative midvolume distillation fraction.¹²

that lead to high levels of NO_x . Therefore, it is necessary to approach the problem from the other direction; that is, to employ the specialized design concepts that give low levels of NO_x and optimize that technology to achieve minimum carbonaceous emissions. In this way, optimum control of all emissions becomes a primary design criterion and a goal that can be achieved during the development of the combustion process for a specific application.

The following discussion identifies key system features that relate to emission control for these two general classes of fuels. Emphasis is placed on nitrogen-containing fuels.

Nitrogen-Free Fuels

Fuels that do not contain chemically bound nitrogen produce only thermal and "prompt" NO_x , for which there is a substantial body of control technology already developed. For stationary heat and steam generation systems, the primary techniques are external flue gas recirculation and burner designs that maximize internal recirculation of relatively cool combustion products. The burner techniques can be coupled with combustion chambers designed to achieve early heat removal, thereby further reducing peak temperature and optimizing the NO_x reduction. These techniques are compatible with low carbonaceous emissions and with low excess air operation for maximum system thermal efficiency. For gas turbines, a number of approaches are being explored. Substantial effort has been devoted to achieving premixed prevaporized primary combustion zones, which can be operated at conditions giving lower flame temperatures (e.g., fuel lean) and, therefore, lower thermal NO_x . These concepts also produce low carbon particulate levels, but may produce excessive CO, particularly over the full operating load range of the engine. This technique is well suited to the gas turbine that normally operates at high excess air levels (i.e., 300 to 400 percent). A major consideration for this concept is burner stability. These relatively conventional technologies are well documented and do not require further discussion.

Nitrogen-Containing Fuels

Nitrogen compounds chemically bound in the fuel are oxidized to form what is termed fuel

NO_x . This is a significant concern for alternate fuels because virtually all untreated coal- and shale-derived fuels have large concentrations of bound nitrogen species. Before processing, the liquid crudes derived from coal and shale have more than 0.5 percent nitrogen. Because sulfur levels are generally below 1 percent, minimum hydrotreating is desirable to limit efficiency and economic penalties. For coal-derived solid fuels (e.g., SRC-I), the nitrogen compounds are not removed to a significant degree by the fuel conversion processes. For both conventional solid and liquid fuels, the nitrogen is bound within the fuel structure as single or multiple heterocyclic ring compounds, and a similar structure is believed to exist in the alternate fuels.

In addition to the absolute amount of nitrogen contained in the fuel, it appears that the degree of control achievable may also depend on nitrogen distribution. The evidence indicates that the nitrogen in the fuel is converted to simple gas-phase species (HCN and NH_3) before it is oxidized to NO or reacts to form N_2 . The heterocyclic nitrogen compound in the parent fuel appears to undergo a sequential pyrolysis through lighter organic forms to HCN or NH_3 . The extent of this pyrolysis depends on temperature, residence time, and ambient conditions (oxidizing or reducing). Although it has been shown that a quantitative conversion of pyridine ($\text{C}_5\text{H}_5\text{N}$) to HCN can be achieved at 1,373 K under inert conditions,¹¹ comparable conversions have not been shown for any real fuel at residence times achievable in practical combustors, even at considerably higher temperatures. The balance of the nitrogen is contained in the fuel residue that may be char or tar. The nitrogen evolved into the gas phase is referred to as "volatile nitrogen." The significance of this distribution of nitrogen compounds is discussed in greater detail below.

The basis of fuel NO_x control techniques is the same regardless of the fuel type. A fuel-rich primary combustion zone is used to facilitate the conversion of fuel nitrogen to molecular nitrogen (N_2). A fraction of the nitrogen is evolved as XN species (e.g., HCN and NH_3), which partially oxidize to form NO . The NO then reacts with the residual SN to form N_2 . Because XN species remaining in the rich mixture undergo high-efficiency conversion to NO in the lean secondary stage and because any NO will be retained almost quantitatively, the rich-zone con-

ditions must give a minimum value of ΣXN (i.e., $\text{HCN} + \text{NH}_3 + \text{NO}$). The stoichiometry required to achieve minimum ΣXN depends on several factors, including:

- The rate of evolution of nitrogen species from the fuel;
- The inevitable distribution of stoichiometries from rich to lean, which exists in an overall fuel-rich zone of a diffusion flame;
- The overall temperature of the reaction zone; and
- The overall residence time in the reaction zone.

The interaction of these four factors depends on the aerodynamic mixing of a turbulent diffusion flame, as well as the nitrogen distribution for a given fuel. It is desirable to extract some energy from the rich products prior to second-stage air addition to reduce the thermal NO_x formation. In the lean second stage, a significant fraction of the gaseous ΣXN and a smaller fraction of any residual nitrogen in the char or tar will be converted to NO_x . Based on evidence for coal char and petroleum coke, the conversion of this nonvolatile nitrogen to NO occurs at a low fraction efficiency (i.e., less than 10 percent) for solid fuels. In fact, the NO_x levels from these fuels are insensitive to burner design changes that significantly reduce NO_x from pulverized coal. This char NO_x may impose a minimum level below which NO_x cannot be reduced for a given primary zone condition. There are indications that the nonvolatile nitrogen species from liquid fuels may undergo higher fractional conversion to NO_x than those in solid fuels.

Emission Performance: Boilers

Primarily because of the small quantities of synthetic liquid fuels available, the data on their combustion emissions and performance in practical systems are limited. Therefore, this discussion will review the available data from experimental systems and compare the performance of synthetic liquids to that of conventional petroleum fuels. The data on some of the earlier work have been summarized previously;¹² only an update is presented below.

Blazowski and Maggitti¹³ believe that the alternative fuel characteristics that are most likely to affect future gas turbine design are the hydrogen and nitrogen content and the thermal stability. Carbon-to-hydrogen ratio influences

soot formation, which leads to increased flame emissivities increasing liner temperatures and smoke emissions. Fuel-bound nitrogen in jet fuels contributes to higher NO_x emissions unless the combustor is designed to minimize fuel nitrogen conversion to NO_x .

Increased NO_x emissions have also been observed when coal- or shale-derived liquids have been burned in boilers. Muzio¹⁴ carried out tests with SRC-II and found that its combustion characteristics were similar to those of No. 2 fuel oil except that NO_x emissions were higher (400 ppm compared to 80 ppm) mainly because the SRC-II contained 1.12 percent nitrogen. However, emissions can be reduced by blending with lower nitrogen petroleum-derived fuels or staged combustion. Similar experiences are reported by Mansour¹⁵ when Paraho shale oil was burned.

The most comprehensive comparison of emission characteristics to fuel properties has been carried out by Heap and coworkers.¹⁶ A variety of petroleum-derived residual oils and synthetic fuels derived from coal and shale have been burned in two experimental systems: a small (20 kW thermal) down-fired tunnel¹⁷ and a 900-kW cold wall axisymmetric combustor that simulates the firetube of a package boiler.¹⁸ The down-fired combustor allowed direct determination of fuel nitrogen conversion by substitution of argon/oxygen for the combustion air, thereby eliminating thermal NO_x . The package boiler simulator allows the smaller scale results to be generalized to practical equipment. The results of these experiments provide significant insight into pollutant control for both petroleum-derived and synthetic fuels. The properties of the petroleum oils have been summarized previously,¹⁷ and properties of the synthetic fuels are shown in Table 1.¹⁶ NO_x emissions for all fuels tested in the tunnel furnace are summarized in Figure 2. Since the data are for a system where very fine oil droplets (about 25 μm) are well dispersed in the oxidizer at a fuel-lean condition, it is not surprising that the fuel NO_x emissions (lower curve) are a strong function of fuel nitrogen content. The NO_x levels are high because the percentage conversion under these premixed conditions is higher (50 to 75 percent) than expected in practical systems (25 to 45 percent). The upper curve shows that thermal NO_x , which is determined using air as the oxidizer, is relatively constant for most fuels. For some

TABLE 1. ALTERNATIVE LIQUID FUEL PROPERTIES¹⁶

	DFM	SRC-II Blend	Shale Derived Residual	SRC-II M:H Dist.	Synthoil	Paraho Shale
Ultimate Analysis						
Carbon, %	86.18	89.91	86.71	85.91	86.30	84.6
Hydrogen, %	13.00	9.27	12.76	8.74	7.44	11.3
Nitrogen, %	0.24	0.45	0.46	0.97	1.36	2.08
Sulfur, %	0.51	0.065	0.038	0.30	0.80	0.63
Conradson Carbon Residue, %	4.1	6.18	0.19	0.51	23.9	2.9
Asphaltene, %	0.036	4.10	0.083	-	16.55	1.33
API Gravity at 60°F	33.1	10.0	29	11	-	-
Viscosity SSU at 140°F	36.1	40.6	54.3	-	10,880	97
Gross Heat of Combustion, Btu/lb	19,430	17,980	19,350	-	16,480	18,290

*Paraho Diesel Fuel Marine

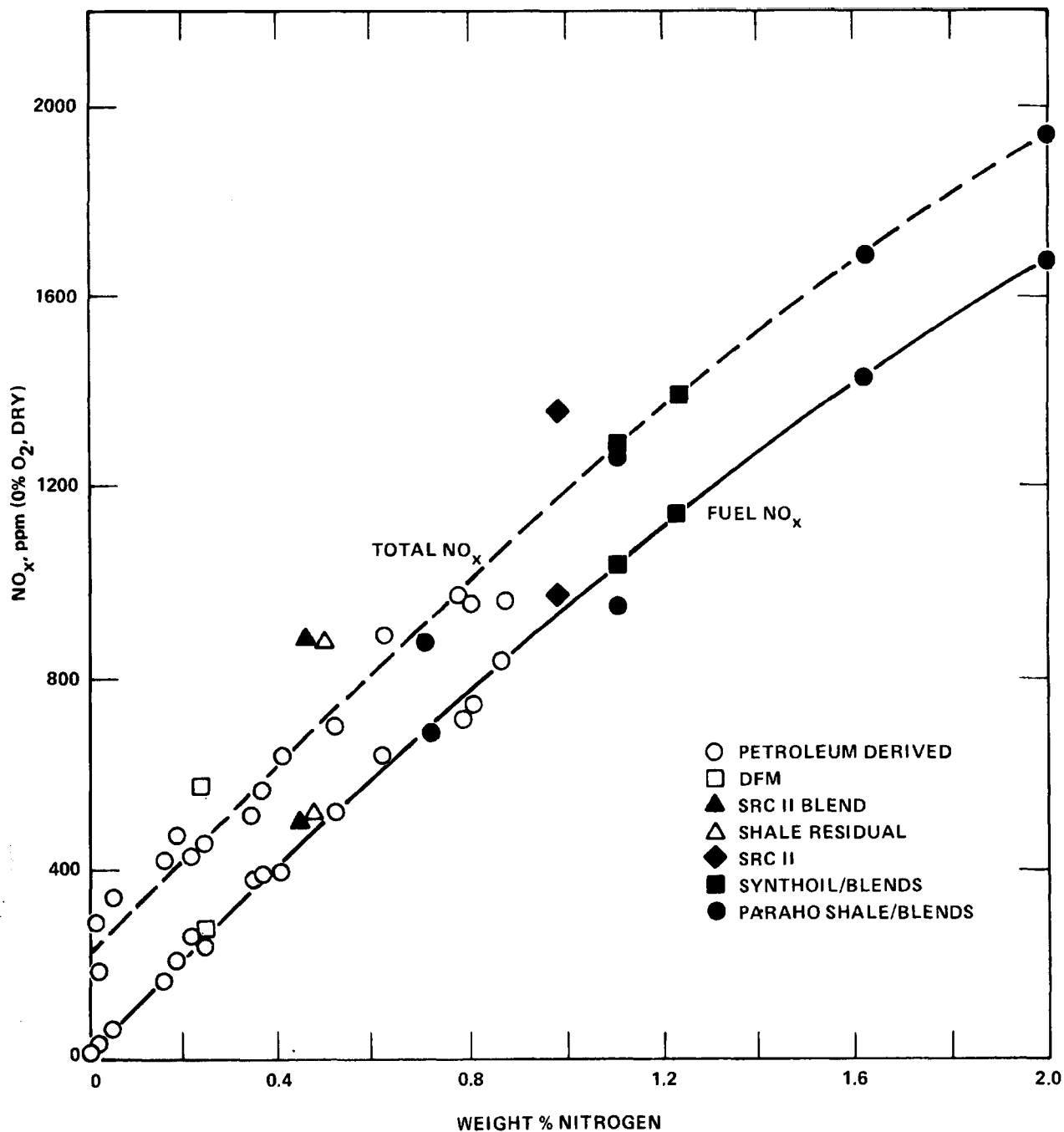


Figure 2. The effect of fuel nitrogen content on total and fuel NO_x (5 percent excess oxygen).¹⁶

unexplained reason, the alternative fuels appear to produce a somewhat higher thermal NO_x level than the petroleum fuels. This points out the need for NO_x control techniques for the alternative fuels.

To examine the effects of control technologies, Heap¹⁶ also ran the tunnel furnace under staged conditions. The total NO_x data for the Paraho crude shale oil, shown in Figure 3 at two primary residence times, indicate that very high levels of control (90 to 95 percent) can be achieved at reasonable primary stage stoichiometries (i.e., 70 to 80 percent theoretical air). Figure 4 compares the results of the shale crude to a residual liquid from the same crude that has been extensively hydrotreated, SRC-II and a blend of SRC-II with the donor solvent. While the uncontrolled levels are substantially different, the minimum levels under staged conditions are quite similar. It is interesting to note that the minimum NO_x for the 2.08-percent nitrogen shale crude is *lower than* for the 0.97-percent nitrogen SRC-II, a result to be discussed at greater length. A comparison of results in the tunnel and in the package boiler simulator is shown in Figure 5. Although conditions were maintained as consistently as possible between the systems, the minimum NO_x from the tunnel furnace is significantly lower than conditions for the simulator using the same type of ultrasonic atomizer (curve B). This might be attributable to differences in a number of primary zone factors including amounts of wall cooling affecting the rate of nitrogen evolution in the primary zone; fuel/air mixing rates creating wider distribution of off-optimum stoichiometries in the boiler simulator; or control of residence time for secondary air addition because of recirculation patterns. Comparison of curves A and B for different nozzles in the boiler simulator shows that nozzle A, which produces a coarser spray than B, has lower baseline emission (primary zone stoichiometric ratio of 1.17) but higher emissions under staged conditions. This points out the importance of optimizing the combustion system for minimum emissions.

These results and others suggested that under staged conditions, factors other than total percent nitrogen affected the minimum attainable emissions. A comparison of minimum NO_x under staged conditions for synthetic and petroleum-derived fuels is shown in Figure 6. For

many fuels with approximately the same fuel nitrogen level (0.4 to 0.6 percent) a significant spread exists. The minimum is a nitrogen- and sulfur-doped distillate fuel where all of the nitrogen is volatile (i.e., has a boiling point of about 400 K), and the maximum is the SRC-II blend. It should also be noted that at fuel nitrogen levels above 0.6 percent, there is only a small increase in the minimum achievable NO_x . In an attempt to relate the effects of fuel properties to emissions, a bench-scale vacuum distillation technique was selected as a relatively simple and rapid method of quantifying the amount of "volatile" nitrogen in the fuel. Each fuel was distilled into as many as five fractions, and the total mass of oil and nitrogen content of each fraction was determined. The data for petroleum oils have been presented previously by Pershing.¹⁹ The results for the specific alternative fuels tested are compared in Figure 7 to those for the range of petroleum oil. The shaded area shows the extremes of individual residual oils from less than 10 percent of the nitrogen evolved at 811 K (1,000° F) to over 40 percent at the same temperature. By comparison, all of the synthetic fuels show greater than 40 percent evolved at 700 K (800° F). It is particularly interesting to note that even the "residual" derived from a highly hydrotreated Paraho crude has bound nitrogen more volatile than in any petroleum-derived residual.

These data were used by Heap¹⁶ to correlate the effectiveness of staged combustion vs. volatile nitrogen for various fuels, as shown in Figure 8 (which uses the same symbols as previous figures). The ratio of NO_x staged to unstaged, which represents the fraction not controlled by staged combustion, increases as the nitrogen volatility decreases. The dotted lines are for the tunnel furnace at two primary residence times, where the lower line is the longer residence time, and the solid line is the package boiler simulator. This figure indicates that for a given system the nitrogen volatility has a strong effect on the degree of NO_x control achievable; however, the system design also is a significant factor.

Emission Performance—Turbines

The information available on combustion of synthetic liquid fuels in gas turbines has been for baseline combustors without NO_x control

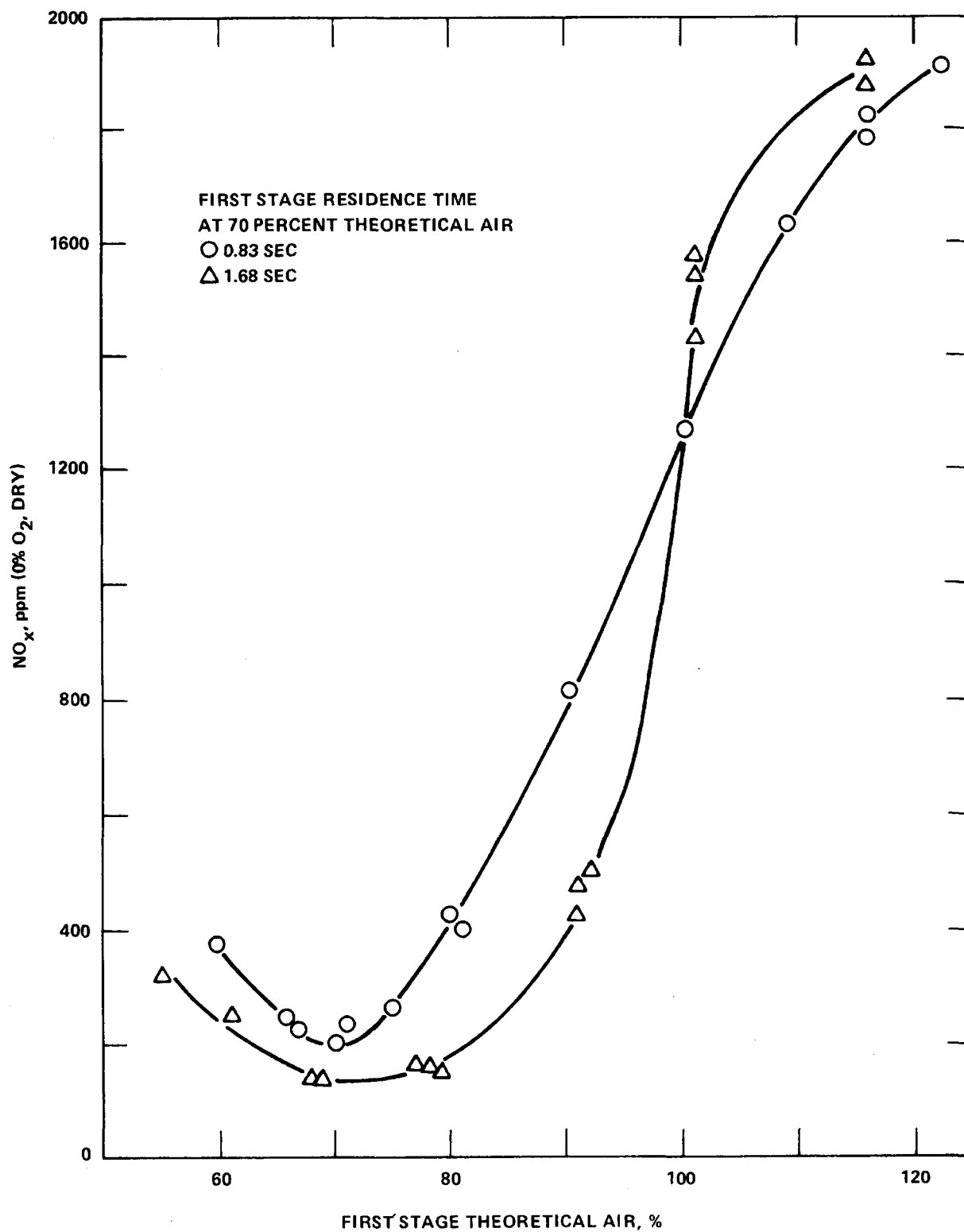


Figure 3. The influence of staged operation in the tunnel furnace on NO_x emissions from the Paraho shale oil (5 percent excess oxygen).¹⁶

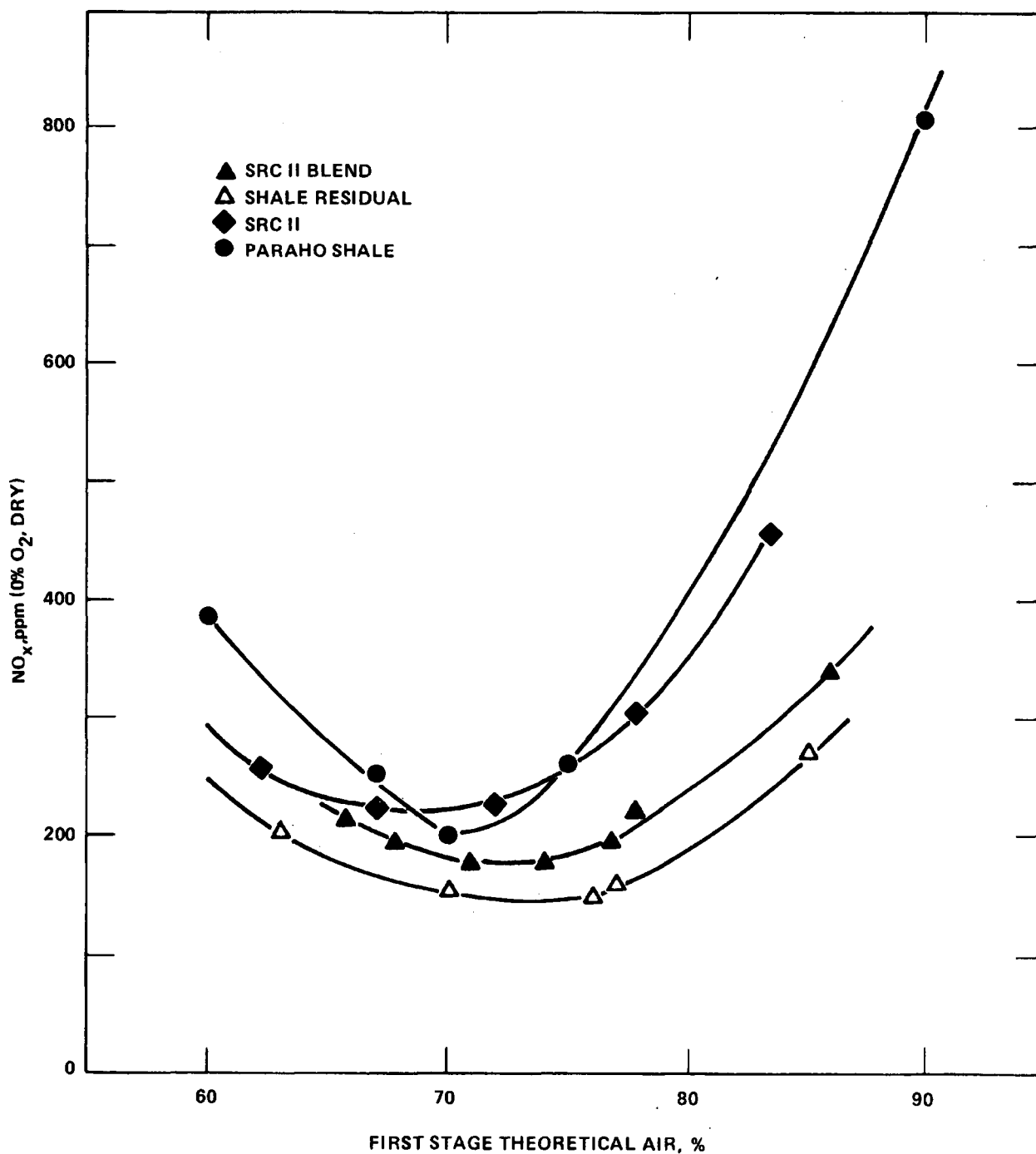


Figure 4. Minimum NO_x levels achieved with alternative fuels (tunnel furnace primary zone residence time 0.83 sec).¹⁶

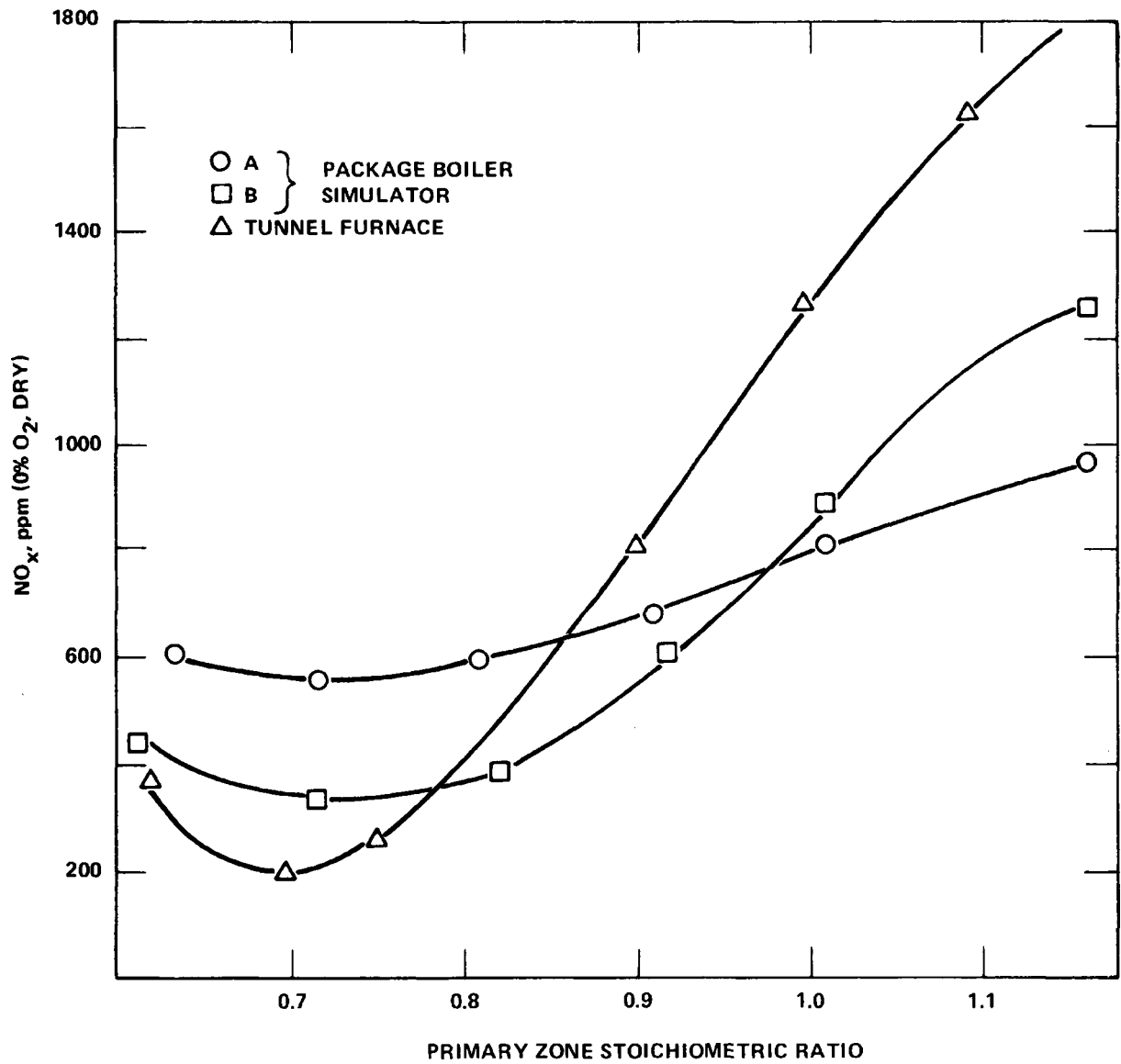


Figure 5. NO_x emissions staged—Paraho shale (5 percent overall excess oxygen).¹⁶

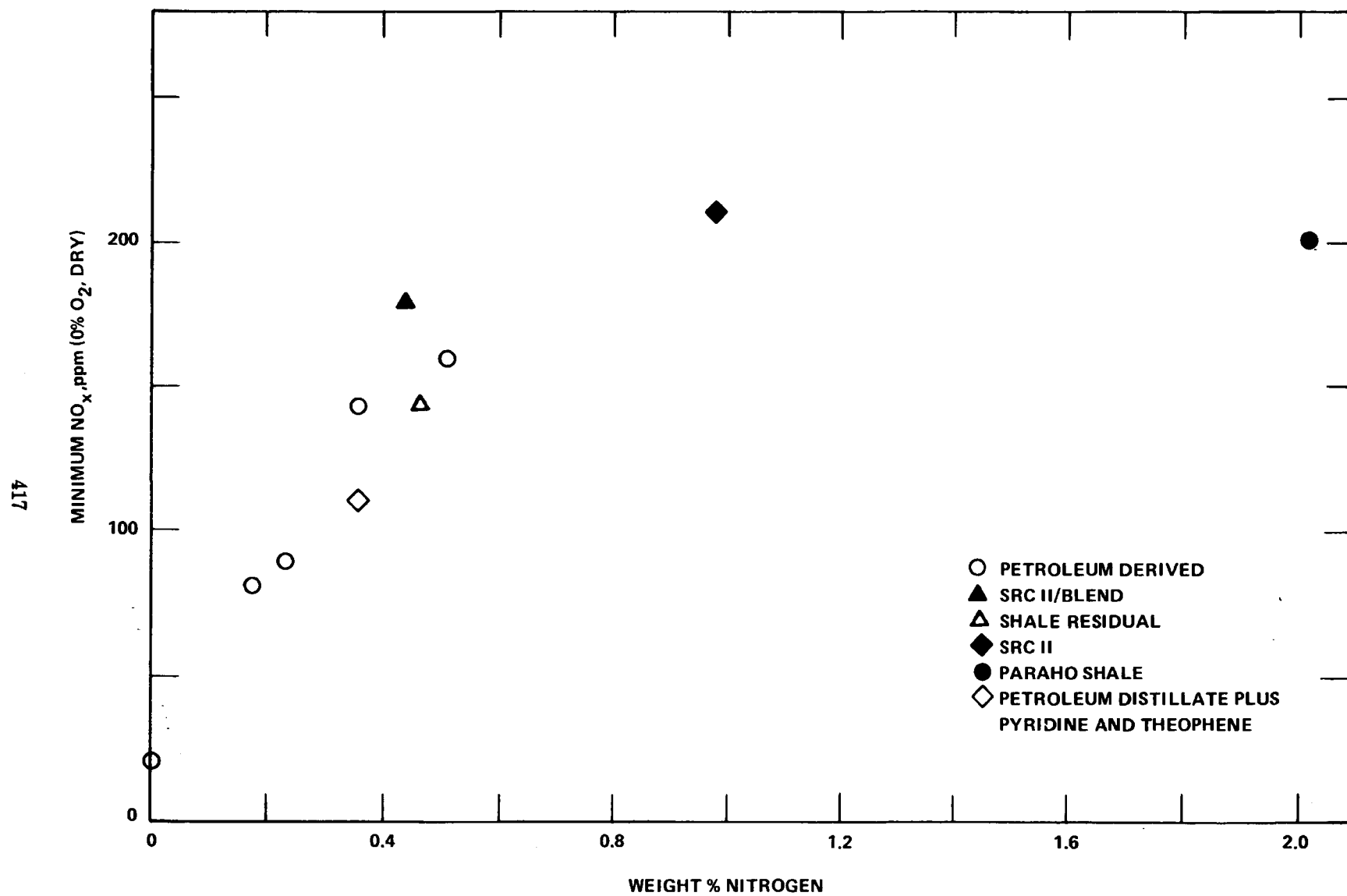


Figure 6. Minimum NO_x levels obtained in the tunnel furnace as a function of fuel-bound nitrogen content.¹⁶

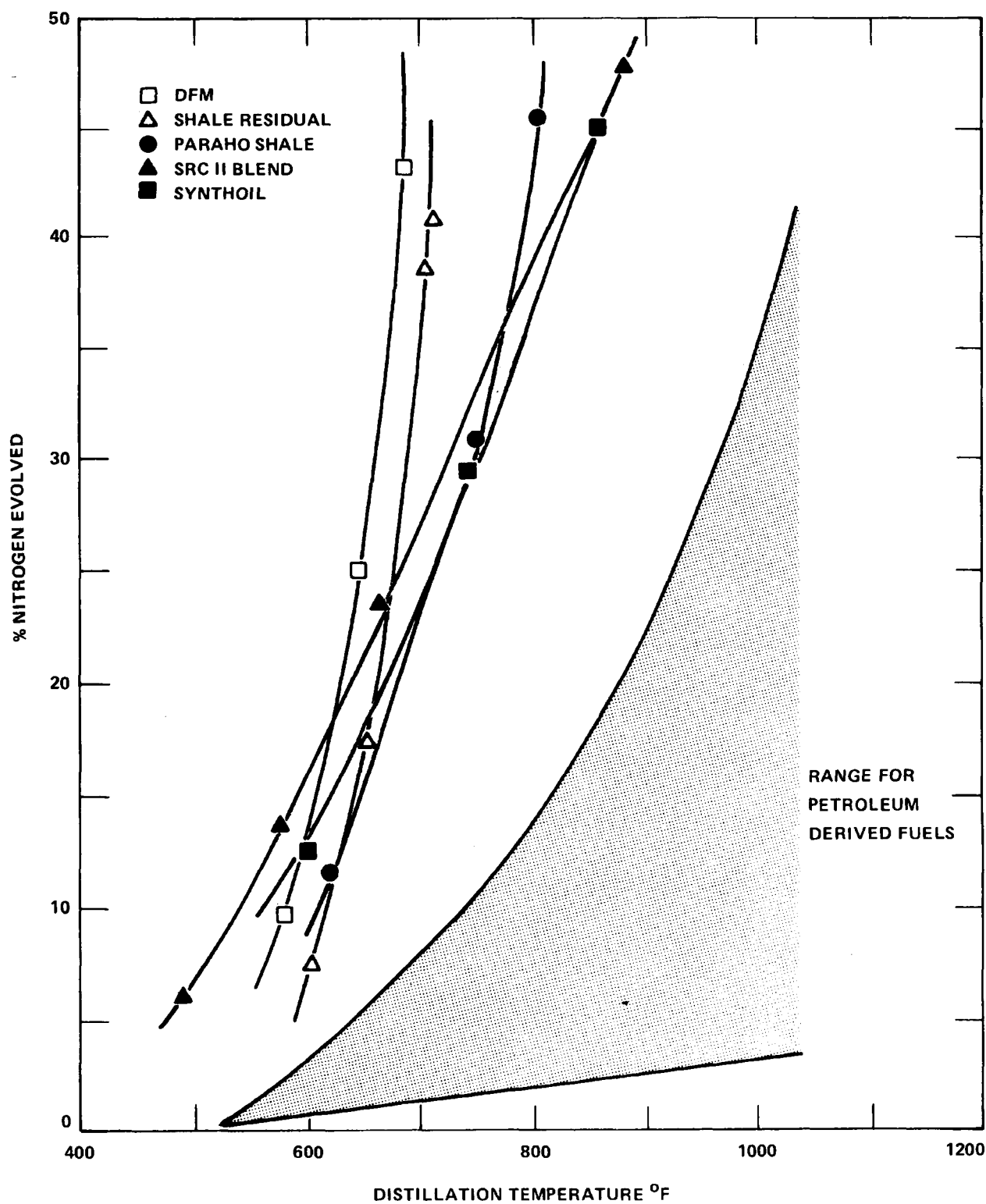


Figure 7. Fuel nitrogen volatility as determined by vacuum distillation.¹⁶

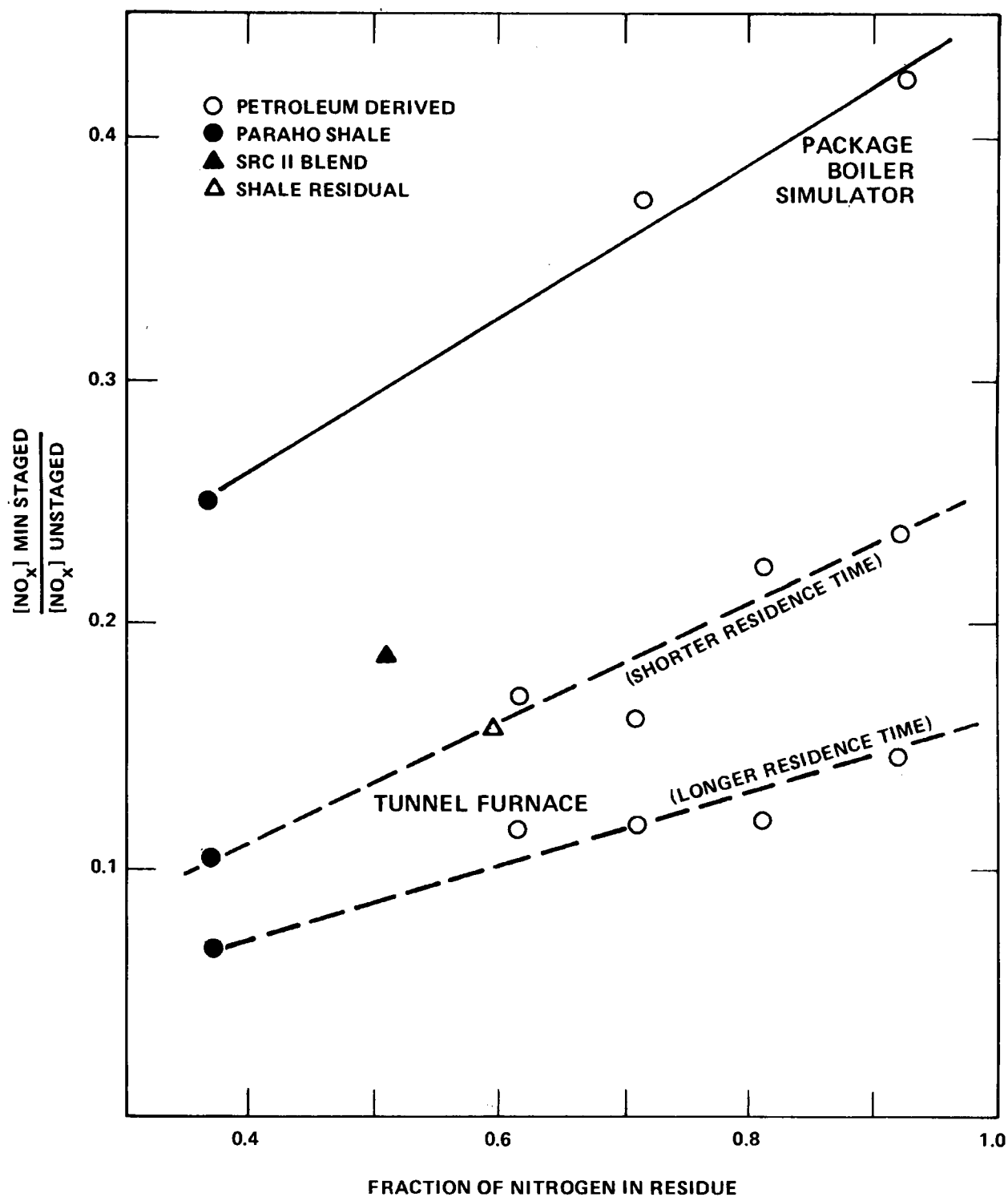


Figure 8. The influence of volatile fuel nitrogen on staging effectiveness (reference 16).

technology applied. There are indications that the wet control techniques designed to control thermal NO_x , such as water injection, will have little beneficial effect on fuel NO_x , and possibly will be detrimental.

A promising low NO_x combustor concept for gas turbine engines has been reported by Pierce.²⁰ The program goals were to achieve NO_x emissions below 50 ppmv (at 15 percent O_2) for clean fuels and 100 ppmv (at 15 percent O_2) for fuels with less than 0.5 wt percent bound nitrogen. The bench-scale version of the combustor, which burns a premixed, prevaporized, fuel-rich fuel and air mixture, followed by rapid addition of secondary air to avoid high peak temperatures during fuel burnout, has achieved minimum emission levels of 20 ppmv (at 15 percent O_2) for No. 2 fuel oil and 35 ppmv (at 15 percent O_2) for No. 2 fuel oil doped with 0.5 wt percent nitrogen as pyridine.²¹

Based on the previous discussion on boiler experience, it may be expected that the nitrogen-doped oil would provide a good indication of the control potential for distillate synthetic liquid fuels, although the NO_x level for the higher boiling nitrogen compounds in these fuels may be somewhat higher. It also appears that the premixed and prevaporized nature of the primary zone should provide the maximum opportunity for minimizing fuel NO_x . The bench-scale combustor has been scaled up to the size of a single can for a practical engine, and preliminary testing appears to show similar performance.

Practical Implications

Based on the above discussion of the combustion characteristics of synthetic liquid fuels, some generalizations about system design and fuel properties are possible.

System Design—

There are some obvious differences in the emission performance between the tunnel furnace and the package boiler simulator¹⁶ that cannot be fully explained at this time; however, speculation is possible if we adopt the volatile nitrogen hypothesis discussed earlier. It may be restated as follows:

- That nitrogen species should be evolved as early as possible in the fuel-rich primary zone to allow maximum possible reaction of nitrogen species (XN) to N_2 ; and

- That residual XN not reacted in the first stage will oxidize to NO_x with a relatively high conversion in the fuel-lean second stage.

The conditions that appear to favor maximum N_2 formation include high temperature to evolve nitrogen species as early as possible and longer residence times. There is also an indication that an atomizer that yields small droplets that are well dispersed in the airstream improves the degree of control achieved; some doubt exists that a completely prevaporized fuel, premixed with air, is desirable, even if possible. While it is obvious that prevaporization is not possible for petroleum-derived residual oils, it may be possible for many of the synthetics (e.g., the shale residual tested). A directly comparable test is required to determine if a well-dispersed spray of small droplets with combustion in a diffusion flame over the range of stoichiometries is superior to premixed combustion of a vaporized fuel at a single stoichiometry.

The degree of success achieved in controlling NO_x from any given fuel will depend on integration of the fuel atomizer, the air mixing device, and the primary zone thermal environment (e.g., cooled or refractory). While the available information is encouraging, additional work is necessary to optimize emissions for systems burning heavy liquids that cannot be completely vaporized.

Fuel Properties—

Compared to petroleum residual oils, the synthetic fuels tested to date appear to have a larger fraction of the nitrogen bound in low-boiling fuel fractions and, therefore, to be more amenable to NO_x control technology. The main problem with this conclusion is that the fuels are not directly comparable. That is, the petroleum residual fuels are the heaviest ends of the crude that contain most nitrogen of the refractory compounds, whereas most of the synthetic fuels should be regarded as crudes. (Note that the one exception, the Paraho residual, results from distilling a heavily hydrotreated crude.) In actual practice it would probably be desirable to distill the synthetic crude, using the lighter fractions for jet fuels and distillate oils, thereby leaving the heavier fractions for boiler fuels. While it may be argued that such a synthetic residual would still contain substantially less

refractory nitrogen compounds than petroleum residual (see Figure 7), such a heavy synthetic must be tested to determine its performance.

The second aspect that remains to be established is the need for hydrotreating the various synthetic fractions. For the lighter jet and distillate fuel fractions, substantial removal of nitrogen compounds is apparently required to enhance storage stability. One approach is to hydrotreat the full crude prior to distillation; however, an alternative is to distill the light fractions and then hydrotreat to remove nitrogen to required levels. The primary decision here would probably be based on an economic tradeoff of the smaller fraction of the crude barrel available as premium fuel vs. the cost of heavy hydrotreating the full crude.

If one assumes that an unhydrotreated residual containing a significant nitrogen content (e.g., more than 1 percent) is to be used as a boiler fuel, a second question of extent of hydrotreating must be addressed. Assuming that the data shown in Figure 6 prove applicable to practical systems, the economic impact of hydrotreating from 2.08 percent nitrogen to about 0.4 percent must be balanced against a 25-percent reduction of NO_x (i.e., 200 vs. 150 ppm NO_x , respectively). However, if the true untreated shale residual produces substantially more NO_x than the crude for a comparable nitrogen content, yet another tradeoff may be possible. The extreme case is to deeply hydrotreat the crude and achieve the relatively low nitrogen residual, with the attendant potential increase in distillate fraction, or to mildly hydrotreat the residual fraction simply to upgrade the nitrogen into a more volatile form without substantial denitrification. In either case it might be expected that the smoke-forming tendencies of the fuels would be decreased by hydrotreating, which might provide yet another consideration in the decision process.

Based on the current state of knowledge, it is not possible to draw a firm conclusion about fuel processing. Careful experimental work on fuels of specific properties is required.

CONCLUSIONS

The data on combustion of synthetic liquids in practical combustion equipment are still very limited. From the available data from experimental apparatus and comparison of emission characteristics of synthetic liquids to petro-

leum-derived fuels, the following conclusions can be drawn:

- Under fuel-lean conditions, the nitrogen content of the fuel is the dominant factor for a given system. Conversion to NO_x is similar for petroleum and synthetic liquids, with fractional yield NO_x decreasing with increased nitrogen content.
- Under staged combustion conditions, the volatility of the fuel nitrogen compounds is an important factor in the degree of control achievable, and the absolute level of NO_x attainable may be a weak function of fuel nitrogen content.
- System design is a significant factor in the degree of control achievable with a given fuel. The key variables appear to be primary zone stoichiometry, residence time, and thermal environment. The methods of atomization and of air/fuel mixing strongly influence the performance of a practical system.
- The experimental results appear to have important implications for fuel treatment strategies, particularly denitrification; however, experiments with a wider range of fractions from a common crude are required.

METRIC CONVERSION

While it is EPA policy to use metric units, the nonmetric data used in this paper have been secured from published literature and have not been altered. Metric conversion can be accomplished with the following factors:

$$^{\circ}\text{C} = 5/9 (^{\circ}\text{F} - 32)$$

$$\text{J/g} = \text{Btu/lb} \times 2.326$$

REFERENCES

1. *Economic Commission for Europe, Second Seminar on Desulfurization of Fuels and Combustion Gases*. Washington, D.C. November 11-20, 1975.
2. Martin, G. B. Environmental Considerations in the Use of Alternate Fuels in Stationary Combustion Processes. In: *Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology*. EPA-650/2-74-118, NTIS PB 238-304/AS. October 1974. p. 259-276.
3. Brown, R. A., H. B. Mason, and R. J. Schreiber. *Systems Analysis Require-*

- ments for Nitrogen Oxide Control of Stationary Sources. Aerotherm-Acurex Corp. EPA-650/2-74-091, NTIS PB 237-367/AS. September 1974.
4. Martin, G. B. Overview of U.S. Environmental Protection Agency's Activities in NO_x Control for Stationary Sources. In: *Joint U.S.-Japan Symposium on Countermeasures for NO_x* . Tokyo, June 28-29, 1974.
 5. Yamagishi, K., M. Nozawa, T. Yoshie, T. Tokumoto, and Y. Kakegawa. *A Study of NO_x Emission Characteristics in Two-Stage Combustion*. (Presented at 15th Symposium [International] on Combustion. Tokyo. August 1974.)
 6. Fenimore, C.P. *Formation of Nitric Oxide in Premixed Hydrocarbon Flames*. (Presented at 13th Symposium [International] on Combustion. Salt Lake City. August 1970.)
 7. Bartik, H., K. Kunchal, D. Switzer, R. Bowen, and R. Edwards. *Final Report: The Production and Refining of Crude Shale Oil into Military Fuels*. Applied Systems Corp. Office of Naval Research Contract N00014-75-C-0055. August 1975.
 8. Ball, J. S., and H. T. Rall. Nonhydrocarbon Components of a California Petroleum. In: *27th Midyear Meeting of the American Petroleum Institute Division of Refinery*. San Francisco, 1962.
 9. Dzuna, E. R. Combustion Tests of Shale Oils. In: *Central States Section of the Combustion Institute*. Columbus, April 5-6, 1976.
 10. Whitaker, R. Scaling up Coal Liquids. *EPRI Journal* 3(7):6-13. September 1978.
 11. Axworthy, A. E., and V. H. Dayan. Chemical Reactions in the Conversion of Fuel Nitrogen to NO_x : Fuel Pyrolysis Studies. In: *Proceedings of the Second Stationary Source Combustion Symposium, Vol. IV: Fundamental Combustion Research*. EPA-600/7-77-073d, NTIS PB 274-029/AS. July 1977. p. 39-78.
 12. Martin, G. B. NO_x Considerations in Alternate Fuel Combustion. In: *Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology*. EPA-600/2-76-149, NTIS PB 257-182/AS. June 1976. p. 373-394.
 13. Blazowski, W. S., and L. Maggitti. Future Fuels in Gas Turbine Engines. In: *Progress in Astronautics and Aeronautics Vol. 62, Alternative Hydrocarbon Fuels: Combustion and Chemical Kinetics*, Bowman, C. T., and Birkeland, J. (ed.). American Institute of Aeronautics and Astronautics, 1978.
 14. Muzio, L. J., and J. K. Arand. *Small Scale Evaluation of the Combustion and Emission Characteristics of SRC Oil* (Paper Presented at the American Chemical Society Fuel Chemistry Symposium on Combustion of Coal and Synthetic Fuels. Anaheim. March 1978)
 15. Mansour, M. N., and D. G. Jones. *Emission Characteristics of Paraho Shale Oil as Tested in a Utility Boiler*. EPRI Report Number AF-709. March 1978.
 16. Heap, M. P., G. C. England, and D. W. Pershing. *Emission Characteristics of Alternative Liquid Fuels*. (Presented at the Institute of Gas Technology Symposium on New Fuels and Advances in Combustion Technology. New Orleans. March 26-30, 1979.)
 17. Heap, M. P., et al. The Influence of Fuel Characteristics on Nitrogen Oxide Formation—Bench Scale Studies. In: *Proceedings of the Third Stationary Source Combustion Symposium, Vol. II*. EPA-600/7-79-050b, NTIS PB 292-540/AS, February 1979. p. 41-71.
 18. England, G. C., et al. The Control of Pollutant Formation in Fuel Oil Flames—The Influence of Oil Properties and Spray Characteristics. In: *Proceedings of the Third Stationary Source Combustion Symposium, Vol. II*. EPA-600/7-79-050b, NTIS PB 292-540/AS, February 1979. p. 3-39.
 19. Pershing, D. W., G. C. England, M. P. Heap, and G. Flament. *Control of NO_x from Liquid Fuel-Fired Industrial Boilers*. (Presented at the 86th National AIChE Meeting. Houston. April 1-5, 1979.
 20. Pierce, R. M., C. E. Smith, and B. S. Hinton. Low NO_x Combustor Development for Stationary Gas Turbine Engines. *Proceedings of the Third Stationary Source Combustion Symposium, Vol. III*. EPA-600/7-79-050c, NTIS PB 292-541/AS. February 1979. p. 137-173.
 21. Pierce, R. M. *Advance Combustor System for Stationary Gas Turbine Engines*. Monthly Progress Report No. 23 on Contract 68-02-2136. December 1977.

Session III: ENVIRONMENTAL CONTROL

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CONTROL ASSAY SCREENING PROCEDURES

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Abstract

Control assay (CA) screening procedures are a significant and important part of the U. S. Environmental Protection Agency's (EPA) overall data acquisition program for environmental assessment of fuel conversion systems. This paper presents a background of the development of CA screening procedures as they relate to the Industrial Environmental Research Laboratory's (IERL) Level 1 sampling protocol. The logic involved in selecting or rejecting specific unit processes is presented. Screening procedures to be used by a field team for gaseous and aqueous waste treatment are described. The development of detailed screening procedures from the CA methodologies required laboratory work for confirmation. Test results, conclusions, and revised CA methodologies are presented in the paper.

Biological oxidation screening procedures were the most difficult problem in the development of CA screening procedures; therefore, laboratory data derived from biological tests along with recommendations for future work are presented. The feasibility of using a dry bacteria culture for biological oxidation is discussed.

Laboratory data are presented from specific gas treatment tests conducted using a modified Source Assessment Sampling System (SASS) train. Setup, operation, and required adjustments to the SASS train for proper field operation are described.

INTRODUCTION

Control assay development (CAD) is the term applied to a field-testing program for determining the best potential control techniques based on Level 1 evaluation of effluent samples before and after treatment by combinations of laboratory procedures that simulate control processes.

The physical and chemical characteristics and

health/ecological effects of waste streams must be determined to establish the potential pollution problem and the need for control technology. The CAD approach for wastewater and for air emissions provides practical and economically feasible screening procedures for a number of treatment technologies without prior knowledge of all pollutant parameters. This is possible when broad criteria such as biological oxygen demand (BOD), chemical oxygen demand (COD), total organics, etc., can be used as a measure of the effectiveness of treatment. Specific pollutants or health/ecological effects will also be determined after completion of the screening tests. The methodologies are designed to produce reliable data indicating the degree of effectiveness of each control process on a Level 1 basis.

During the formulation of CAD methodologies, it became apparent that certain procedures should be verified in the laboratory before being adopted for use in the final protocols.

The objectives of the laboratory study were:

- To determine logistical problems of sample handling.
- To assess the adequacy of the proposed designs and operation of appropriate test units.
- To examine the possibility of using a dry bacterial culture for biological oxidation studies.
- To evaluate the feasibility of using Source Assessment Sampling System (SASS) components for air testing.

CAD field procedures for coal conversion wastewater treatment require processing relatively large volumes of water as compared to standard process development testing procedures for determining treatability of a given waste. Volumes of 200 L or more have to be processed to accommodate normal system requirements and to provide 10-L samples for the Industrial Environmental Research Laboratory's (IERL) Level 1 analyses.

CAD air methodologies specify the use of a

*Speaker.

modified SASS. The minimum sample volume required by IERL Level 1 air analyses for particulate, organic, and inorganic materials is 1,000 ft³. This volume allows for collection of sufficient quantities of trace components to reach detectable levels.

The principal control approaches for solids (e.g., incineration and fixation) are not easily conducted in the field. Incineration equipment becomes impractical to outfit and operate in a mobile facility. Chemical fixation or encapsulation techniques are proprietary in nature and cannot be satisfactorily duplicated in the CAD test program. Samples would have to be forwarded to a selected process vendor if data are to be developed. These approaches are not reasonable until a Level 1 analysis establishes the need for treatment; therefore, no screening procedures have been recommended for solid waste evaluation.

WASTEWATER SCREENING PROCEDURES

Wastewater streams encountered during CAD testing are expected to contain phenolic compounds, ammonia, sulfides, and cyanide. These materials should be present in large enough quantities to make their recovery economical in a full-scale plant; however, pilot-plant operations may not be able to afford the capital investment for recovery equipment. It is expected that CAD testing procedures will be employed using wastewater streams produced by pilot plants. Therefore, it becomes necessary to provide pretreatment of these samples in order to simulate the characteristics of the waste effluent that could be expected from a full-scale plant.

The analytical effort expected of the field team members is not extensive for any of the CAD testing. However, during pretreatment some analyses must be performed to evaluate the need for pretreatment and the efficiency of removal when a sample is processed through a pretreatment step. The individual streams used to make up the composite sample will be analyzed with inexpensive test kits, and a decision will be made by the team leader as to which streams will be subjected to byproduct removal treatment before compositing. After byproduct removal and compositing, the sample will be an-

alyzed to determine the effectiveness of any pretreatment steps that have been employed.

Phenolic compounds will be removed by liquid-liquid extraction by using isopropyl ether as the solvent. Ammonia and sulfides will be removed by air stripping at appropriate pH ranges. A high percent removal rate of hydrogen sulfide can be accomplished in a matter of minutes at pH 7. Ammonia stripping will take place at a pH of 11, and the wastewater will be heated to 60° C to reduce the required stripping time. Complete destruction of the cyanide ion will be accomplished by the addition of sodium hypochlorite with agitation.

Figure 1 shows the preliminary test sequence for wastewater screening. The recommended screening procedures are not intended to provide design data for a treatment plant but will indicate the applicability of a particular treatment process and provide information to be used as a basis for further studies. The tests have been limited to those unit processes that have proven to be most successful in practice and that have been most universally applied. Two other processes (wet air oxidation and evaporation/distillation) were initially considered for wastewater methodology, but both were rejected because they are normally used in special applications and would require more sophisticated testing procedures than are warranted for CA screening.

To accomplish the proposed objectives of this portion of CAD, a 200-L synthetic wastewater sample was processed as it would be by a sampling team in the field, with the exception of the byproduct recovery steps and the treatment by chemical oxidation. Complete Level 1 analytical procedures were not applied to the treated samples because of time and cost restrictions. Instead, traditional wastewater parameters (COD, BOD, solids, and metals analyses) were used to measure the performance of each unit process. Separate studies were conducted to determine the effectiveness of using dry bacteria vs. an acclimated activated sludge for the biological oxidation assessment.

Synthetic Wastewater

Because of the difficulty of obtaining an actual coal conversion process waste, it was decided to use a synthetically prepared waste for

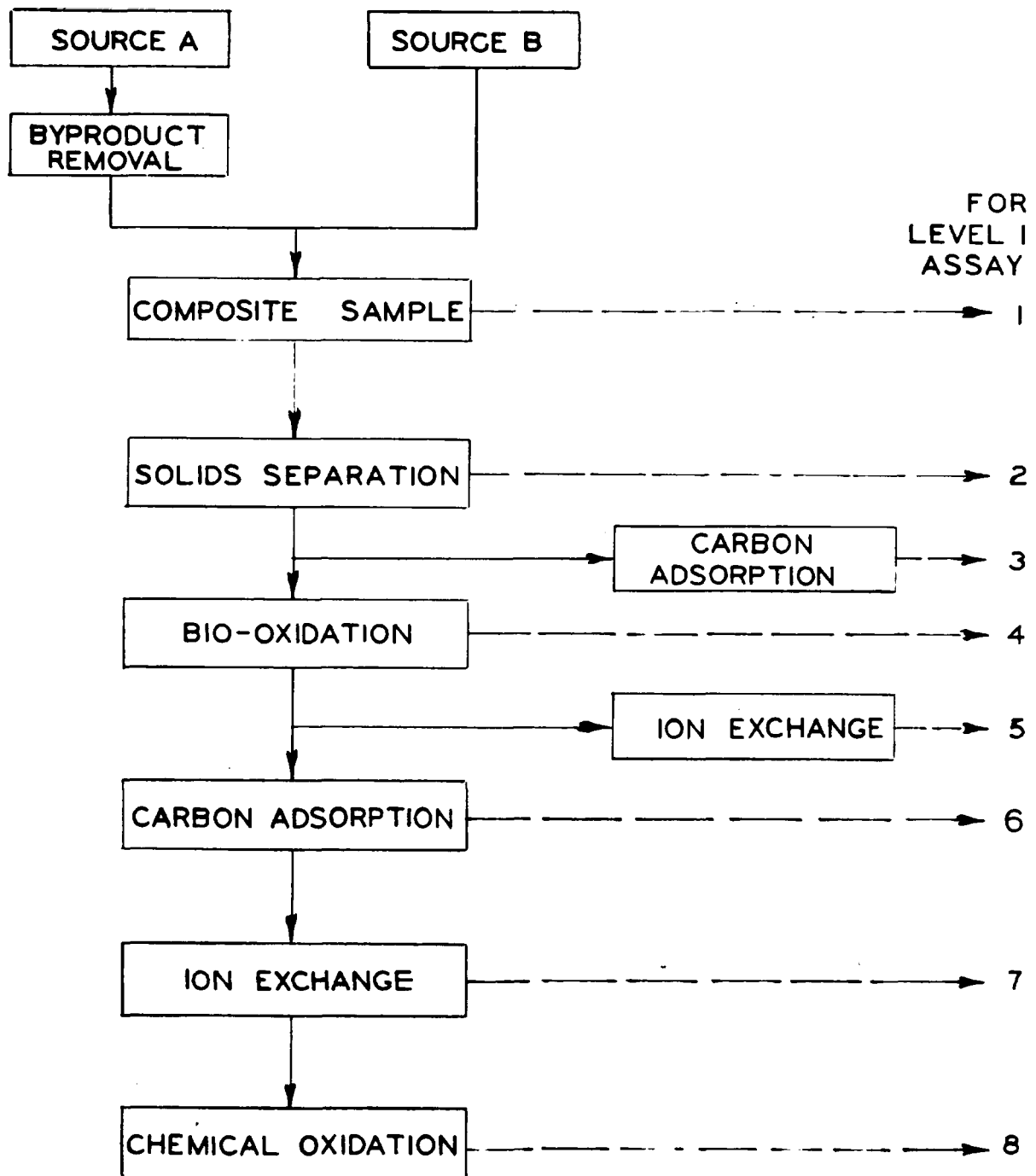


Figure 1. Preliminary wastewater test sequence.

TABLE 1. ORGANIC COMPOSITION OF SYNTHETIC WASTE

Compound	Waste A Concentration mg/l	Synthetic Waste Concentration mg/l
1. Phenol	2000	200
2. Resorcinol	1000	500
3. Catechol	1000	500
4. Acetic Acid	400	400
5. o-Cresol	400	40
6. p-Cresol	250	25
7. 3,4 Xylenol	250	25
8. 2,3 Xylenol	250	25
9. Pyridine	120	120
10. Benzoic Acid	100	100
11. 4-Ethylpyridine	100	100
12. 4-Methylcatechol	100	50
13. Acetophenone	50	50
14. 2-Indanol	50	-
15. Indene	50	50
15. Indole	50	50
17. 5-Methylresorcinol	50	25
18. 2-Naphthol	50	50
19. 2,3,5 Trimethylphenol	50	5
20. 2-Methylquinoline	40	40
21. 3,5 Xylenol	40	4
22. 3-Ethylphenol	30	3
23. Aniline	20	20
24. Hexanoic Acid	20	20
25. 1-Naphthol	20	20
26. Quinoline	10	10
27. Naphthalene	5	5
28. Anthracene	0.2	0.2

the laboratory verification studies. The organic portion of the synthetic wastewater used for verification purposes was derived from a formulation developed by Dr. Philip Singer from research conducted at the University of North Carolina, Chapel Hill.¹ The concentrations of organic compounds proposed by Dr. Singer defined a coal gasification wastewater with no byproduct recovery steps. Because the laboratory verification was intended to test CAD methodologies after byproduct recovery, the initial organic concentrations were modified to simulate a phenol recovery step. The Phenosolvan® process was selected as a typical phenol extraction process. Extraction recoveries expected from this process were estimated to be 99.5 percent monohydric phenols, 60.0 percent polyhydric phenols, and 5.0 percent for other organics.²

The phenolic compounds listed for waste A (Table 1) were segregated by chemical structure, and values of 90 percent and 50 percent removal were used to calculate the concentrations remaining after byproduct recovery of monohydric and polyhydric phenols, respectively. No concentration adjustments were made for "other organics."

The inorganic components of the synthetic mix were selected after actual sample data from several operating plants were reviewed. Table 2 lists the target inorganic concentrations in the synthetic mixture.

Solids Separation

Four candidate approaches were considered for separation of solids by physical means: centrifugation, sand filtration, microstraining, and cartridge filtration. Although it was felt that all the above physical separation methods would be applicable, the first three were discarded after evaluation of various factors including degree of solids removal required; the kind of specialized apparatus needed; the question of logistics for storing, transporting, and obtaining new filter media; the ease of operation; and the reproducibility of results.

Filtration of the composite sample using a polypropylene cartridge was deemed to be the most favorable method for solids removal in the CA screening procedure. A pore size of 75 μm was selected as being descriptive of the particle

TABLE 2. INORGANIC COMPONENTS OF SYNTHETIC WASTE

<u>Component</u>	<u>Concentration (mg/l)</u>
F	2.0
Fe	0.2
Pb	0.04
Hg	0.007
PO ₄	2.5
S	12.0
Zn	0.08
As	0.2
Cd	0.02
Cr	0.03
Cu	0.1
Cn ⁻	1.0

size discharged from a well-designed primary settler. A 200-L sample of synthetically prepared waste was passed through the cartridge filter with no difficulty. The synthetic waste typically had a fairly low suspended solids level at the outset, and no problems with filter plugging were encountered. It was noted, however, that the waste did exhibit a tendency to precipitate solids from solution upon standing. Several filtrations were made at various times during the laboratory study and the 200-L sample could be passed through the filter in 15 min or less using a standard laboratory pump. Aeration occurred because of the pumping action, which caused some foaming in the sample; but this situation was not considered to be a significant problem. It is possible that actual wastewater samples will have a much higher level of solids than was encountered in the synthetic waste. Also, during chemical pretreatment for byproduct recovery, conditions could develop conducive to the formation of precipitates, thereby increasing the total amount of suspended solids in the sample.

The filter cartridges are relatively inexpensive and easy to change when their filtering capacity has been exhausted. It would be possi-

ble to make several filter changes during a run, if it became necessary, without a significant loss of time. Cartridge filters are also available in various pore sizes, and two or more filters of gradually decreasing size could be used in series to obtain a higher degree of solids removal, if required. The synthetic waste had no visible effect on the integrity of the cartridge or the filter holder (both polypropylene).

Activated Carbon

Evaluation of the effects of activated carbon as a unit operation involves selection of a particular carbon, measurement of adsorptive capacity using batch isotherms, and development of a breakthrough curve and regenerability characteristics determined from a continuous-flow pilot column test. In a detailed concept design study, a number of different carbons are examined using a particular wastewater before the best candidate is selected for the column tests. Considering the basic purposes for CA screening procedures and the field time constraints imposed, the use of a single, somewhat broad-based carbon is proposed. This approach may not produce data using the best suited carbon, but the results will be sufficiently indicative of the applicability of carbon as a treatment step and will still keep the investigations within practical bounds.

Because it is a relatively simple matter to perform carbon isotherms on a wastewater sample in the field to determine the approximate organic loading and optimum pH conditions for a specific wastewater, they have been included as a prescreening procedure. Results of isotherm testing provide useful guidelines for the column test runs in addition to the data they furnish directly.

Two methods were considered for treating the composite sample by activated carbon: continuous feeding through a series of carbon columns, and batch testing. Each batch treatment of a composite sample represents only one equilibrium condition. It is anticipated that a micro-filtration step for removal of suspended carbon fines would be necessary before subsequent processing steps could be performed.

Pilot column testing normally requires continuous sampling throughout the run at several points in the carbon system to determine wave-

front movement and breakthrough, which are among the data needed for an actual column design. Because only a limited number of samples can be taken during CA screening, it is not proposed, nor is it necessary, to conduct this detailed type of design study. Based on the foregoing considerations, continuous column operation was selected for use in screening; however, the number of samples to be collected was limited to the feed and the composite effluent. The volume of the feed to the carbon system will be the amount needed to produce the samples for analysis after the carbon test as well as from any subsequent screening procedures, plus the amount needed to displace "fill water" in the columns. The feed volume will be contained in a single vessel, pumped continuously through the carbon beds, and collected in another vessel at the effluent end. After an aliquot sample is withdrawn for subsequent laboratory analysis, the remaining effluent becomes the influent for screening steps to follow. To determine general column operation parameters, several isotherms are to be run on a small quantity of the feed sample prior to the continuous run.

Table 3 summarizes the results of the activated carbon verification testing. A Freundlich isotherm was developed on the synthetic waste sample to establish the effectiveness of carbon treatment and to gain some insight into the amount of carbon required to produce acceptable organic removal rates. The standard COD analysis was used as a measure of organic removal. The values of X/M (quantity of COD adsorbed per unit weight of carbon) were calculated and plotted vs. concentration of residual COD in solution. The plot of the data shows a definite break at carbon dosages of 20 g/L and higher. The sudden change in slope indicates that two (or more) classes of organics present are not uniformly adsorbable (Figure 2).

Carbon column runs were made using the column design specified by the CAD wastewater methodology—four 2-in I.D. glass columns connected in series, each charged to the 3-ft level with activated carbon (7.8 lb of carbon). The test sequence for CAD (Figure 1) requires the use of carbon at two points, before and after bio-oxidation. After filtration the sample was equally divided (84 L per run) for use during the column tests.

In view of the apparent dual-adsorption re-

TABLE 3. CARBON ISOTHERM RESULTS

Carbon Dose (M) (gm/l Sample) (*)	COD Remaining (C) (mg/l)	COD Removed (x) (mg/l)	X/M (mg COD/gm Carbon) (**)
0	5000	0	0
1	4653	347	347
5	3931	1069	214
10	3657	1343	134
20	3259	1741	87
50	1866	3134	63
100	1000	4000	40

(*) Corrected for 100 ml sample size used.

(**) Equivalent to 1b. COD adsorbed/1000 lb. Carbon.

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CARBON COLUMN TEST RESULTS

Run Number	Linear Flow Rate (ml/min.)	Loading Rate (gpm/ft ²)	Influent Concentration		Effluent Concentration (+)		% Removal	
			COD mg/l	BOD mg/l	COD mg/l	BOD mg/l	COD	
<u>BOD</u>								
1A	190	2.3	6864	2200	1714	440	75	
80								
1B	190	2.3	1714	440	334	186	80	
58								
1 (A&B)	190	2.3	6864	2200	334	186	95	91
2	200	2.4	3581	1940	347	197	90	90

(+) Corrected for dilution water in columns.

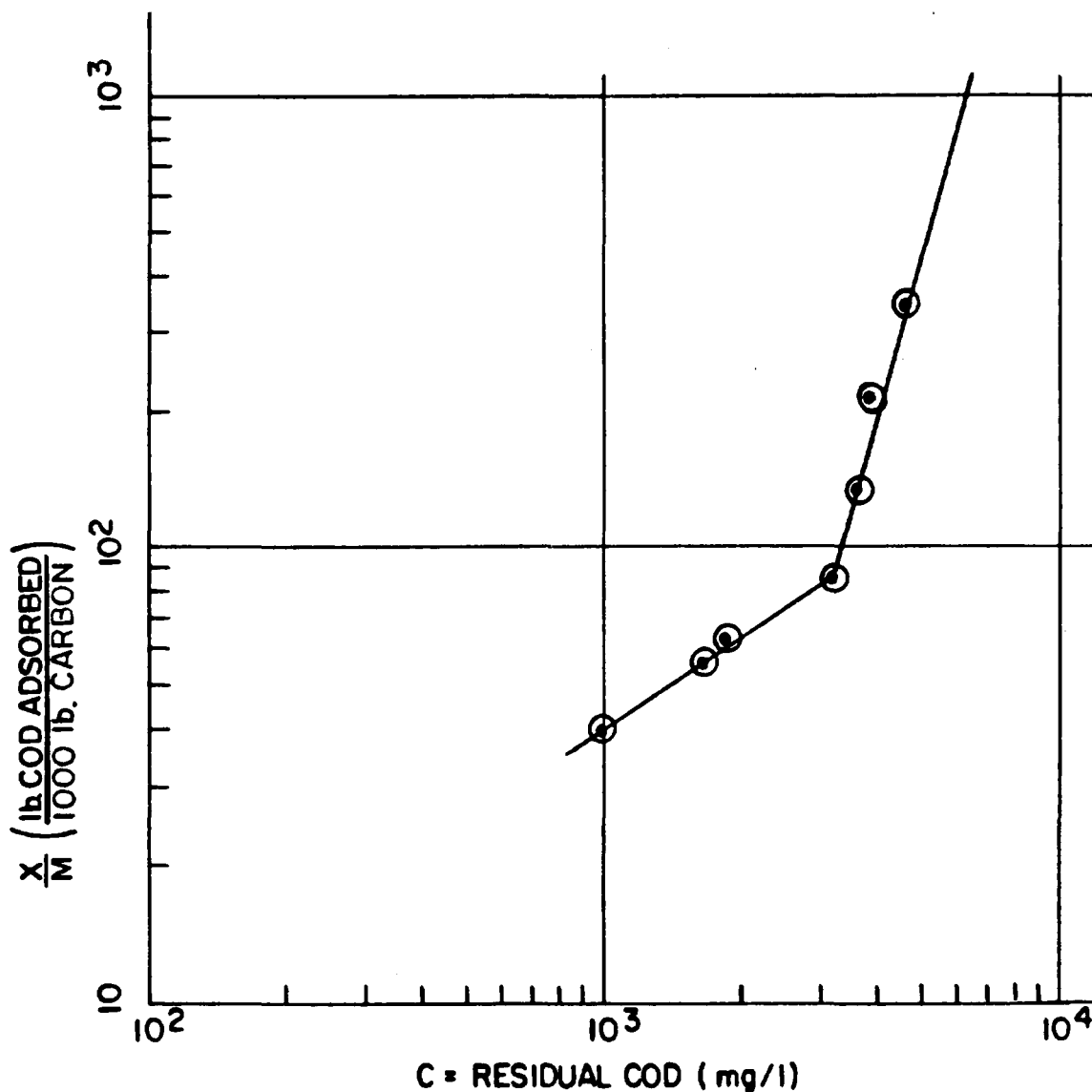


Figure 2. Carbon adsorption isotherm.

gimes demonstrated by the batch isotherm, it was decided to collect data during the first test run in two stages. The 84 L of filtered waste was pumped through fresh carbon in the columns, and the effluent was retained (Run A). After the columns were rebbed with new carbon, the effluent from Run A was used as the influent to Run B.

The second portion of synthetic waste was treated by the bio-oxidation screening procedure and then fed to fresh carbon in the columns. Results of this test are indicated as Run

2. To varying degrees, carbon is effective in reducing the COD and BOD of the synthetic waste sample in both applications. By referring to Table 3, it is seen that the combined Run 1 achieved essentially the same effluent COD and BOD concentrations and percent removals as Run 2. It must be recalled, however, that Run 1 was conducted in two stages and that twice the carbon was bedded. The specified CA screening procedures are more closely simulated by Run 1 alone. The data show that substantially fewer (BOD/COD) organics are removed than in Run 2,

which follows bio-oxidation.

It can be postulated that lower molecular weight organics were not retained in the four-column system but were captured in an equivalent eight-column setup. Apparently, the four-column system was able to produce a better effluent quality after one pass by virtue of the reactions taking place during the bio-oxidation procedure.

The run time required to process an 84-L sample through the four-column system at a superficial velocity of 2 to 3 g/min/ft² is approximately 8 hr. By increasing the column size to 3-in I.D., the sample could be processed in slightly less than 3 hr at an identical superficial velocity. On the other hand, the amount of carbon available would be increased more than twice.

One disadvantage of increasing the column size is that the dilution from the "fill" water existing in the carbon bed at the beginning of the run becomes larger in relation to the size of the sample being passed through the columns. In any event, the dilution factor has to be considered when test results are interpreted and should not substantially affect the evaluation of activated carbon as a unit process, provided that a sufficiently large sample is processed.

The synthetic waste demonstrated a tendency to form some additional solids on standing, which were removed by the carbon bed. If real wastes react similarly, it may be necessary to perform a supplemental cartridge filtration before feeding the sample to the columns to prevent bed blinding.

The column design was modified slightly because plugging problems arose using the original fitted glass support materials. These were removed and replaced with 50-mesh screen, which was satisfactory for all subsequent runs.

Biological Oxidation

The original intent of wastewater treatment evaluation was to have a field team onsite to perform all aqueous screening procedures in approximately 1 week. Standard biological treatability testing using activated sludge normally requires 2 weeks to 1 mo of continuous operation for acclimation of the biomass to the specific waste being studied. After acclimation, an additional 3 to 4 weeks of data gathering under steady-state conditions are required to provide

system performance and design parameters for that particular wastewater. Control assay screening procedures are not developed for the purpose of obtaining design data; therefore, the continuous sampling after acclimation is not necessary. However, to properly evaluate a biological system as a unit process, it is imperative that an acclimated seed be used.

The requirement for an acclimated seed onsite posed several problems. A "wet" seed must be continuously aerated and provided with some type of feed substrate during transportation to a plant and on location. The possibility of acclimating a sludge from a local municipal treatment plant was also considered. While a viable option, such an approach could introduce unwanted contaminants to the system, depending on the type of industrial waste normally treated at the local plant. Biological sludge from a plant that normally treats coke oven wastes would be ideal because components of this type of wastewater are similar to many materials found in coal conversion wastes. However, the likelihood of being near this type of treatment plant would be small and could not be realistically incorporated into the screening methods. In essence, it was desirable to determine if there were any feasible alternatives to using a wet seed for the screening procedure.

By private communication, one investigator reports experimentation examining the possibility of quick-freezing activated sludge for subsequent use. While interesting, the work is still in an early trial stage and the results are too tentative for inclusion in a screening procedure at this time. A second alternative is the use of dry bacterial cultures offered commercially by several vendors.

Dry bacterial cultures are grown on an inert material. The organisms are selectively mutated and segregated in accordance with their ability to biologically degrade specific classes of compounds. One such culture is purported to specifically oxidize phenolic compounds, cyanides, and other similar contaminants. The culture is marketed in a dry powder form and, according to the vendor, the organisms are reactivated when added to warm water and aerated for 24 hr. The dry bacterial culture route offers a potential solution for the transportation and acclimation problems posed by CA methodology.

It was decided to test a dry bacterial culture to ascertain whether or not it would serve as a practical alternative for a wet seed and/or to try to establish a relationship between system performance using dry bacteria as compared with a seed acclimated to a waste in the more usual manner. Tests performed to evaluate biological screening procedures were divided into two categories: batch testing and continuous systems. Additionally, experimental work was conducted to gain better familiarity with the characteristics and application of the dry bacterial culture; and to explore some side issues that arose during the test work that were relevant to the overall bio-oxidation verification procedures.

The batch tests were performed either in 2-L glass beakers or in 7-L cylindrical, stainless steel containers. Vessels used for the continuous systems testing were 7.5-L capacity stainless steel tanks fitted with baffle plates at the outlet to provide a quiescent zone for solids settling. The volume of the aerated portion of these tanks was about 6 L.

An attempt was made to start a continuous system using the dry bacterial culture. After several days of feeding with dilute synthetic wastewater, there was no apparent biological growth. It was believed that the bacteria were present as a dispersed growth and were being lost in the effluent because there was no measurable solids production in the system and effluent COD values were consistently higher than the feed analyses. Millipore filtration of the effluent samples did not significantly reduce the effluent COD results.

Data collected during the early exploratory work with the dry bacterial culture contained two anomalies:

- Effluent COD concentrations were higher than influent values.
- The COD concentration in the open feed container dropped rapidly on standing.

The latter effect was substantially reduced—but not totally eliminated—by covering the feed vessel during the subsequent continuous biotesting studies.

The phenomenon of organic (BOD/COD) loss from the synthetic waste mixture was addressed several times during verification testing through studies involving aeration of different batches of synthetic waste under varying

test conditions. The data collected during these runs are presented in Tables 4, 5, and 6.

Air-stripping tests were performed on batch samples of the synthetic waste to quantify the loss of COD material (presumably) by volatilization and/or oxidation of the organic compounds in the waste (Table 4). At the same time, tests were conducted to determine the amounts of COD and BOD added to a batch system by the dry bacterial culture alone (Table 7). A supplemental air stripping/oxidation run was conducted near the end of the laboratory test to examine the effect of volume size on BOD/COD reductions. For convenience, these data are shown in Table 5.

The bulk of the results support the proposition that the losses occur primarily through volatilization. However, there is some evidence that chemical oxidation of the organics could also be involved. Whatever the actual mechanisms might be, Tables 4 and 6 (Unit 1) show that the cumulative effect of air stripping/oxidation is essentially reached after 48 hr of aeration. Table 5 evaluates the effect of volume size on BOD/COD reduction. A stripping action is definitely indicated by the fact that the (smaller) units with greater air-to-liquid ratios demonstrated higher reductions.

The supplier's recommended standard procedure was followed for reactivating the dry bacterial culture. First, a measured amount (25 g) of bacteria/substrate material was added to 3 L of distilled water, heated to 38° C (100° F), and mixed for 2 hr. The batch was then aerated for 24 hr, and aliquots were taken to produce various concentrations for analysis. The test results indicated that the BOD and COD concentration will increase as a result of adding the dry culture. Relationships are depicted in Figure 3.

The zero hour time did not include the initial 24-hr aeration period; therefore, the total aeration time from start of reactivation to the end of the test was actually 96 hr. These tests indicated that the substrate material will provide the bacteria with an adequate nutrient supply for at least 72 hr, while also adding organic food (COD) material to the system. Measurements of oxygen uptake rates on similar systems confirmed the continued high biological activity over the same time period.

Dry bacterial cultures can also be used as an additive to an existing biological system. Be-

TABLE 4. AIR STRIPPING/OXIDATION TESTS

Aeration Time (hrs)	Run #1		Run #2		Run #3				Run #4			
	COD (mg/l)	Rem. %	COD (mg/l)	Rem. %	COD (mg/l)	Rem. %	BOD (mg/l)	Rem. %	COD (mg/l)	Rem. %	BOD (mg/l)	Rem. %
0	5660	0	5504	0	4761	0	3306	0	4280	0	2340	0
1	4228	25.3										
2	2686	52.5										
4	2412	57.4										
24	1965	65.3	2046	62.8	2637	44.6	1408	57.4	3412	20.0	1980	15.4
48			1450	73.7	2030	57.4	960	71.0	2410	43.7		
72			1580	71.3	1834	61.5	760	77.0	2222	48.1	1200	48.7

NOTE: Sample volume used was 15 liters.

TABLE 5. EFFECT OF VOLUME SIZE ON AIR STRIPPING/OXIDATION

Parameter	Infl. (mg/l)	Run #5- 22 gal. Volume				Run #6- 7 liter Volume			
		Aeration Only		Dry Bacteria		Aeration Only		Dry Bacteria	
		Effl. (mg/l)	Rem. (%)	Effl. (mg/l)	Rem. (%)	Effl. (mg/l)	Rem. (%)	Effl. (mg/l)	Rem. (%)
BOD	1080	780	27.8	740	31.5	780	27.8	870	18.4
COD	7560	5520	27.0	5680	24.9	3760	50.3	3840	49.2

NOTE: 24 hours aeration period on all units

TABLE 6. BIOLOGICAL OXIDATION BATCH REACTOR RESULTS

	Unit #1-Air Stripping/Oxidation			Unit #2-Coke Oven Sludge			Unit #3-Coke Oven Sludge + Dry Bacteria			Unit #4-Dry Bacteria			Aeration (hrs)
	Influent	Effluent	% Removal	Influent	Effluent	% Removal	Influent	Effluent	% Removal	Influent	Effluent	% Removal	
BOD (mg/l)	2823	1694	39.9	2520	1120	55.5	2630	1260	52.1	2570	1330	48.2	24
COD (mg/l)	4848	2698	44.3	4806	2078	56.7	4886	2368	51.5	4860	2162	55.5	
BOD (mg/l)	2823	960	65.9	2520	930	63.1	2630	660	74.9	2570	1130	56.0	48
COD (mg/l)	4848	1980	59.1	4806	1584	67.0	4886	1467	70.0	4860	2043	57.9	
BOD (mg/l)	2823	980	65.3	2520	510	79.7	2630	540	79.4	2570	840	67.3	72
COD (mg/l)	4848	1879	61.2	4806	1404	70.7	4886	1275	73.9	4860	1577	67.5	

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NOTES

Unit #1 contained 1.0 liter tapwater plus 4.5 liters of waste.

Unit #2 contained 1.0 liter of activated sludge from continuous Unit A plus 4.5 liters of waste.

Unit #3 contained 1.0 liter of activated sludge from continuous Unit B plus 4.5 liters of waste.

Unit #4 contained 1.0 liter 35 reactivated dry bacteria (8.75 gms/l) plus 4.5 liters of waste.

TABLE 7. DRY BACTERIA—COD AND BOD DATA

Aeration Time (hours)	BOD Dry Bacteria Concentration								Average Adjusted Value
	0.75 gm/l	Adjusted Value*	1.5 gm/l	Adjusted Value*	2.25 gm/l	Adjusted Value*	3.0 gm/l	Adjusted Value*	
24	44	59	92	61	290	128	386	128	94
48	60	80	112	75	274	121	268	89	91
72	86	115	106	71	140	62	314	104	88

Average BOD increase: 91 mg/l/gm Dry Bacteria added

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Aeration Time (hours)	COD Dry Bacteria Concentration								Average Adjusted Value
	0.75 gm/l	Adjusted Value*	1.5 gm/l	Adjusted Value*	2.25 gm/l	Adjusted Value*	3.0 gm/l	Adjusted Value*	
24	80	107	165	110	490	217	722	240	169
48	102	136	177	120	500	222	725	242	180
72	245	327	280	187	578	256	895	298	267

Average COD increase: 205 mg/l/gm Dry Bacteria added

*Mathematically adjusted to a Dry Bacteria concentration of one mg/l.

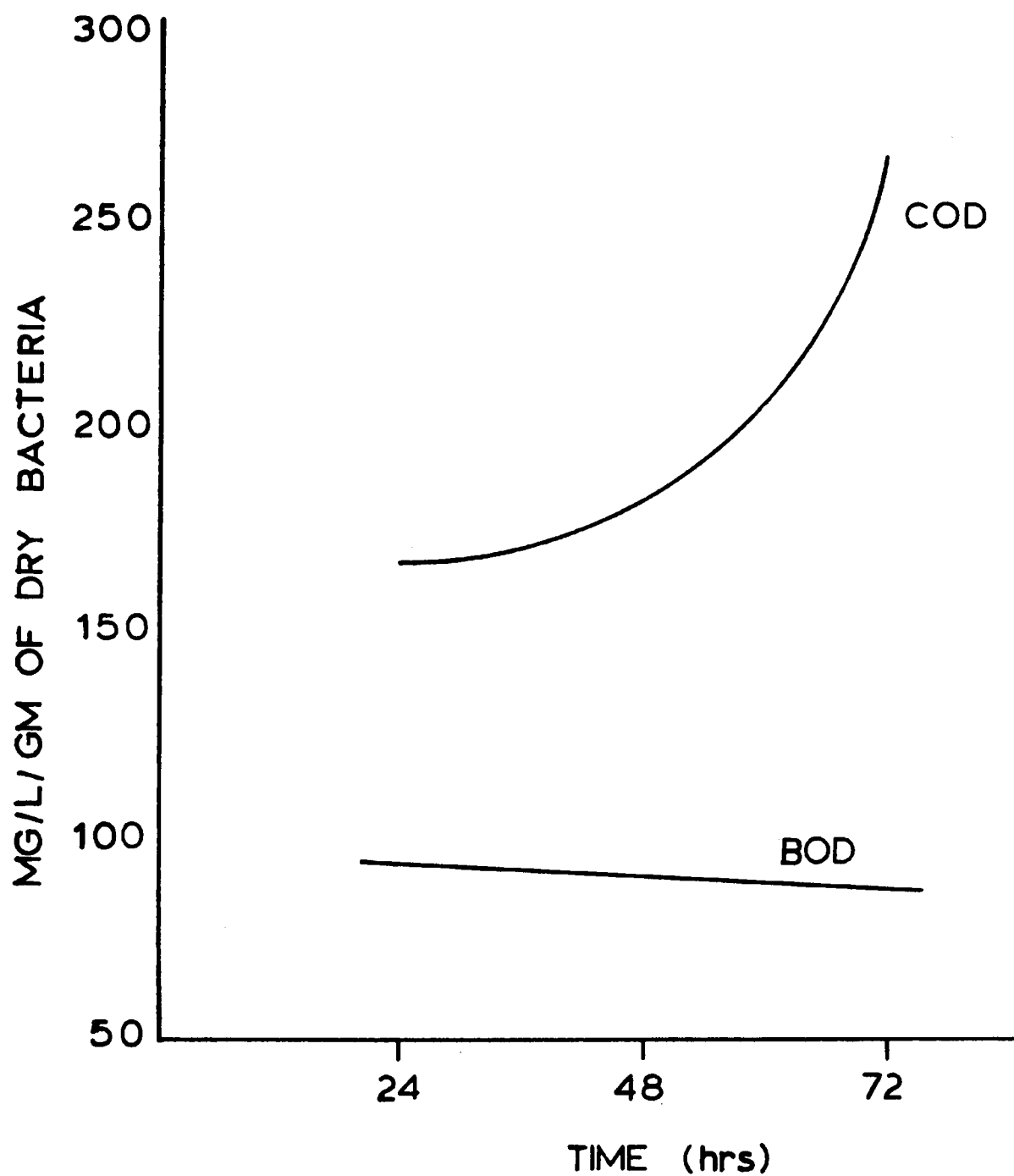


Figure 3. COD and BOD addition by dry bacteria.

cause poor results were being obtained from the continuous system, this operation was discontinued and replaced by two new continuous units, each containing biomass taken from a coke oven waste treatment plant. Identical amounts of the synthetic waste were fed to each of the units. Additionally, doses of the dry bacterial culture were introduced to one of the units on a daily schedule prescribed by the supplier's instructions. Gradually decreasing amounts of dry culture were added to this system until a "maintenance" dosage level (2 g/6 L) had been reached. This dosage was continued for the duration of the testing period. Sludge from these units was later used for additional batch tests. Results of the continuous reactor testing will be discussed later in this report.

Batch Testing

Three sets of batch tests were conducted, each set consisting of four batch reactors aerated for 72 hr. Samples from the reactors were taken every 24 hr and analyzed for COD and BOD. Air flow to each system was stopped for 1 hr before sampling to allow for solids settling. One reactor (Unit 1) in each series contained wastewater only (no biologically active seed introduced) for the purpose of comparing the effects of air stripping/oxidation of the waste to biological oxidation. The contents of the other three reactors were prepared as follows:

- Unit 2—Wastewater plus coke oven sludge (from continuous Unit A).
- Unit 3—Wastewater plus coke oven sludge with dry bacteria (from continuous Unit B).
- Unit 4—Wastewater plus dry bacteria.

The batch testing (Table 6) revealed no significant differences in BOD and COD removals between the dry bacteria system (Unit 4) and the air stripping system (Unit 1).

Both of the systems (Units 2 and 3) using coke-oven-activated sludge as the bulk of the seed, performed similarly, with better removals than the stripping unit and the dry bacteria unit. In these batch tests, no significant difference was observed between coke oven sludge alone (Unit 2) and the system containing supplemental dry bacterial culture (Unit 3).

Average COD and BOD removals were calculated to compare the effectiveness of the differ-

ent units. After 24 hr, there was little difference among any of the reactors in either BOD or COD removal, except for Unit 1, which was somewhat lower. The units containing coke oven sludge (with and without dry bacteria) began to show greater removals at 48 hr, and this trend continued for the 72-hr samples. The reactor containing dry bacteria alone showed very little, if any, superiority over the air stripping/oxidation reactor during the first day; and by the end of the test, the removals were essentially equivalent. Unit 3 (coke oven sludge plus dry bacteria) had a slightly higher COD removal rate than Unit 4 (coke oven sludge only), but the difference was so small that it cannot be attributed to the dry bacteria. BOD removals for these two units were identical.

Two continuous units were set up and operated for approximately 2 1/2 mo. Both units (A and B) were seeded with a coke oven sludge; one unit (Unit B) also received a daily dose of dry bacteria. The systems were contained in identical stainless steel reactor tanks each having a removable baffle to aid in clarification of the effluent streams. The influent to both systems was from a common tank, and various concentrations of synthetic wastewater were used as the feed material. Initially, the synthetic waste was diluted to one-tenth of the original strength and later changed to one-quarter strength. During the final 3 weeks of testing, both units were fed full-strength synthetic wastewater.

Figure 4 shows influent and effluent COD data for both continuous units during the entire test period. During the early part of the run, the unit with dry bacteria addition (Unit B) showed higher effluent values. Vendor instructions on the use of the dry bacterial culture as a supplemental addition were followed in Unit B. The procedure specified a relatively high initial dose followed by a dosage rate decreasing to a point where only a maintenance dose is applied daily. Presumably, the effluent COD pattern demonstrated in Unit B reflects the changing dosage rate of the bacterial culture. (The effect of culture dose on effluent COD has already been discussed.) When the dry bacteria addition reached the maintenance dosage level, COD removals for this system (Unit B) reached a level equivalent to the coke oven sludge system (Unit A).

During the final 3 weeks of testing, both units were fed full-strength waste. The unit with the

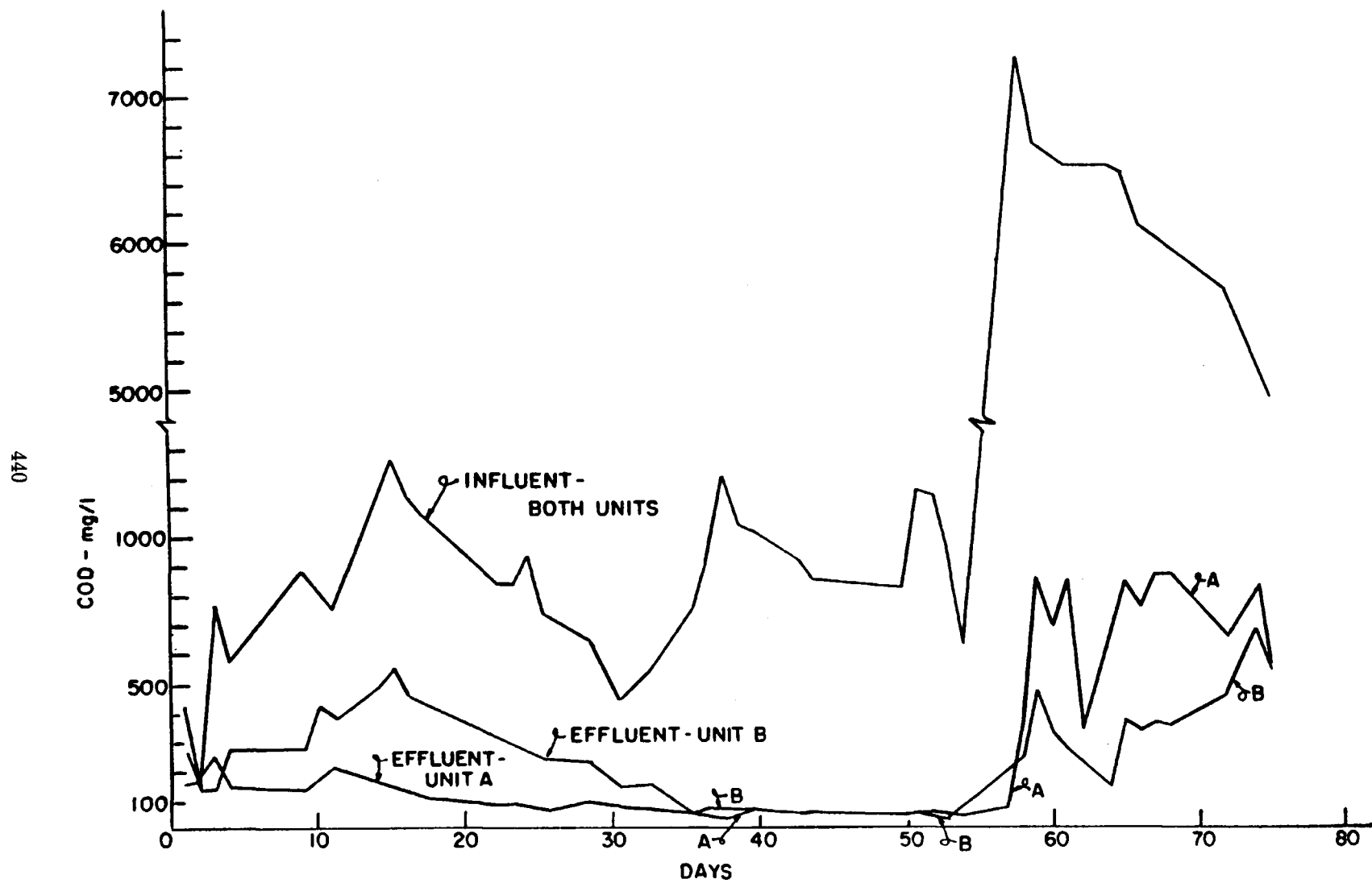


Figure 4. Continuous biological reactor results.

dry bacteria showed a much greater ability to cope with the shock loading conditions encountered when the feed was abruptly changed to full strength. The companion unit was adversely affected by the change in feed, although it gradually recovered over a 3-week period when, because of time limitations, operation of all units was discontinued.

Results from verification testing of the bio-oxidation screening procedure have produced valuable information relevant to CAD wastewater methodology. If the synthetic waste mixture used in the experimental work closely simulates a real-life coal conversion aqueous waste, then a substantial portion of the organic removals usually attributed to oxidation by biological organisms may well be physically stripped from the bioreactor as an air emission. Consequently, a simple aeration step in parallel with the biological treatment step appears warranted to ascertain the extent to which organic removal through stripping/oxidation is occurring.

Based on results developed with one commercial dry bacterial culture mixture, the use of this type of dehydrated product as a biological seed does not meet the needs of the screening procedure. A wet seed approach must be adopted. Moreover, the wet seed must be acclimated for about 3 weeks to a waste stream that is generally descriptive of the material that will eventually be tested by the CA procedure.

Clearly, two choices present themselves. One is to disregard the biological oxidation step entirely, which is not really reasonable, since this approach will eliminate consideration of the effects of a major waste treatment unit process. The second option is to begin biological acclimation (using a locally available activated sludge as seed) 3 weeks in advance of the wastewater screening study. During this time, the CA team could be generating the air samples for IERL Level 1 analyses.

At the outset of biotesting verification, it was presumed that the team would use COD analyses as the prime performance monitoring method, backed up by an occasional reference BOD. In view of the experience gained during this test work, some doubt is now cast upon the validity of using COD for these purposes. Changes produced by aeration in the oxidation state of dissolved waste organics may be clouding the

dichromate chemistry and possibly producing misleading data. It is recommended that the team should be equipped with a TOC analyzer for quantification of waste organic content and for process monitoring purposes.

Ion Exchange

After discussions with an ion exchange resins manufacturer, it was decided to employ a three-glass (2-in I.D.) column system set up in series. The first column contained a strong-acid type resin, the second column was filled with a weak-acid resin, and the final column contained a strong-base resin. Prior experience by the manufacturer suggested that this combination of resins would remove the majority of ions expected to be present in a typical coal conversion wastewater. To minimize pumping requirements, a single pump was to be used to introduce the sample into the first column and, by proper positioning of the second and third columns, a continuous gravity flow would be maintained.

The ion exchange system was tested to evaluate its ability to process the required aqueous sample within 1 work day. Excess solids in the wastewater caused a flow rate problem in the columns that was solved by filtering the sample through the 75- μ m cartridge and changing the resin bed support media. A single pump was used to introduce the wastewater into the first column, and gravity flow was employed through the second and third columns. Constant adjustments to the column height and piping were necessary to produce a continuous flow through all of the columns.

CAD methodology specifies the use of ion exchange at two points in the test sequence (Figure 1): after bio-oxidation and after bio-oxidation plus carbon adsorption. Reference analyses of a few selected metals were made for these runs and the results are shown in Table 8.

The gravity flow concept was not acceptable because unequal pressure drops through the columns, caused primarily by differences in resin particle diameters, necessitated constant adjustments to the column heights to maintain a continuous flow. It has been determined that the sample should be pumped through one column at a time to eliminate this problem. Furthermore, to reduce the possibility of plugging

TABLE 8. RESULTS OF ION EXCHANGE TESTING

<u>Parameter</u>	<u>Influent</u>	<u>Run #1 Effluent</u>	<u>Run #2 Effluent</u>
Iron as Fe, mg/l	0.7	1.5	0.7
Copper as Cu, mg/l	0.18	N.D.	0.034
Cadmium as Cd, mg/l	0.06	0.05	0.05
Zinc as Zn, mg/l	0.36	0.22	0.15

Notes:

Run #1 was made on a sample after bio-oxidation plus carbon adsorption.

Run #2 was made on a sample after bio-oxidation only.

N.D. Indicates Not Detectable (less than 0.05 mmg/l).

the resins with solids, a cartridge filter should be placed in-line before the first resin column.

The analytical data indicate that the ion exchange resins did remove metals, although there was some performance variability from metal to metal. The principal impact on CAD methodology is that an overall comparison of the effluents from both runs shows them to be reasonably similar; therefore, two ion exchange runs are not required for CAD purposes. The ion exchange run after carbon adsorption is the more appropriate site selection in the test sequence.

In view of the increase in column size (from 2-in to 3-in I.D.) suggested for the carbon screening procedure, it is logical to also change the ion exchange column size to 3 in. This alteration will gain some time during the ion exchange test run and will serve to standardize the column sizes for both screening procedures.

Chemical Oxidation

Phenolic compounds and numerous other organic chemicals can be destroyed by reaction with an oxidizing agent. The choice of an oxidizing agent rests primarily on its rate of reaction, selectivity, cost, and ease of handling. Some commonly used chemical oxidants are:

- Ozone and oxygen,
- Hydrogen peroxide,

- Potassium permanganate, and
- Chlorine and chlorine-containing compounds.

For thermodynamically reversible reactions, the oxidation reduction potentials can be used as a quantitative measure of oxidizing power. However, most reactions involving oxidation of organic chemicals are irreversible and, therefore, the redox potentials are of little use for predicting expected behavior.

Hydrogen peroxide will be added to the sample to oxidize any organic components remaining after being processed through the classical treatment processes. This procedure was not tested during laboratory verification.

Conclusions and Recommendations

Laboratory verification of the CA screening procedures revealed several problems with the original wastewater methodologies. Minor equipment changes were made to facilitate sample handling, and a revision of the biological oxidation procedure was necessary. Figure 5 shows the steps in the initial CAD treatment sequence and includes verification testing results for those processes examined.

Conclusions and recommendations developed from the study are:

- Solids separation using an in-line cartridge filter presented no difficulties, and this ap-

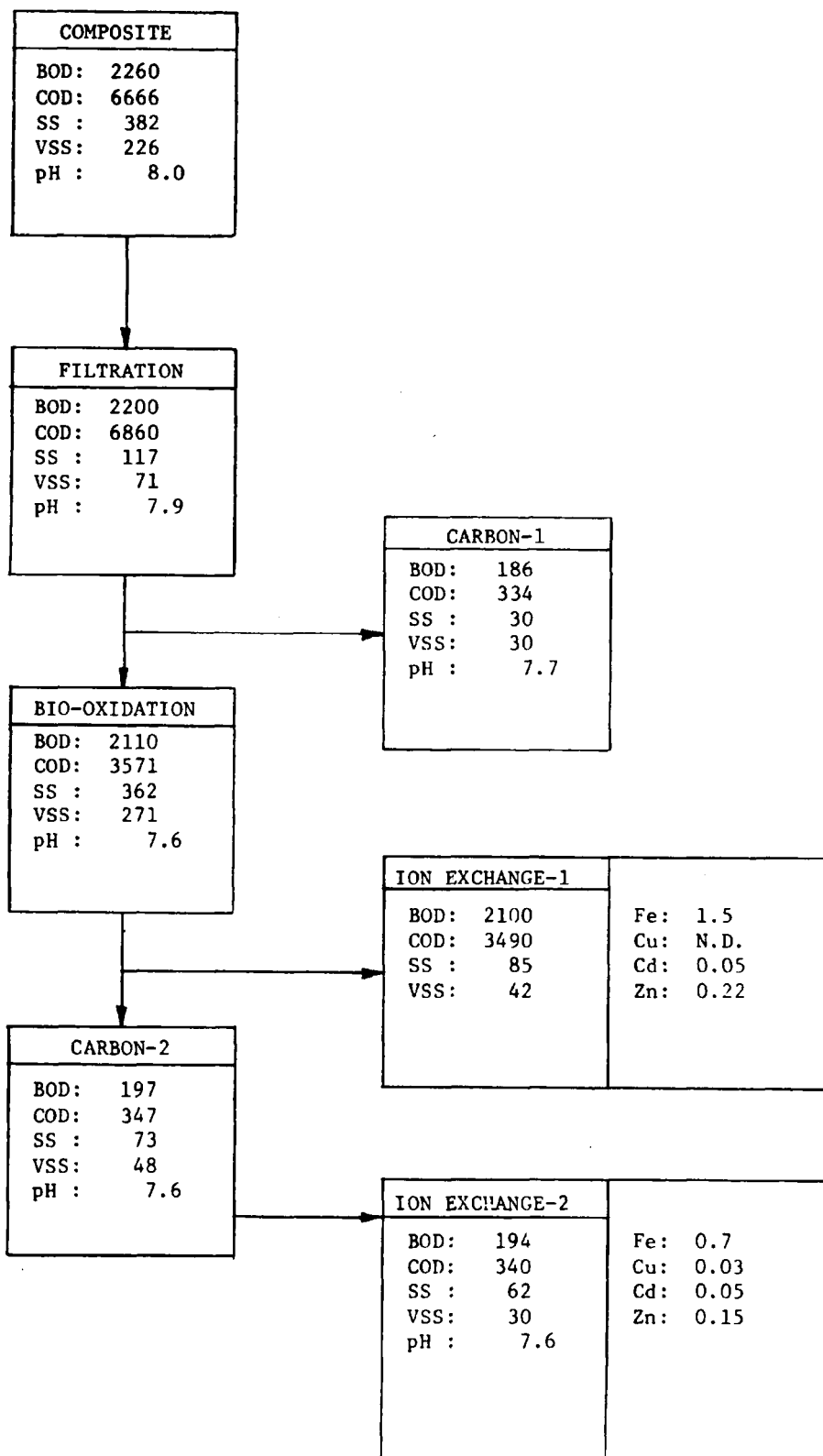


Figure 5. Results for synthetic waste sample.

proach will be adopted as originally conceived. If precipitates form in the wastewater sample, supplemental solids filtrations may be required to prevent blinding of the carbon and/or ion exchange resin beds.

- The effect of carbon adsorption should remain where proposed by the CAD wastewater methodology; i.e., both before and after bio-oxidation.
- The carbon column diameter should be changed from the 2-in I.D. specified to 3 in. A few minor column design modifications are also suggested.
- Verification testing data strongly support the proposition that a substantial portion of the BOD and COD removals demonstrated during the bio-oxidation screening procedure can be attributed to air stripping (volatilization). Therefore, the CAD wastewater methodology should be modified to include an air-stripping step running in parallel with the specified bio-oxidation screening procedure.
- Insufficient benefit is derived from the use of a dry bacterial culture during the bio-oxidation screening procedure to warrant its adoption in the testing protocol.
- To be effective, bio-oxidation screening must use an activated sludge that has been acclimated to the wastewaters under consideration for a period of 3 weeks prior to the formal initiation of the CAD wastewater methodology. While acclimation is underway, it is anticipated that the CAD team would be pursuing the screening procedures specified by CAD air methodologies.
- Based on experience derived during the verification testing, the use of COD analyses as the monitoring method should be replaced by TOC to provide a faster and more accurate analysis of the organic composition of the samples.
- The gravity flow concept through the ion exchange columns is not acceptable as a CAD screening procedure. The wastewater sample should be pumped through each column.
- Evaluation of the effects of ion exchange should be studied only after carbon adsorption and not before. The wastewater testing sequence should be altered accordingly.
- The ion exchange column diameter should be standardized at 3 in.

Figure 6 shows the final version of the wastewater screening test sequence.

GASEOUS EMISSIONS SCREENING

Control technology for screening gaseous samples to determine potential treatment methods must include unit operations for the removal of particulates and gases/vapors of concern. Either class of materials may be organic or inorganic. The types of control technology for gas treatment include mechanical collection, electrostatic precipitators, filters, liquid scrubbers/contactors, condensers, solid sorbents, and incineration.

Sampling of air streams for Level 1 CAD is much more difficult than the simple grab procedures specified for liquids. The inability to bring sufficient sample volume into the CAD mobile test facility, as is possible with liquid samples, limits the use of a number of unit operations and/or desirable strategy that can be applied in the air methodology. The practicality of performing certain types or large numbers of CAD tests at the source may be restricted by such factors as limited working space on a platform, logistical problems servicing a platform, plant restrictions on use of nonexplosion-proof equipment, personnel safety, requirement for specialized equipment (e.g., SASS train), and the analytical load generated by a broad test plan.

Based upon the above considerations, the Level 1 air methodology was developed to be flexible but more reliant on process information. This permits the user of CAD to be selective in choosing a screening system and may allow a more simplified approach to certain streams. The various screening sequences available in Level 1 CAD are presented in Figure 7.

Unit operations considered for the air methodology but not being evaluated in the sequence are electrostatic precipitation, flaring, and incineration. The following sections indicate the reasons for their exclusion.

Electrostatic Precipitation

The selection of electrostatic precipitation technology depends heavily on conductivity and resistivity properties of the gas stream. Instead of testing a prototype electrostatic precipitator unit as a CA screening procedure, measurement of the following properties is recommended to

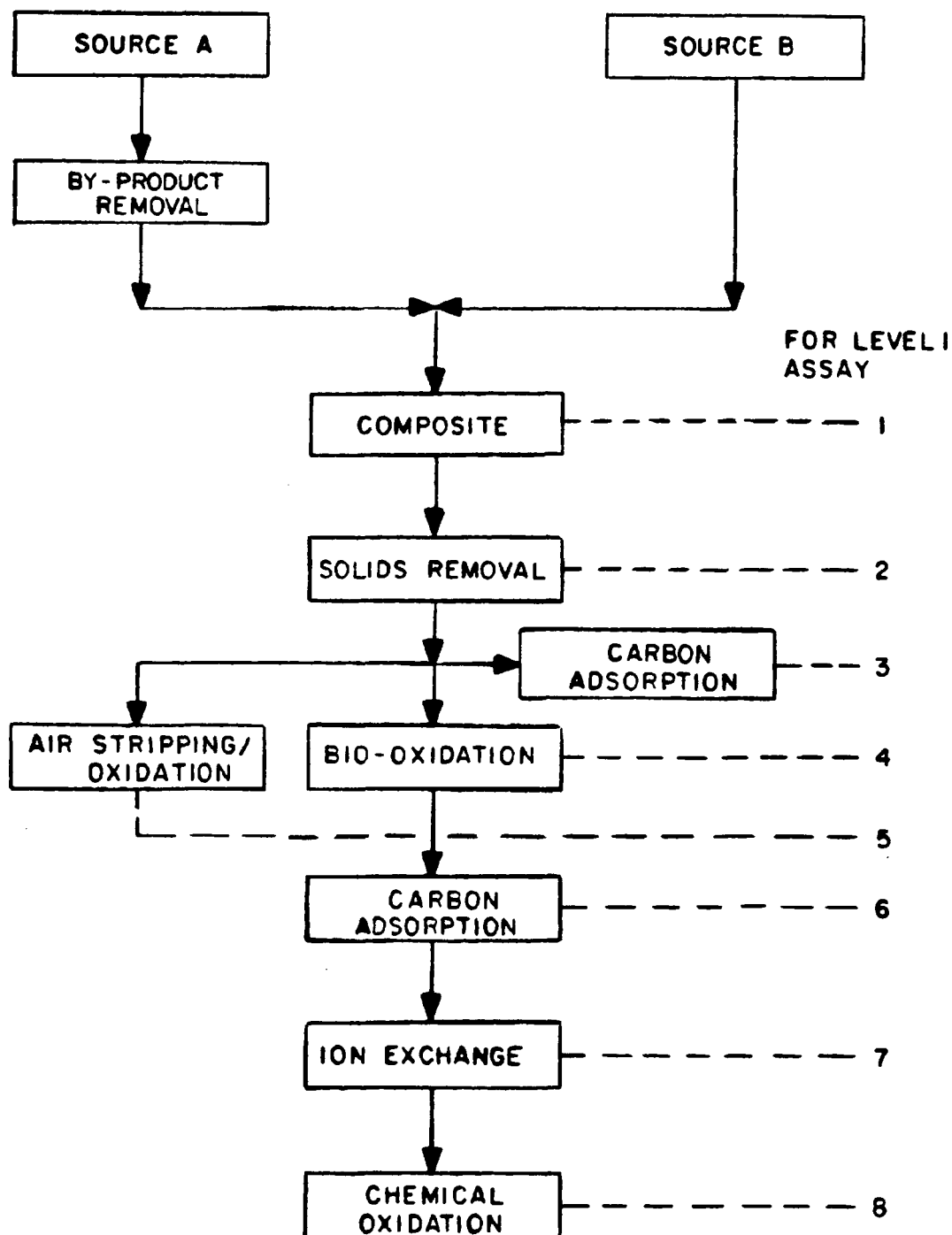


Figure 6. Final wastewater test sequence.

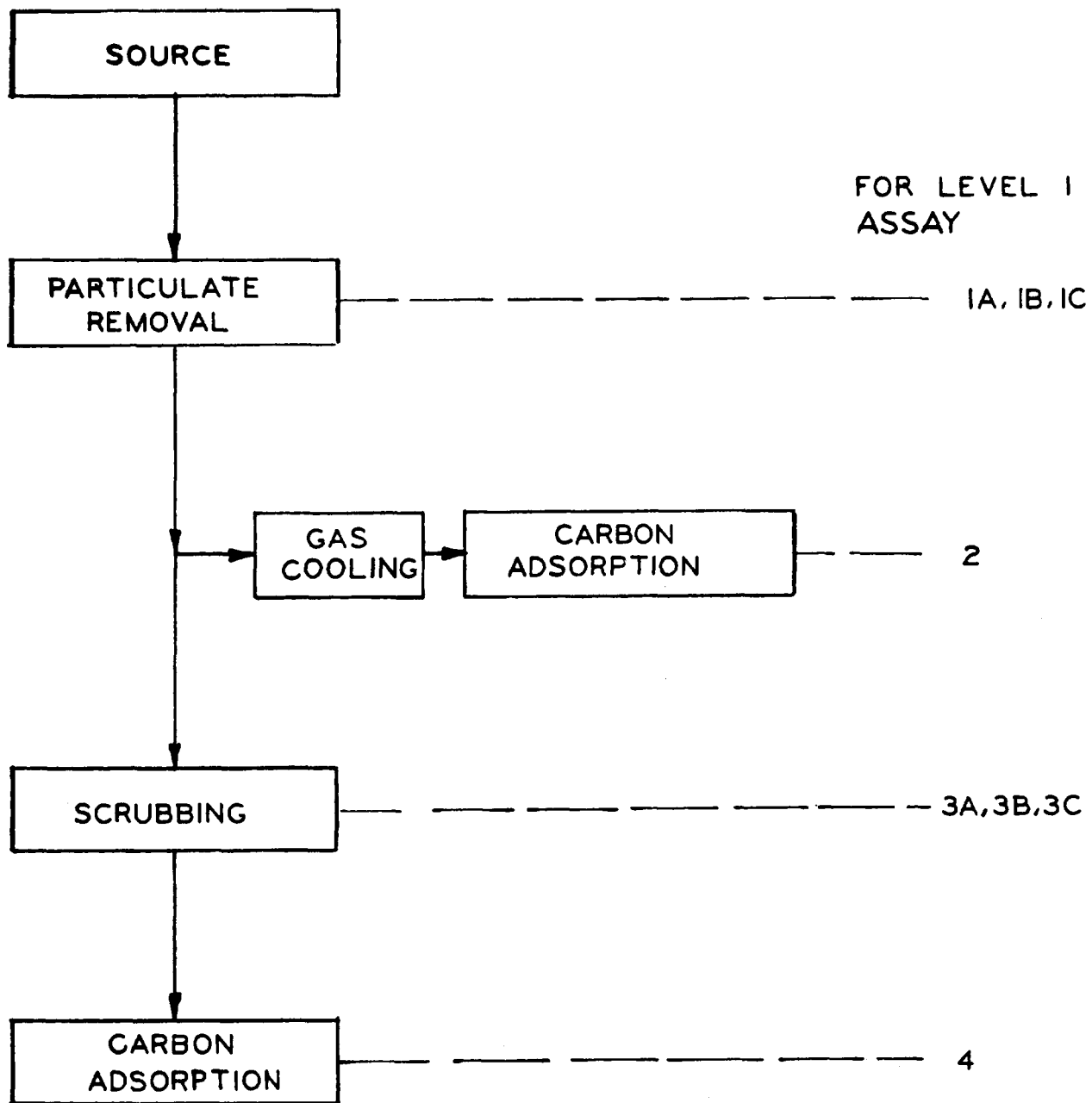


Figure 7. Preliminary air testing sequence.

supplement existing Level 1 protocols:

- Particle resistivity,
- Particle size—average diameter,
- Specific gravity,
- Bulk density, and
- Particle size distribution curve.

Direct Combustion (Flare)

Flaring is acceptable control technology for a number of applications, principally in the petroleum refining and other industries where upset conditions involving large volumes of flammable gases can be economically handled. It is not recognized or recommended as best available control technology by regulatory agencies due primarily to lack of a sufficient data base. A major disadvantage is the absence of equipment and practical techniques to sample the products of combustion and monitor performance. Methods and equipment sizes used in pilot-plant test runs are not practical for CAD and have not yielded data that can be used for scaleup design or prediction of performance. The disadvantages of flares are presently too great for the unit operation to be useful in CAD.

Direct Flame Incineration

Thermal incineration is one of the most effective means for disposal of hazardous waste gases and, despite high capital and operating costs, will likely be specified more frequently in the future for problem pollutants. A proper evaluation of the capability of incineration would involve study of key parameters such as residence time and temperature. The manipulation of a number of variables is beyond the scope of Level 1 CAD and, coupled with the general difficulty of handling large volumes of sample, screening tests on incineration become impractical and are not recommended. Incinerator manufacturers, however, have compiled a large data base on the thermal oxidation of organic materials, and there is also a high level of confidence that almost any organic material can be destructed.

The Level 1 air methodology is applicable to any point source where a Level 1 environmental assessment might be performed. This is generally intended to mean those sources that discharge directly to the atmosphere and does not

normally include process lines, internal recycle, or waste gas lines directed to control devices.

Open vents or stacks that are considered sources of uncontrolled fugitive emissions are not recommended for CAD. Examples of these sources include relief systems, pressure let-down or control systems, emergency vents, leaks, spills, etc. They are normally highly variable in composition, rate, frequency, and duration, and control technology is often uneconomical or difficult to apply. When the materials are hazardous, it is common to collect the vapors in an exhaust system and direct the combined flow into a central control system such as a scrubber or flare. Discharges from control systems are usually of interest to CAD.

Vents, stacks, and other point sources of air emissions are usually too numerous in the plant site to permit a CAD assessment of each discharge. A cost-effective program can best be achieved by performing a reasonably complete engineering review of the available data before finalizing sample points. Process and engineering flow sheets, process and treatment description, and all other information should be studied prior to a preliminary site visit. During the visit, information gaps may be filled by discussions with plant personnel and/or inspection of equipment and devices. If it can be established, for example, that the emission is a vapor and contains no particulate matter, the most complex and costly test configuration requiring particulate sampling modules can be avoided. Furthermore, if the source is a pure, single-component organic material (such as breathing and filling vapors from a storage tank), CAD may not be needed at all because emissions can be calculated and potential control technology selected based on the material properties.

IERL Level 1 sampling protocols are employed in Level 1 CAD air methodology. The sampling apparatus for a Level 1 assessment are the grab bulb, for gaseous samples only, and the SASS, for gaseous streams containing particulate. The control technologies recommended for CAD air methodology are particulate removal, gas cooling (condensation), liquid scrubbing, and carbon adsorption. The equipment for these operations is constructed and assembled as modules (Figures 7 and 8). Following is a brief description of each module and its function in CAD.

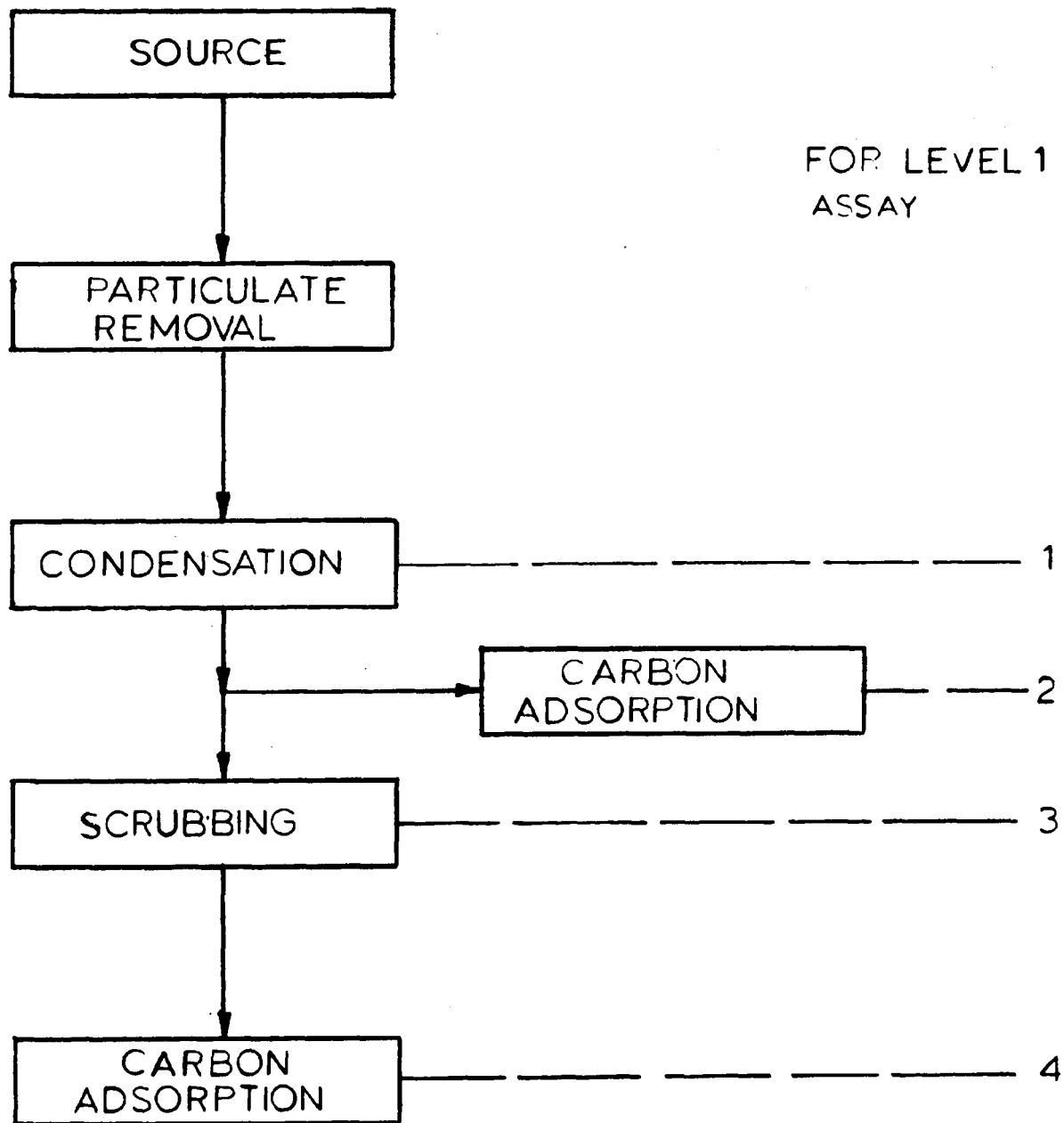


Figure 8. Final air testing sequence.

Particulate Removal

The module is a standard SASS train cyclone/filter assembly, contained in a heated oven. For CA screening purposes, this module serves only to pretreat the gas when particulate is present.

Gas Cooling

Hot gases must be cooled to at least 55° C (130° F) before entering an activated carbon module. In commercial practice, gases are often cooled to permit use of cheaper materials of construction (e.g., plastics) in downstream ducts and equipment. In addition to cooling as a protective measure, condensation of volatile material is a valuable control technology. This module also will be a standard SASS train component, except that the sorbent cartridge is not used and will be taken out of line.

Scrubbing

Liquid scrubbing, using an aqueous alkaline solution, is specified as the primary control technology in Level 1 CAD screening for removal of pollutants in acid gases. Several media were investigated and sodium carbonate was selected. CO₂ is a common component in many gaseous streams and will be absorbed in media such as sodium hydroxide, requiring a large volume of solution and causing logistical problems. The capacity to remove acidic components at expected concentrations cannot be handled in the standard SASS impinger assembly. Therefore, a small counter-current scrubber must be used.

Carbon Adsorption

Activated carbon is being studied for removal of trace quantities of organic and inorganic materials. The economics of regeneration usually preclude carbon being used as the primary technology for removal of high concentrations of organics. Regeneration will not be studied in Level 1 CAD. The module is a column canister sized to contain a sufficient quantity of activated carbon. Calculations show that the capacity of a standard SASS sorbent module is not adequate for CAD studies.

The general principles of IERL sampling ap-

ply to CA but may be modified to accommodate a more flexible approach in air methodology. This is illustrated in Figure 8, which outlines alternative screening arrangements and associated sampling requirements. For CA screening procedures, the standard SASS modules are used in the following manner:

- The particulate removal module (cyclones and filter) is used for preconditioning of the stream prior to entering control devices.
- The gas-cooling module of the SASS train is used in CAD for evaluating condensation control technology. Operating this module according to Level 1 assessment parameters will serve both as condensation screening technology and the means to provide a sample for evaluation of the applicability and effectiveness of condensation.
- The XAD-2 cartridge and the impinger module in the sampling system (see Figure 9) is designed to collect the residual. A side benefit is the removal of corrosive material that would cause damage to the vacuum pump, dry gas meter, and other components downstream.

The complete Level 1 analytical protocols shall be performed on the gas samples produced. The CAD sample sizes shall meet the requirements for Level 1 analytical protocols. These are presently:

- GC analysis: 3 L (grab);
- Physical/chemical testing and health effects: 30 m³ (passed through SASS train); and
- Ecology effects: 1,360 L (grab).

Laboratory Verification

In developing the CAD air methodologies, typical unit operations needed to remove particulates and gases/vapors from air emissions were evaluated. For various reasons, some of these operations had to be excluded from consideration as CA screening procedures. Control technologies eventually selected for the CAD methodology included particulate removal, gas cooling (condensation), carbon adsorption, and liquid scrubbing.

The SASS, developed for IERL Level 1 sampling, made use of all these mechanisms for separation and collection of gas stream contaminants and therefore initially seemed to be an ideal system for use in CA screening proce-

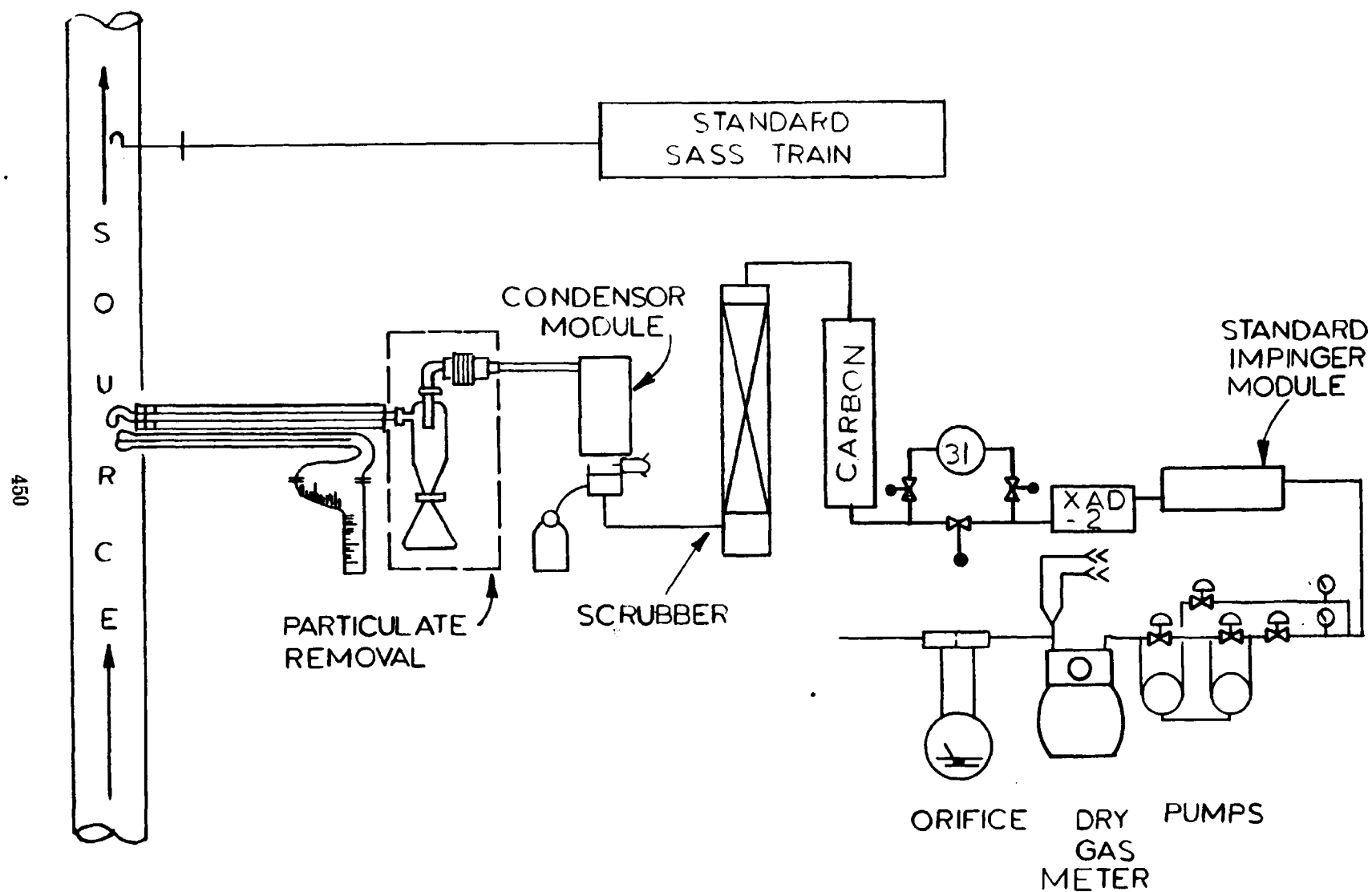


Figure 9. Combined screening train.

dures. It was thought that activated carbon could replace XAD-2 in the same cartridge. However, subsequent calculations showed that the capacity of the standard XAD sorbent module used in the SASS train would not be adequate for these studies.

Several scrubbing media were investigated and sodium carbonate was selected as the most promising. The capacity needed to remove acidic components at expected concentrations was also calculated, and it was determined that the standard SASS impinger assembly would not hold the required volume. The existing condensation module in the SASS train was not expected to be a problem because sample flow rates and test duration would be similar to those encountered in IERL Level 1 sampling.

In order to provide the extra capacity required for scrubbing, a counter-current, packed-column scrubber with an 8-L reservoir was designed. A 4-in I.D. by 5-ft glass column containing 3 ft of Raschig rings as packing was used during verification testing.

Likewise, a larger canister to contain the activated carbon was specified. A 4-in I.D. by 3-ft glass column containing 10 lb of activated carbon (3-ft bed depth) was used for testing.

Figure 9 shows the configuration of the modified screening train as assembled to evaluate scrubbing followed by activated carbon. Both control technologies can be evaluated separately if a process review indicates no need to study both systems in series.

The solids removal module of the standard SASS has been incorporated into the train. However, particulate removal technology will not be evaluated during screening because data for evaluating the effects of solids removal technologies/control devices are obtained by the standard IERL Level 1 sampling protocols, as amended by CAD methodologies. When a gas stream with a high particulate loading is sampled, this module will prevent particle buildup on the activated carbon. The condenser module serves two purposes: for cooling of the gas stream (to a carbon influent temperature of 55° C or less), and as a separate unit process for removal of low-boiling organics.

The standard SASS train presently requires two vane-type pumps arranged in parallel in order to maintain a sample flow rate of 4 ft³/min through the sample collection portion of the train.

During a sampling run, particulates gradually build up on the filter causing an increase in vacuum at the pumps. If this vacuum becomes too great, the desired flow rate cannot be maintained and the system must be shut down in order to replace the filter. Incorporating two additional modules in the train (scrubber and carbon adsorption modules) increases the total pressure drop across the system.

A SASS train was obtained from the manufacturer to quantify the effects of the added components on the system. Testing was accomplished by drawing room air through the SASS train alone, SASS train with carbon in-line, and the complete system (SASS plus carbon canister and scrubber modules). Vacuum hoses with an I.D. of 1/4 in were used to connect the extra modules to the SASS train. Tests were also performed to determine the pressure drop across these lines. All vacuum readings were taken from the gauges supplied with the pumps, and gas flow rate measurements were made using the gas meter and timer that are part of the SASS train control unit. Before the tests were conducted, a filter was placed in the filter holder, three of the impingers were each filled with 750 mL of tap water, and the fourth impinger was charged with silica gel. XAD-2 resin was placed in the sorbent cartridge assembly. Results of these tests are presented in Table 9.

Proper operation of the cyclones is dependent on the sample gas flow rate through the system, with 4 ft³/min being the optimum design flow rate. At this rate, a typical test run collecting 1,000 ft³ of sample has an approximate duration of 4.5 hr. Depending on particulate loading in the gas stream, it may become impossible to maintain a 4-ft³/min flow rate through the modified SASS train (scrubber and carbon modules in line); however, the only problem this presents is an extended sampling period. For the purposes of the screening procedures, it is not absolutely necessary to maintain the 4-ft³/min flow rate.

The sample flow piping in the standard train is 1/2-in I.D.; it is recommended that this size tubing be used for the design of the actual screening train to eliminate the pressure drop caused by the smaller diameter tubing. The modular construction of the entire screening train makes it a simple matter to add or delete components or rearrange the sequence of any of

TABLE 9. SCREENING TRAIN PRESSURE DROP TESTING

	Flow Rate (cfm)	Vacuum (in. Hg)	Flow Rate (cfm)	Vacuum (in. Hg)
Standard SASS	4.0	8.5	3.0	6.0
Scrubber and Connecting Lines	4.0	8.5	3.0	5.0
Connecting Lines (Only)	4.0	<u>6.5</u>	3.0	<u>4.0</u>
Scrubber	4.0	2.0	3.0	1.0
Carbon Columns and Connecting Lines	4.0	5.0	3.0	4.0
Connecting Lines (Only)	4.0	<u>4.5</u>	3.0	<u>3.5</u>
Carbon Columns	4.0	0.5	3.0	0.5
TOTAL SYSTEM	4.0	18.5	3.0	9.0
(Standard SASS with both scrubber and carbon columns on-line)			3.7	15.0

the units, depending on prior knowledge of the gas stream constituents and/or the desired application of the train at a particular source.

Preliminary calculations indicated that 8 L of scrubbing solution (1-Normal sodium carbonate) would be required to scrub 1,000 ft³ of sample with an H₂S concentration of approximately 2,000 ppmv. Additional calculations indicated that 5 lb of activated carbon would be adequate for removal of organic compounds expected in a waste gas stream. To verify these calculations, the special gas blend with the following composition was utilized:

- Carbon dioxide 70 percent
- Nitrogen 29.55 percent
- Hydrogen sulfide 2,000 ppmv
- Ethylene 2,500 ppmv

Two gas cylinders were required to obtain this blend, the first containing the N₂, H₂S, and C₂H₄, and the second containing the CO₂. Flow rates from both cylinders were monitored by the use of rotometers and dry gas meters and were adjusted to obtain the desired final gas composition (Figure 10).

The gases were first introduced into a mixing chamber where initial samples were taken to

determine both H₂S and total hydrocarbon concentrations. From the mixing chamber, the gases then flowed through the scrubber unit and the carbon canister. Several test runs were made on each unit separately, and one run was conducted to determine H₂S and hydrocarbon removals with both units in series. Total hydrocarbons were measured by taking a 100-cm³ gas sample and injecting directly into a gas chromatograph equipped with a flame ionization detector. Methane was used as the standardization gas, and, therefore, the results are presented as total hydrocarbons expressed as methane. Hydrogen sulfide levels were measured by drawing a sample of the gas directly through H₂S detector tubes. Results of the testing are presented in Table 10.

The results of pilot scrubber testing indicate that 8 L of sodium carbonate scrubbing solution will not be adequate when a 1,000-ft³ sample is drawn that has an acid-gas concentration (H₂S, SO₂, etc.) of 2,000 ppmv or greater. It was observed during the test period that the scrubber solution became totally ineffective at a pH of 10.0 or less. It is recommended that the solution concentration be increased to 2-Normal,

Ⓢ - SAMPLE POINTS
 ----OPTIONAL SCRUBBER BYPASS

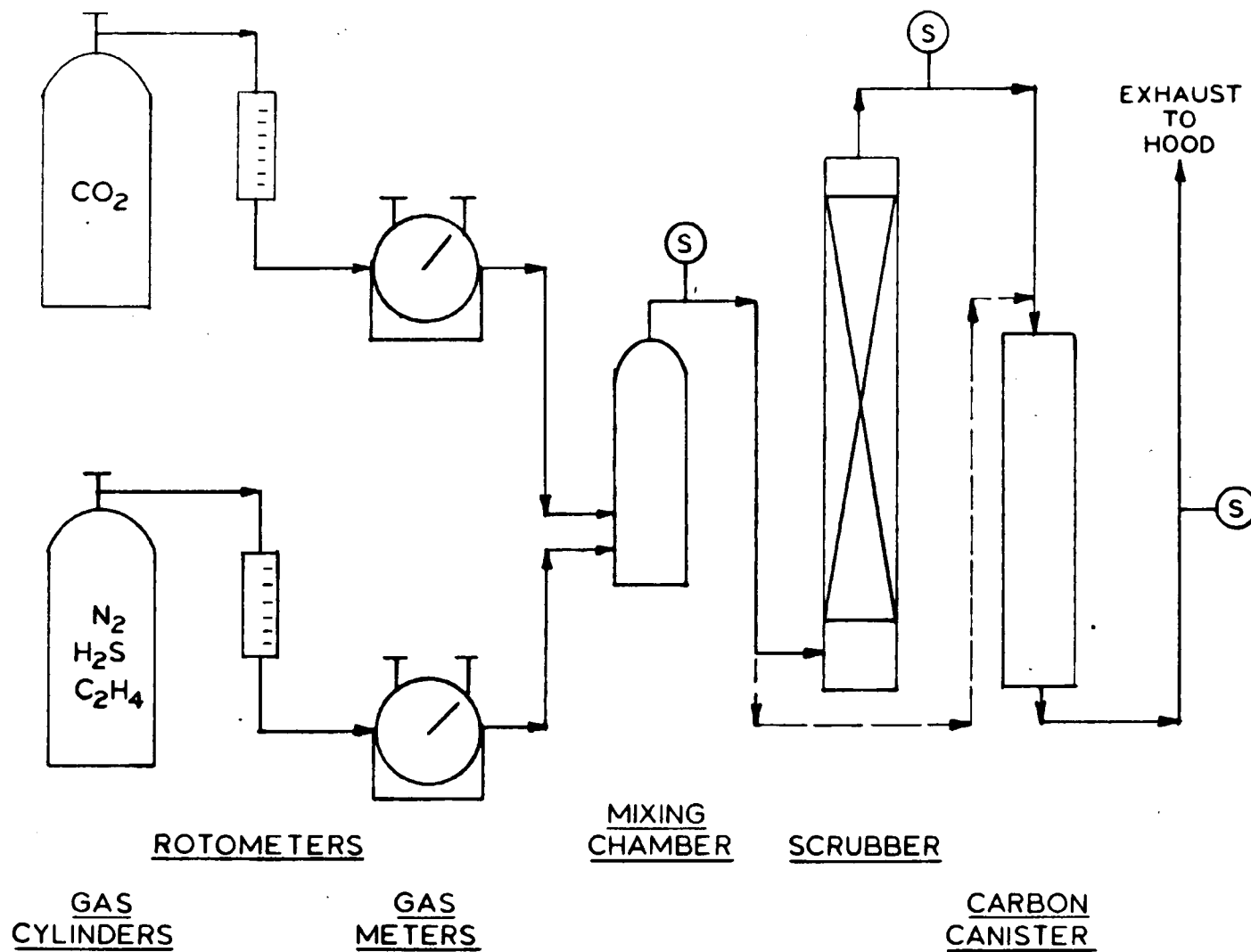
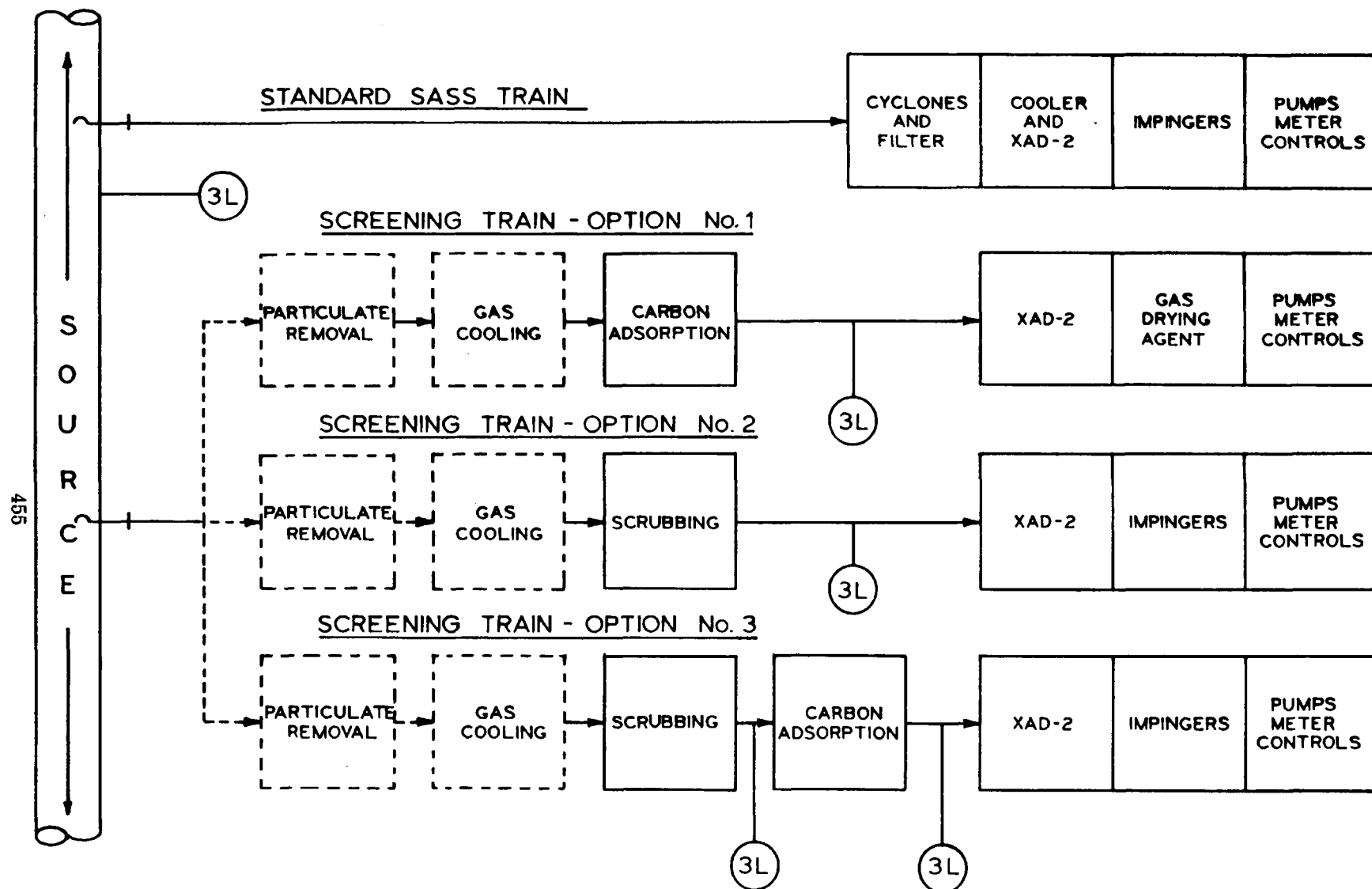


Figure 10. Pilot scrubber and carbon adsorber test apparatus.

TABLE 10. RUN #1—SCRUBBING FOLLOWED BY CARBON ADSORPTION

Time (minutes)	Gas Volume (cubic feet)	Inlet Concentration		Outlet Concentration		% Removal	
		H ₂ S (ppm)	Total Hydrocarbon*	H ₂ S (ppm)	Total Hydrocarbon*	H ₂ S	Total Hydrocarbon
0	-	2400	1060	5	1000	99.8	5.7
25	37.2	2400	1250	10	1275	99.6	-
60	94.6	2100	-	40	-	98.1	-
90	143.2	2200	-	100	-	95.4	-
105	167.1	2400	-	240	-	90.0	-
120	192.6	2200	-	500	-	77.2	-
150	240.6	2400	-	1250	-	47.9	-

* (ppm as methane)



-----OPTIONAL - DEPENDS ON PROCESS INFORMATION

Figure 11. Screening train options.

and that the total volume available in the reservoir be increased to 16 L. As an extra precaution, a pH meter should be used to monitor the condition of the scrubbing medium. If it is necessary to halt the run for a filter change at any time during the test, the scrubbing solution should also be replaced at that time.

Removal of ethylene from the test gas stream by activated carbon was very poor. It is not known whether this was due to an inherently low adsorption capacity for this compound onto the test carbon, or if the large quantity of carbon dioxide present in the stream resulted in flushing the ethylene through the system. Organics with higher molecular weights stand a much better chance of being adsorbed on the carbon and, for this reason, it is recommended that the carbon module be retained in the screening program. It is not practical to substantially increase the amount of carbon used in the screening train because the train already consists of many modules large enough to present problems when the sample location is difficult to reach, and space at the sample point will be restricted in most cases. The screening procedure for carbon during Level 1 may be somewhat limited, but will, nevertheless, be indicative of the potential of the process for removing organic contaminants and will serve as a guide for future studies.

In order to obtain meaningful results from the tests, it is imperative that each source to be evaluated be sampled according to the Level 1 IERL methods, in addition to the screening sampling. Ideally, both tests will be run simultaneously. If this is not possible, process data for each source must be evaluated to determine the constancy of operation, and judgment must be used to assess the reliability of comparing data from two nonsimultaneous test runs.

The 3-L grab samples will be taken as shown in Figure 11. In addition, an optional sample of

1,360 L will be taken at these sample points for use in the stress ethylene test. This sample is listed as optional at this time pending modifications of the analytical procedure.

Conclusions and Recommendations

A summary of conclusions and recommendations based on the laboratory work with simulated waste gas is presented below:

- The screening procedures using scrubbing, carbon adsorption, and condensation should be adopted.
- Special supplemental scrubber and adsorber modules will be required to be used in conjunction with the SASS equipment.
- The supplemental modules increase the pressure drop across the sampling system. It is recommended that the sample flow rate be reduced to 3 ft³/min (Level 1 IERL procedures specify 4 ft³/min for optimum operation of the particle sizing module).
- A 2.0 normal solution of sodium carbonate will be used as the scrubbing media. This solution should be replaced during the test whenever the pH falls below 10.0 standard units.
- Figure 11 shows the screening train options available for air sampling.

REFERENCES

1. Singer, P. C., et al. *Assessment of Coal Conversion Wastewater: Characterization and Preliminary Biotreatability*. EPA 600/7/78-181. p. 95.
2. Beychok, Milton R. *Coal Gasification and the Phenosolvan Process*. (Presented at the 168th National Meeting of the American Chemical Society, Division of Fuel Chemistry. Atlantic City. September 1974.) Volume 19, No. 5. p. 85-93.

EVALUATION OF COAL CONVERSION WASTEWATER TREATABILITY

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Abstract

This paper describes preliminary results from an experimental program that evaluates biological treatability of coal conversion wastewater. The experimental approach includes preparation of a synthetic wastewater designed to simulate a practical coal conversion discharge. Design and operation of four biological reactors and the preliminary results from the first few months of synthetic wastewater treatment are described. Data analyzed include chromatographic analyses of the wastewater and reactor effluents, as well as cytotoxicity analyses using Chinese hamster V79 cells.

INTRODUCTION

Most coal conversion technologies incorporate or project aerobic biological treatment as the principal means of removing phenols and other organic impurities from process wastewaters. However, the nature and biodegradability of many of these other organic materials are not known, and the extent to which they can be removed by biological treatment cannot be reliably predicted. Synergisms and antagonisms resulting from the complex nature of real wastewaters are especially uncertain. Because even well-operated biological treatment processes typically remove only 85 to 95 percent of the influent BOD and a significant portion of the wastewater organics may not be biodegradable, biological treatment alone may not provide an environmentally acceptable discharge. In view of these considerations, a need exists to identify the nature and characteristics of aqueous discharges from coal conversion processes, assess their environmental impact, and develop satisfactory waste-

water treatment so they may be disposed of in an environmentally acceptable fashion.

In an earlier report, Singer et al.¹ presented the results of a literature review and survey showing that the composition of wastewaters from different coal gasification and liquefaction technologies is relatively uniform, especially with regard to the phenolic constituents. Phenol appears to be the major organic constituent, and phenolics as a class constitute 60 to 80 percent of the total organic carbon (TOC) in the wastewater. Other classes of organics, such as mono- and polycyclic nitrogen-containing aromatics, oxygen- and sulfur-containing heterocyclics, and polynuclear aromatic hydrocarbons, appear to be present at significant concentrations. In this paper, the preliminary results of a study directed at evaluating the biological treatability of coal conversion wastewater is presented.

APPROACH

Biotreatability studies require the use of acclimatized microbial cultures to insure accurate evaluation of biological treatment systems and for preliminary assessment of key parameters in establishing the effectiveness of such treatment. Meaningful assessment of potential toxicity of wastewater constituents in biological treatment is impossible unless the test cultures have been acclimatized to the wastewater in question.

Ideally, biotreatability studies should be conducted using the specific wastewater for which the treatment is being developed. In this study, however, it is not feasible to use actual wastewaters from coal conversion operations because coal conversion processes are still in the developmental stage and it is unlikely that a suitable, consistent, and representative wastewater could be obtained. Accordingly, a synthetic organic wastewater was formulated

*Speaker.

to provide a mixture of organic compounds, at known and reproducible concentrations, to be used in acclimatizing and maintaining microbial cultures for preliminary biotreatability studies. The synthetic wastewater is used to feed several bench-scale pilot reactors. In addition to generating acclimatized organisms for biodegradability studies (to be reported elsewhere), analysis of effluents from the reactors provides information on wastewater characteristics at various levels of biological treatment.

FORMULATION OF SYNTHETIC COAL CONVERSION WASTEWATER

Several criteria were employed in choosing specific compounds and their concentrations to be included in the synthetic wastewater. Because this waste would be used as a means of developing an acclimatized culture of microorganisms, most of the compounds selected are known or thought to be biodegradable. However, not all of the identified constituents of coal conversion wastewaters can be used by microorganisms. Accordingly, some compounds presumed to be slowly degradable or nondegradable, as deduced from earlier biodegradation experiments,¹ were included (e.g., 2-indanol, indene, 2-methylquinoline, and 3,5-xyleneol).

When the composition of the synthetic wastewater was formulated, it was desired that concentrations of the various components should be similar to those encountered in real wastewaters. Accordingly, reference was made to a summary of the constituents identified in coal conversion wastewaters¹ and the range, midrange, and median concentrations were determined for each constituent and for each class of compounds (e.g., cresols, xylenols, heterocyclic N-compounds, etc.). From each class, one or more compounds were chosen based on biodegradability and reported concentration. The specific compounds chosen were usually the compounds within each class that were reported at the highest concentrations in the real wastewaters. Often, if a class contained many components, or if differences in biodegradability among the components of a given class were anticipated, more than one chemical from that class was chosen. The concentration selected was the median value reported for that compound in the real waste-

water, or the median of the class if only one compound from that class was picked. When the concentration of a specific compound selected was not known, it was included in the synthetic wastewater at the median concentration for its class.

Table 1 presents the composition of the wastewater formulated in this manner. Twenty-eight organic components are included, as well as inorganic nutrients and pH-buffers. The synthetic wastewater represents all major classes of organics present in real wastewaters for which data are available, and virtually all specific organic compounds that have been reported to be present at high concentration. The total organic carbon (TOC) concentration of all the components is 4,636 mg/L.

DESCRIPTION OF PILOT UNITS

Four 25-L biological reactors were constructed for use in the initial phases of the pilot program. Each reactor consists of a 7½ in ID lucite tube, 4 ft long, fitted at the bottom to a stainless steel cone with a 45° slope (Figure 1). Each reactor has overflow and sampling connections located at appropriate heights to retain the desired volume of contents in the reactor and to permit withdrawal of samples from desired elevations. The stainless steel cone is equipped with connections to permit draining of the unit and nipples for introducing air and feed solution at the bottom of the cone.

A compressor, operating through a pressure regulator, supplies air to each reactor at a rate adequate to insure thorough mixing and maintenance of aerobic conditions in the mixed liquor at all times. The rate of air supply is controlled through the use of rotameters and needle valves.

The units are fed synthetic wastewater from a glass storage reservoir mounted on a large magnetic mixer. The wastewater is fed to each reactor by a variable-speed peristaltic pump. The reactors are operated as continuous-flow activated sludge systems with no recycle of solids (biomass). Hence, solids residence time or sludge age equals hydraulic detention time. The pump feeding Reactor 1 (with a 5-day hydraulic detention time) is operated continuously. Pumps supplying feed to the other three reactors (operated at 10-, 20-, and 20-day hydraulic detention times, respectively) are ac-

TABLE 1. COMPOSITION OF SYNTHETIC COAL CONVERSION WASTEWATER

<u>Compound</u>	<u>Concentration, mg/l</u>
1. Phenol	2000
2. Resorcinol	1000
3. Catechol	1000
4. Acetic Acid	400
5. o-Cresol	400
6. p-Cresol	250
7. 3,4-Xylenol	250
8. 2,3-Xylenol	250
9. Pyridine	120
10. Benzoic Acid	100
11. 4-Ethylpyridine	100
12. 4-Methylcatechol	100
13. Acetophenone	50
14. 2-Indanol	50
15. Indene	50
16. Indole	50
17. 5-Methylresorcinol	50
18. 2-Naphthol	50
19. 2,3,5-Trimethylphenol	50
20. 2-Methylquinoline	40
21. 3,5-Xylenol	40
22. 3-Ethylphenol	30
23. Aniline	20
24. Hexanoic Acid	20
25. 1-Naphthol	20
26. Quinoline	10
27. Naphthalene	5
28. Anthracene	0.2

theoretical Σ TOC = 4636 mg/l

NH ₄ Cl (1000 mg/l as N)	3820
MgSO ₄ · 7H ₂ O	22.5
CaCl ₂	27.5
FeNaEDTA	0.34
Phosphate Buffer: KH ₂ PO ₄	170
K ₂ HPO ₄	435
Na ₂ HPO ₄ · 7H ₂ O	668

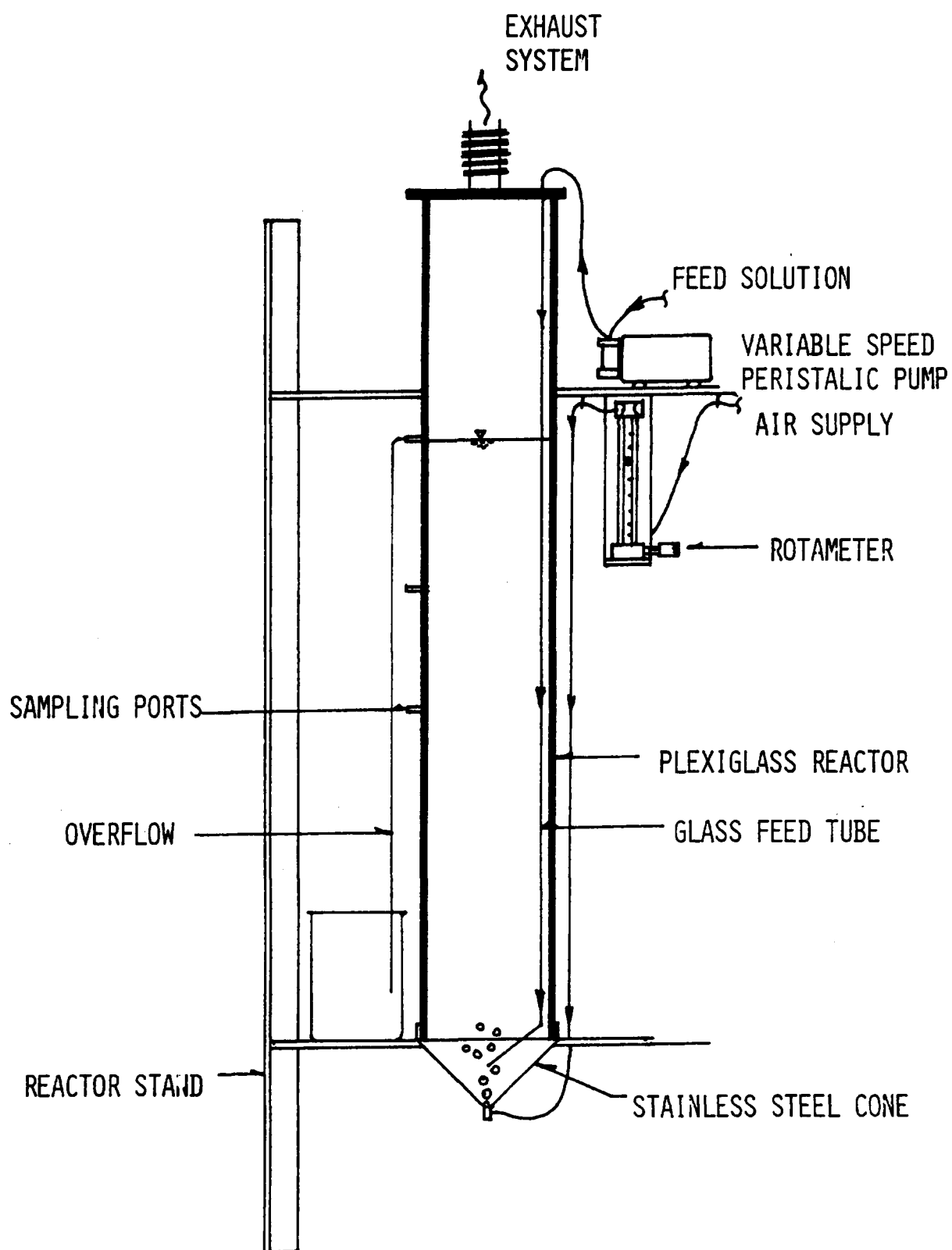


Figure 1. Schematic of experimental biological reactors.

tuated by a clock that operates them for a predetermined time once every half hour. (Two reactors operate at the same 20-day detention time to allow one reactor to be isolated for use as a chemostat to provide seed organisms for parallel biodegradation investigations; the other 20-day reactor is used with the 5- and 10-day reactors to provide operating data to characterize reactor performance as a function of solids residence time.) Overflow from each reactor is collected in a glass reservoir and the amount of wastewater actually fed is determined daily by measuring the amount of effluent collected in that container.

Because of the potential hazard of some chemicals in the wastewater and the need to eliminate objectional odors in the working area, an exhaust system was installed to vent the units continuously to the outside of the building. The exhaust system consists of a blower mounted at the outside wall, thereby maintaining the air ducts under a slight vacuum to insure that gases from the reactors always flow into the exhaust system and not into the room. The feed reservoir is also vented to the exhaust system to prevent the escape of gases from that unit into the room.

OPERATION OF PILOT UNITS

The synthetic wastewater is made up in 16 L batches. Carbon-filtered Chapel Hill, North Carolina, tap water is used as dilution water to which the 28 constituents, shown in Table 1, are added. This is accomplished by adding appropriate quantities from concentrated stock solutions which are prepared periodically from reagent grade chemicals and stored under refrigeration until use. In order to prepare some of the concentrated solutions containing compounds of limited aqueous solubility, an organic solvent was required to maintain solubility in the stock solutions. Accordingly, acetone was employed for this purpose. While this introduced an extra constituent into the wastewater, it was believed that much of the acetone would be removed through air stripping during the long detention times in the reactors. Hence, the TOC concentration of the raw wastewater is actually somewhat higher than that shown in Table 1.

The reactors were started up using activated sludge from one of the Durham, North

Carolina, municipal wastewater treatment plants. The feed of synthetic wastewater was increased gradually over a period of several days to allow time for acclimatization of the microorganisms to the wastewater. However, during the first few weeks after startup, all of the units began to fail as evidenced by increased TOC concentration in the effluents and decreased solids concentration in the reactors. Failure occurred first in the 5-day reactor, then in the 10- and 20-day reactors. The exact reason for failure is unknown, but several possibilities have been considered. Operating procedures during the early stages of the investigation were uncertain and made it possible for the concentration of dissolved oxygen in the reactors to drop occasionally to zero. Also, the pH decreased to low levels (approximately 4.0) and remained there for extended periods. Further, there is a possibility that some wastewater constituents could have exerted a toxic effect on the microorganisms as concentrations of the constituents built up in the reactor during the period following startup. The pattern of failure, in order of increasing reactor detention time, is consistent with the latter hypothesis.

Because of the possibility of toxic effects and a desire to stabilize operations as quickly as possible, it was decided to reduce the strength of the synthetic feed during these initial investigations to one-quarter of that listed in Table 1. Other investigators have had to resort to similar dilution procedures in order to treat coal conversion wastewaters biologically. The resulting diluted version, with a theoretical TOC of 1,159 mg/L, is not inconsistent when compared with biotreatability experiments being conducted by others. (The concentration of TOC measured in the feed averaged 1,600 mg/L over the course of the runs because of the addition of acetone to solubilize the organic constituents in the feed.) At a later date, the question of treating the synthetic wastewater at higher strengths will be addressed. Accordingly, the reactors were started up again using a synthetic wastewater diluted to one-quarter of the concentration specified in Table 1.

A significant change in the color of the synthetic feed solution was observed over the several days during which it is used to feed the reactors. Attempts have been made to determine possible changes in wastewater composition during this time through periodic meas-

urements of TOC and chromatographic scans using high performance liquid chromatography (HPLC). Chemical changes accompanying the change in color from clear to brown appear to be minimal.

Routine sampling of each reactor is performed three times a week. Parameters measured include temperature, pH, mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), sludge volume index (SVI), and TOC. PH is measured potentiometrically. MLSS concentrations are determined using glass fiber filters in a Buchner funnel, followed by drying of the filter in an aluminum dish at 103°C for 24 hr. Filtrates from MLSS analyses are collected for TOC determinations using a Beckman 915 Carbon Analyzer. SVI is determined by allowing mixed liquor from the reactors to settle for 30 min in a 1-L graduated cylinder and calculating the settled volume occupied by the MLSS.

Other samples are collected as desired for the measurement of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and for more detailed analyses such as specific organic compounds using HPLC and GC/MS, aquatic bioassays, and assessment of health effects. BOD and COD analyses are conducted on samples from which suspended materials have been removed through glass fiber filtration. Samples for HPLC and GC/MS analysis and for aquatic bioassay and health effects assessment are centrifuged, filtered, and frozen.

PRELIMINARY RESULTS

Figures 2 through 5 show performance characteristics for each reactor over the period from May to October 1978. The reactors operated without serious incident from the beginning of May to the middle of June. The operational data suggested that they had reached approximate steady-state performance, and intensive data collection for this pattern of operation was initiated in early June. Five sets of filtered samples from the reactors were analyzed for BOD, COD, nitrogen species, and phosphorus, as shown in Table 2.

It had been planned that the analyses would be continued at intervals of 2 days over a period of at least 2 weeks. If the data then indicated that steady-state had been attained, in-

tensive sampling would have been discontinued and the operations modified to another set of reactor conditions. During the intensive sampling period in early June, however, the data for TOC and MLSS indicated clearly that steady-state operation had not been attained. Effluent TOC in all of the reactors rose sharply, beginning about June 9, leading to a decision to postpone the intensive analysis program until a more consistent performance could be achieved.

The exact cause for the substantial change in performance that occurred in June is unknown. However, a short time earlier the time clock controlling the feed to the reactors malfunctioned, resulting in an overfeed of Reactors 2, 3, and 4.

During July, August, and September, MLSS and TOC data indicated a reasonably steady performance, with the possible exception of Reactor 1 (5-day hydraulic detention time), which had performed irregularly since startup. In all units there was a pronounced tendency for pH to drift downward during this period, although the change in pH did not appear to affect the stability of the MLSS and effluent TOC. Accordingly, additional samples were taken during September for detailed chemical analysis, as shown in Table 2. Because of its erratic performance, Reactor 1 was not sampled intensively during this period. Reactors 2, 3, and 4 produced very low effluent BODs, indicating that almost all of the biodegradable material had been removed. The COD reductions were consistent with the reduction in TOC exhibited in Figures 2 through 5. The nitrogen and phosphorus measurements indicated that nutrients were sufficient for biological activity and that microbial growth was not inhibited by a lack of nutrients. The distribution among the nitrogen species showed that no nitrification took place.

Although the performance of the reactors appeared to be reasonably consistent during the September sampling period, the pH was unstable and continued to drift downward, indicating clearly that steady-state operation had not been attained. During October, the pH in the reactors reached levels lower than 4.0, causing concern about reactor stability. This concern was compounded by sharp rises in effluent TOC following loss of aeration for several hours because of compressor failure.

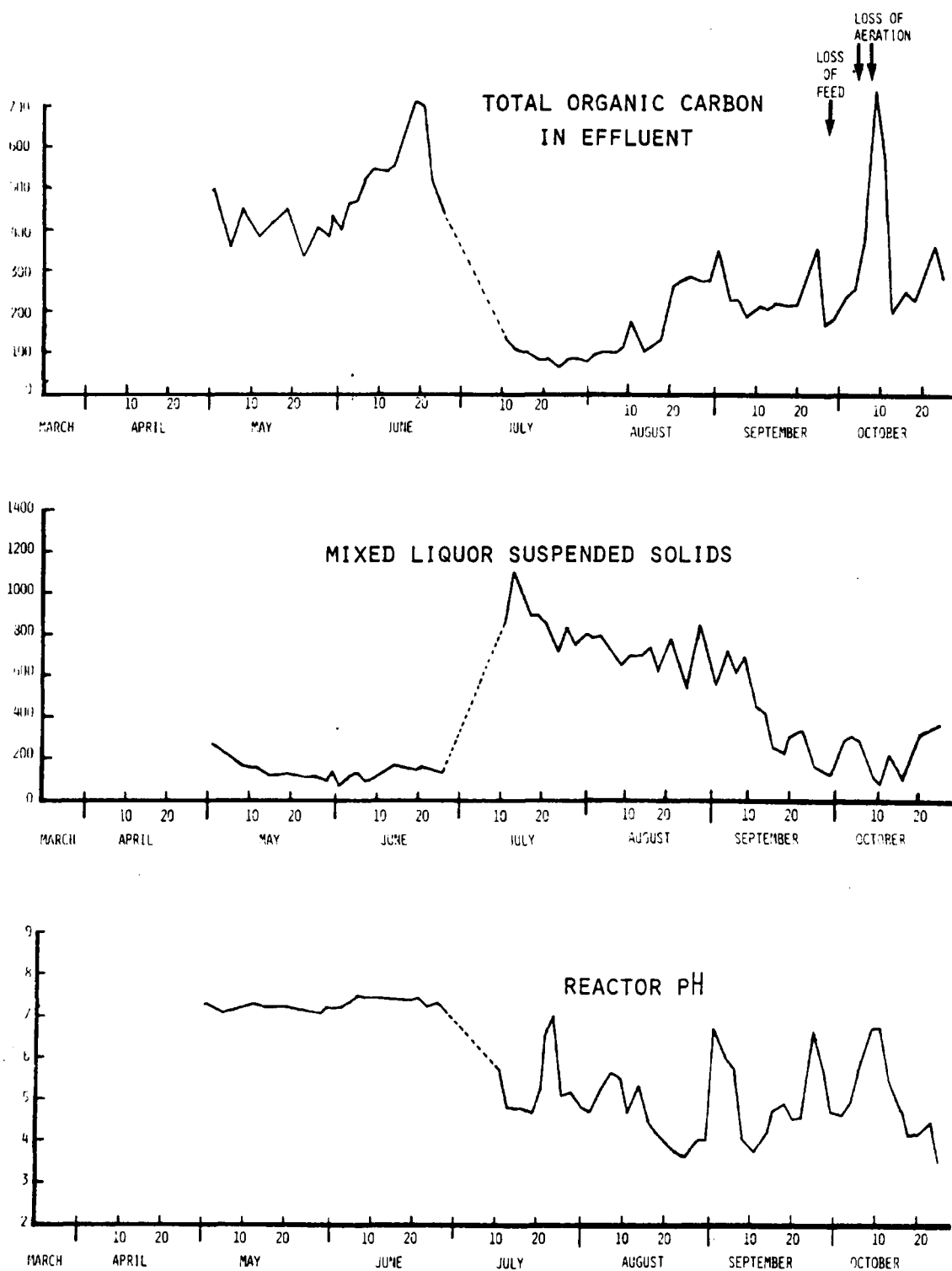


Figure 2. Performance characteristics of Reactor 1 with 5-day residence time.

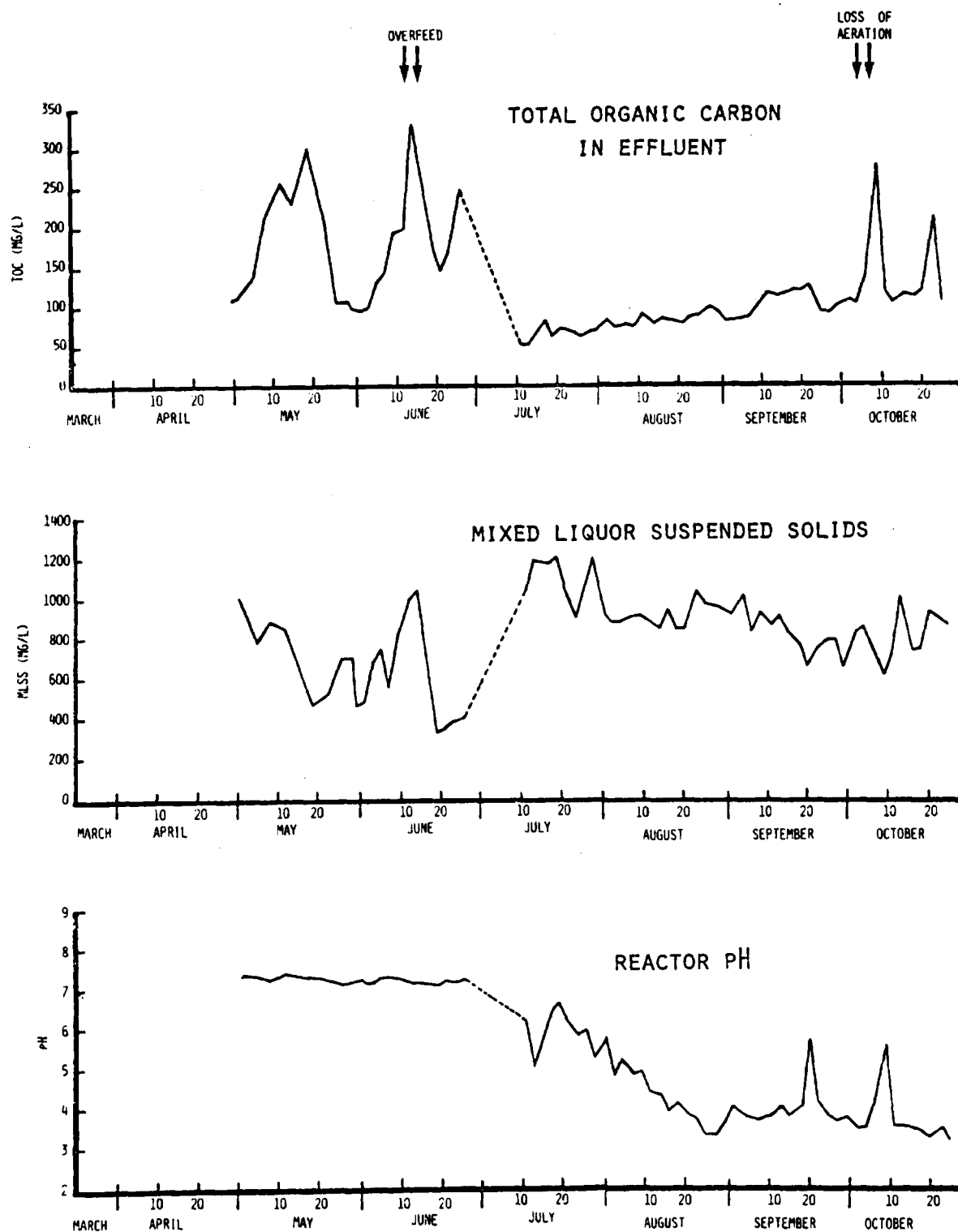


Figure 3. Performance characteristics of Reactor 2 with 10-day residence time.

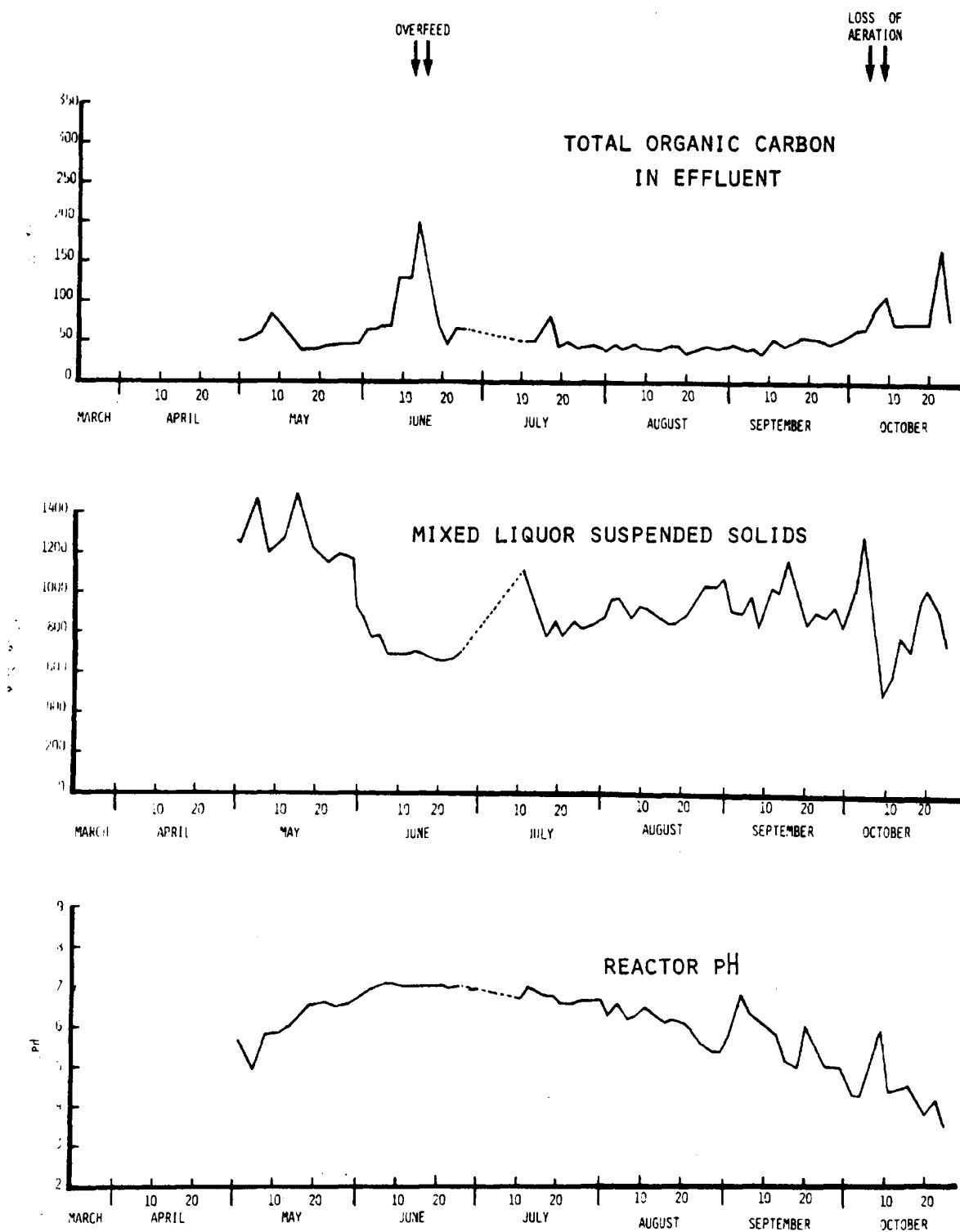


Figure 4. Performance characteristics of Reactor 3 with 20-day residence time.

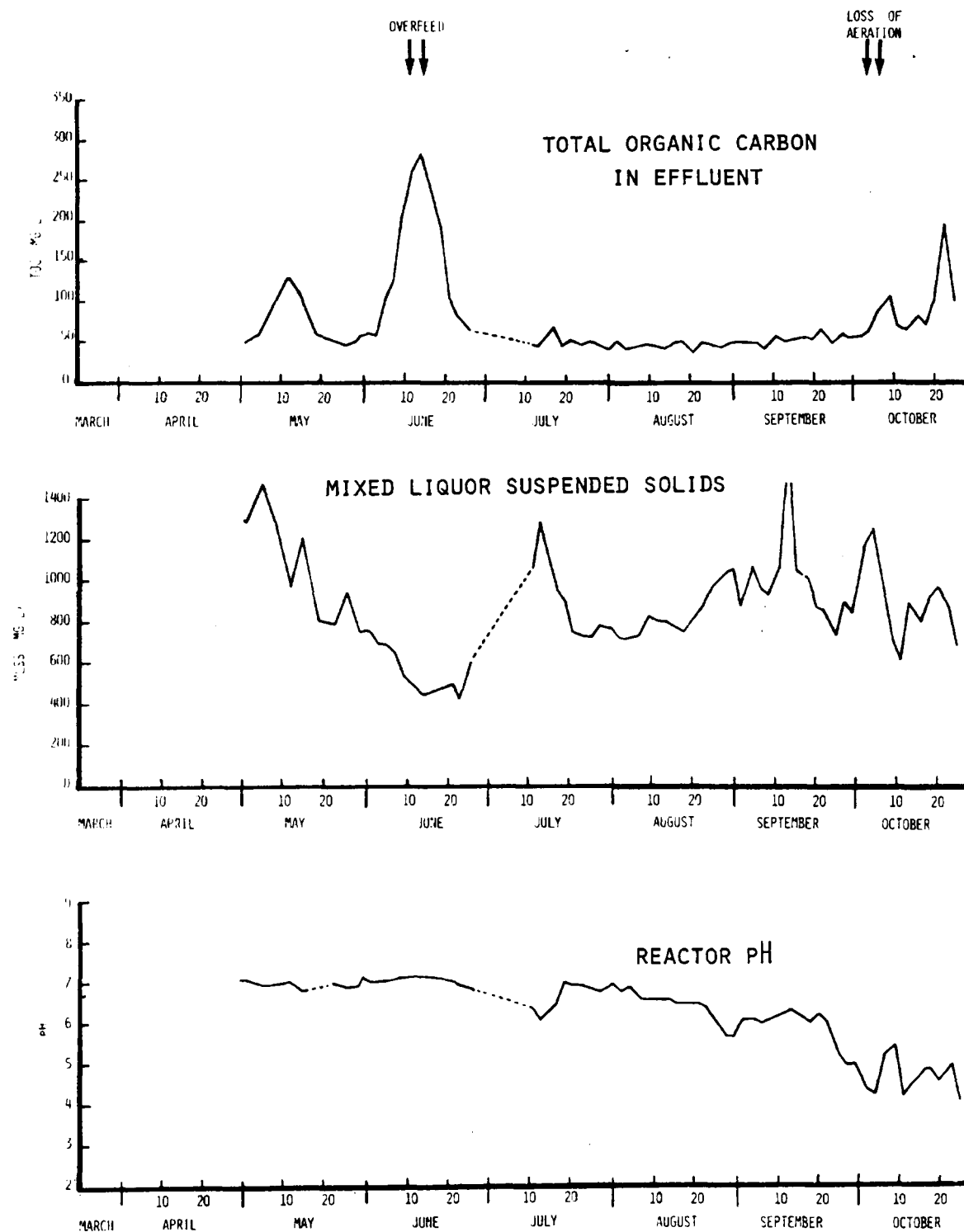


Figure 5. Performance characteristics of Reactor 4 with 20-day residence time.

TABLE 2. SUMMARY OF REACTOR PERFORMANCE:
MAY TO SEPTEMBER, 1978

Date	Sample	TOC mg/1	BOD mg/1	COD mg/1	NO ₂ mg/1 as N	NO ₃ mg/1 as N	NH ₃ mg/1 as N	TKN mg/1 as N	Total Phos. mg/1	Ortho. Phos. mg/1
5/30	Raw Waste		3520	5880	<0.03	11.0	243	239	423	---
6/5	" "		2880	5800						
9/12	" "		4140	5450						
5/30	Reactor 1	430	1115	1600	0.005	3.3	228	243	68	46
6/1	"	399	870	1648			228	273		
6/3	"	463	960	1728						
6/5	"	469	1055	1744						
6/7	"	521	1100	2112	0.12	6.8	209	370	42	50
5/30	Reactor 2	95	179	400	0.064	2.0	234	231	106	99
6/1	"	93	140	360			222	243		
6/3	"	98	171	488						
6/5	"	130	245	532						
6/7	"	143	240	616	0.05	5.6	222	330	35	38
9/8	"	90	443	----						
9/12	"	112	26	275						
9/14	"	112	25	315						
9/16	"	116	33	330						
9/18	"	119	----	320						
5/30	Reactor 3	47	47	340	0.07	5.5	217	242	369	333
6/1	"	64	30	348			231	246		
6/3	"	65	45	352						
6/5	"	70	80	400						
6/7	"	70	52	368	0.07	5.6	225	330	42	41
9/8	"	34	5	----						
9/12	"	51	7	190						
9/14	"	47	8	180						
9/16	"	53	7	210						
9/18	"	57	----	190						
5/30	Reactor 4	57	73	292	0.07	3.2	247	244	435	400
6/1	"	59	18	280			249	254		
6/3	"	57	38	356						
6/5	"	99	170	496						
6/7	"	123	183	552	0.06	4.4	240	290	50	51
9/8	"	39	5	----						
9/12	"	53	5	200						
9/14	"	51	4	195						
9/16	"	54	7	220						
9/18	"	56	----	240						

Accordingly, in late October this series of experiments was terminated.

DISCUSSION OF PRELIMINARY RESULTS

Overall performance of the units from March through October may be summarized with a few pertinent observations. All of the reactors have shown excellent TOC removals from the feed level of approximately 1,600 mg/L. Figure 6 summarizes TOC removal data for the months of July, August, and September before major excursions in pH were experienced. With 5-day detention, Reactor 1 was capable of producing an average effluent TOC of about 200 mg/L, with a range extending from about 80 to 300 mg/L. Reactor 2 (10-day detention) produced an average effluent BOD of about 80 mg/L, with more consistent performance as shown by the narrower range of approximately 60 to 120 mg/L. Reactors 3 and 4 (both with 20-day detention) performed in substantially identical fashion, with effluent TOCs averaging 45 mg/L and a rather narrow operating range of approximately 40 to 60 mg/L. Table 3 summarizes the average performance of the reactors for the months of July, August, and September, taken from the data in Figures 2 through 5 and Table 2.

Kinetic Analysis

In order to design an activated sludge process for treatment of coal conversion wastewater, the parameters describing the kinetics of microbial growth and substrate utilization

for the given wastewater must be determined. The data collected to date can be used to make a preliminary determination of these requisite microbial growth coefficients as follows:

The kinetics of microbial growth can be described by the equation²

$$dx/dt = y ds/dt - k_d x \quad (1)$$

where:

x = concentration of microorganisms (biomass) in mg of MLSS per L;

s = substrate concentration, in mg per L, on a BOD, COD, or TOC basis;

t = time, in days;

y = microbial yield coefficient, in mg of biomass (MLSS) produced per mg of substrate (on a BOD, COD or TOC basis) consumed;

k_d = microbial die-away coefficient, in days⁻¹.

Taking finite differences in equation (1) and dividing through by $\bar{x}$, the mean biomass concentration over the time period Δt , yields

$$(\Delta x / \Delta t) / \bar{x} = y (\Delta s / \Delta t) / \bar{x} - k_d \quad (2)$$

For the continuous-flow, completely-mixed reactors used in this investigation, $\bar{x}$ is the steady-state biomass concentration in each reactor, and Δt is the detention time of the reactor. Equation (2) can be rewritten as

$$1/\theta_c = y U - k_d \quad (3)$$

TABLE 3. AVERAGE QUALITY OF EFFLUENT FROM BIOLOGICAL TREATMENT UNITS (ALL VALUES IN mg/L)

	Raw Waste	Reactor Detention Time (Days)			
		5	10	20	20
BOD	3510	1020	32	7	5
COD	5710	1770	310	192	214
TOC	1600	200	80	45	45
MLSS	---	700	900	950	900

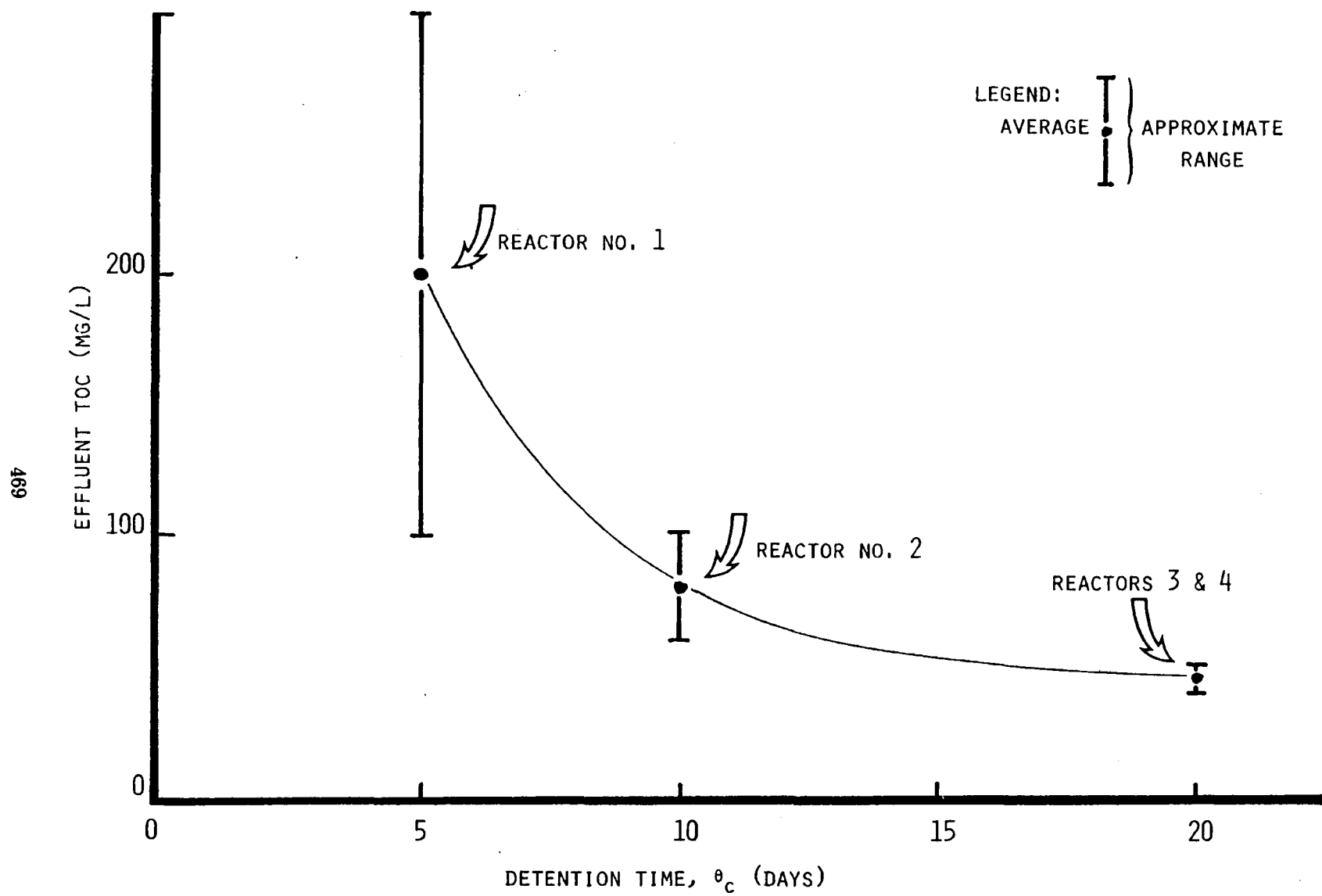


Figure 6. Effect of residence time on reactor performance and stability.

Here, θ_c can be defined as the mean cell residence time, solids retention time, or sludge age, and is equal to the steady-state quantity of biomass in the reactor, divided by the rate of biomass production. θ_c has units of time and for reactor operation with no recycle of biomass, the solids residence time is equal to the hydraulic retention time. The quantity U in equation (3) is defined as the process loading factor, or food to microorganism ratio, and is equal to the quantity of substrate consumed during the given reactor detention period divided by the steady-state biomass concentration (compare equations (2) and (3)). The process loading factor can be computed on a BOD, COD, or TOC basis. If the reciprocal of the sludge age is plotted against the process loading factor in accordance with equation (3), a straight line should result and the microbial kinetic coefficients y and k_d can be determined.

Table 4 gives the calculated values of the process loading factors based upon the summary data in Table 3. The linear plots in accordance with equation (3) are shown in Figures 7 through 9. The yield coefficients computed from the slopes of the straight lines are 0.27, 0.18, and 0.52 based upon BOD, COD, and TOC utilization, respectively. The die-away coefficient determined from the intercepts at zero-loading is approximately 0.005 days^{-1} . The COD yield coefficient is in the same range as those reported by Luthy and Tallon for full-strength, ammonia-stripped, and diluted Hygas wastewater.³

Chromatographic Analysis

High performance liquid chromatograms of

the effluent from the four reactors are shown in Figure 10 along with a chromatogram of the raw feed. The difference in detector sensitivities should be noted. Identities of the chromatographic peaks for the reactor feed are given in Table 5. The chromatograms have been generated using a C_{18} μ -Bondak column, gradient elution with an acetonitrile/water mixture, and 254 nm UV absorbance detection. When these chromatograms are interpreted, it should be noted that polarity decreases with increasing elution volume, so the elution volumes corresponding to the chromatographic peaks can be correlated to the polarity of the various organic compounds in the mixture. Also, each peak may contain more than one compound.

Several observations can be made in comparing the chromatograms of the various reactor effluents. The concentration of highly polar compounds (e.g., aliphatic and aromatic acids, etc.) does not appear to decrease with increasing degrees of treatment, i.e., detention times. This may be attributed to the production of some aliphatic acids from the bacterial degradation of phenolic compounds.

On the other end of the chromatograms (at the high elution volumes), a greater reduction of the more nonpolar compounds can be seen in the two 20-day reactors when compared to the 5- and 10-day reactors. This implies a greater removal of the xylenols, pyridines, quinolines, indoles, naphthols, and trimethylphenol in the 20-day reactors. However, it does not necessarily indicate that these compounds were not removed efficiently in the 5- and 10-day reactors. The nonpolar chromatographic peaks for the 5- and 10-day reactors could be due to non-

TABLE 4. CALCULATED PROCESS LOADING FACTORS FOR BIOLOGICAL REACTORS

θ_c , Days	5	10	20	20
U_B , mg BOD/mg MLSS-day	0.71	0.39	0.18	0.19
U_C , mg COD/mg MLSS-day	1.13	0.60	0.29	0.31
U_T , mg TOC/mg MLSS-day	0.40	0.17	0.082	0.08

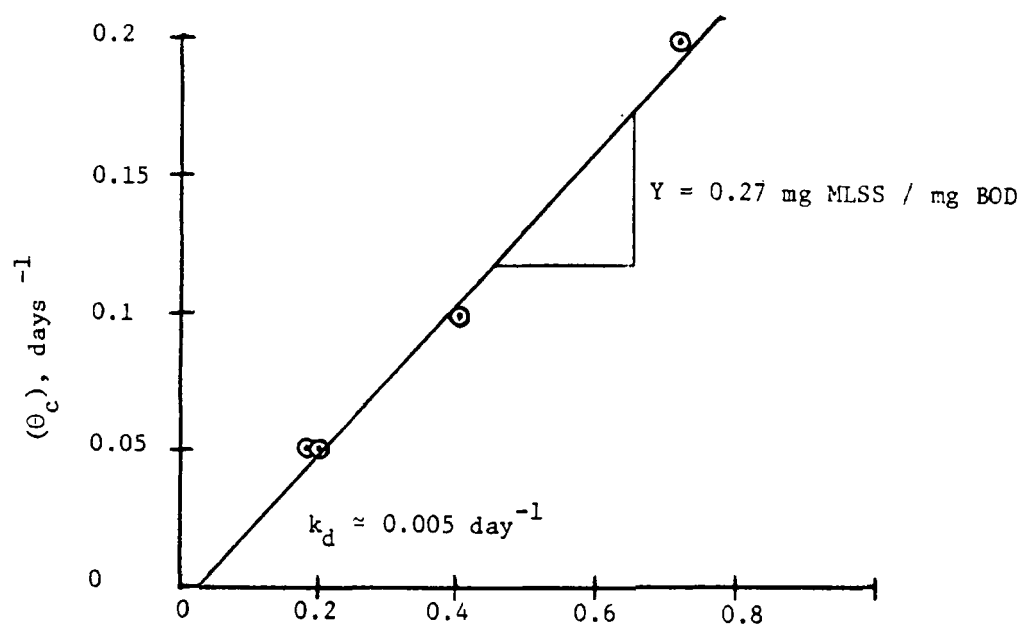


Figure 7. Effect of solids residence time on BOD loading.

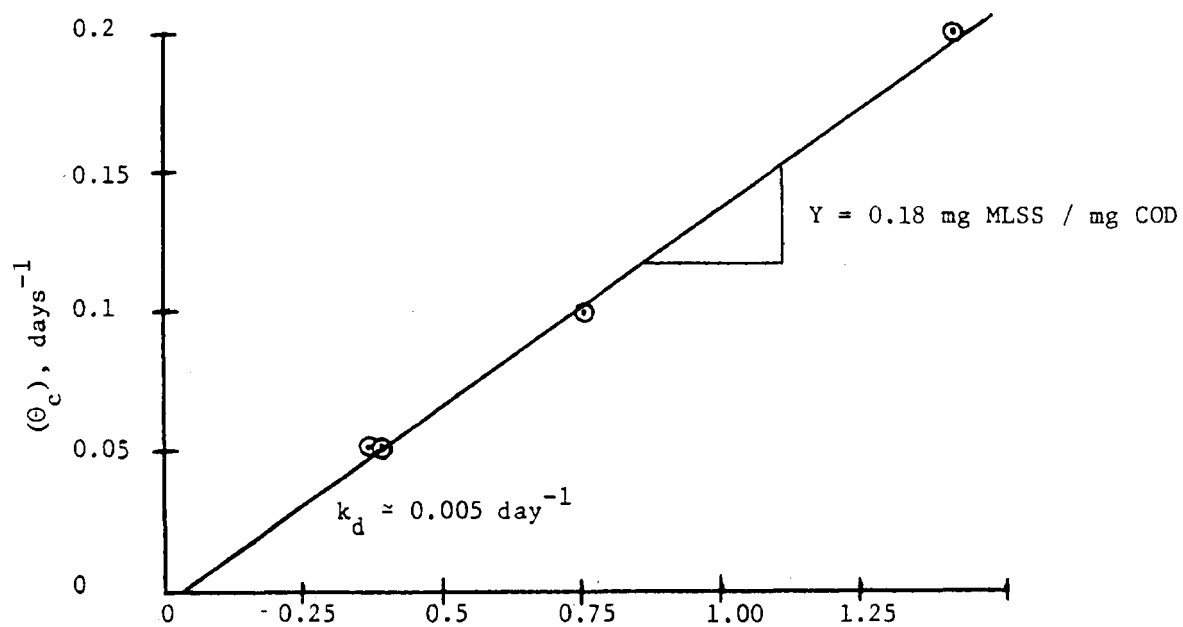


Figure 8. Effect of solids residence time on COD loading.

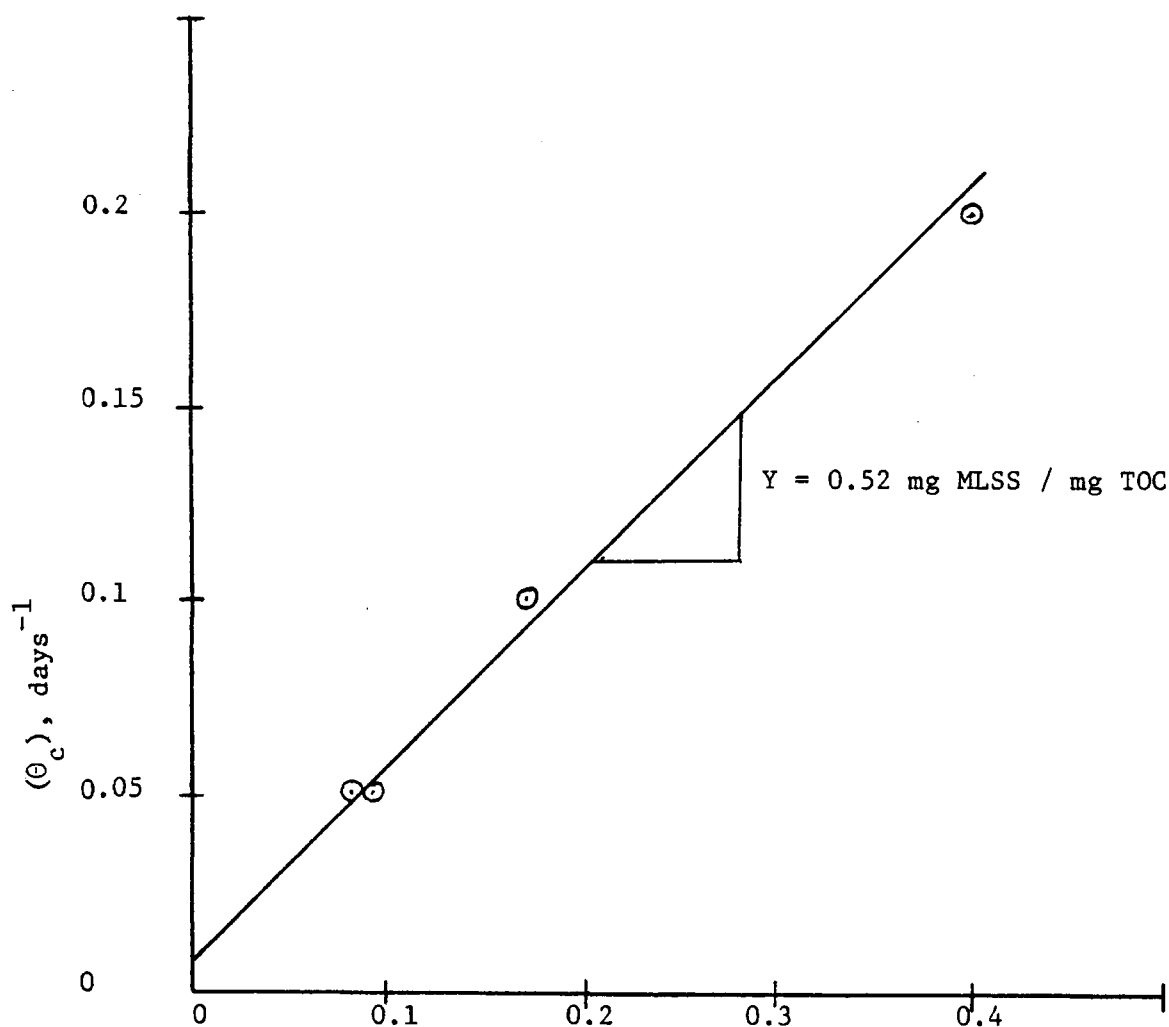


Figure 9. Effect of solids residence time on TOC loading.

polar cellular metabolites of these compounds. More complete analyses are necessary to quantify the removal of the raw synthetic wastewater constituents as a function of residence time in the biological reactors and to ascertain the nature of the components comprising the residual peaks.

These chromatograms have been compared with others using 254 nm UV absorbance detection and simultaneous fluorescence detection at 275 nm excitation and 310 nm emission wavelengths. (Fluorescence spectrophotometry combined with HPLC is a much more sensitive and selective detection technique than simple UV absorbance.) From the relative responses of each peak, these comparisons in-

dicate that very little of the residual organic material is phenolic. This is important from the standpoint of reactor performance because a large portion of the organic carbon in the reactor feed is comprised of phenolic compounds.

HPLC traces of the reactor effluents were used to obtain approximate concentration values for several of the major constituents fed to the reactors. These data are given in Table 6. The maximum effluent concentrations listed in Table 6 should be interpreted with great care because they have been calculated by assuming that a particular chromatographic peak is caused entirely by the specific compound in question. It is more likely, however, that each peak is due to several compounds. Therefore,

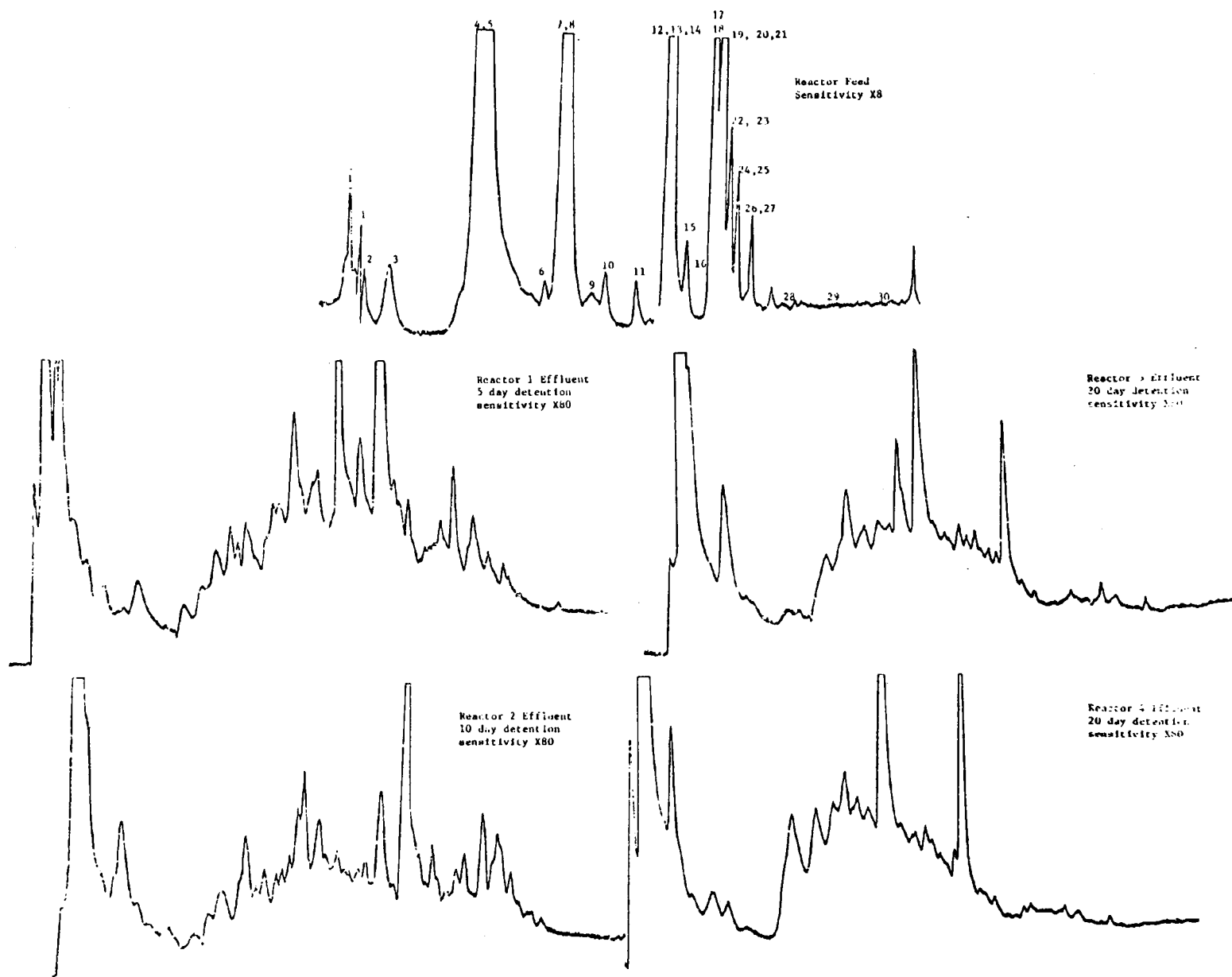


Figure 10. HPLC chromatograms of raw synthetic feed and reactor effluents.

TABLE 5. IDENTIFICATION OF HPLC CHROMATOGRAPHIC PEAKS FOR RAW FEED

1. Acetic Acid, Benzoic Acid, Hexanoic Acid	16. 4-Ethylpyridine
2. Solvent	17. Pyridine
3. Acetone	18. Quinoline
4. Resorcinol	19. 3, 4-Xylenol
5. Catechol	20. 3, 5-Xylenol
6. Aniline	21. 2, 3-Xylenol
7. Phenol	22. Indole
8. 5-Methylresorcinol	23. 3-Ethylphenol
9. 4-Methylcatechol	24. 2-Methylquinoline
10. Unidentified	25. 1-Naphthol
11. Unidentified	26. 2-Naphthol
12. p-Cresol	27. 2, 3, 5-Trimethylphenol
13. o-Cresol	28. Indene
14. 2-Indanol	29. Naphthalene
15. Acetophenone	30. Anthracene

the actual effluent concentrations are probably much less than those listed in the table. Recent studies on the reactor effluents using fluorescence/HPLC have indicated that effluent concentrations of the compounds listed in Table 6 are probably much less than those reported there.

Cytotoxicity Analysis

A clonal toxicity assay, employing the Chinese hamster V79 cell line, was used to compare the relative acute toxicities of the effluents from the biological reactors and the raw synthetic wastewater. This assay measures the colony forming ability of cells exposed to toxicants. The purpose of this test was to

evaluate the effectiveness of biological treatment in alleviating potential human health effects associated with coal conversion wastewaters.

Effluent samples were collected from Reactors 2, 3, and 4 on September 17, 1978, and from Reactor 1 on October 28, 1978. The samples were centrifuged and then filtered through a series of Nuclepore polycarbonate filters consisting of a 1.0- μ m prefilter and a 0.2- μ m ultimate filter. The filtrates were collected and aliquoted in small glass prescription bottles, which were then frozen and stored at -80° C. A sample of the raw synthetic wastewater, which had been aged for 2 days, was collected, treated, and stored in a similar manner. Individual aliquots of frozen reactor effluents and

TABLE 6. REMOVAL OF SELECTED CONSTITUENTS BASED ON HPLC-UV ABSORBANCE ANALYSIS

Compound	Feed Concentration mg/l	REACTOR 2		REACTOR 3		REACTOR 4	
		Maximum Effluent Concentration mg/l	Minimum % Removal	Maximum Effluent Concentration mg/l	Minimum % Removal	Maximum Effluent Concentration mg/l	Minimum % Removal
Resorcinol	250	1.24	99.5	1.2	99.5	1.2	99.5
Aniline	5	0.6	87.8	0.4	92.2	0.4	92.8
Phenol	500	4.2	99.2	6.6	98.7	6.7	98.7
p-Cresol	62.5	8.0	87.2	5.1	91.9	5.2	91.6
o-Cresol	100	2.6	97.4	1.2	98.8	1.5	98.6
Pyridine	30	0.6	98.2	0.4	98.8	0.5	98.5
Quinoline	2.5						
Xylenols	135	3.5	97.4	1.4	99.0	1.7	98.7

raw feed were thawed immediately prior to their use and the remainder of that aliquot was discarded at the end of the day.

A series of dilutions of each wastewater was made in distilled-deionized water. The addition of 2× or 4× nutrient medium to the dilution tubes maintained physiological conditions at final test concentrations ranging from 0.25 to 75 percent of the wastewater sample being tested. Two hundred cells were seeded per 60 mm of tissue culture dish and allowed to incubate and attach for 3 hr in 3 mL of normal cell growth medium. Duplicate dishes were then treated with appropriate dilutions of a test wastewater. Each pair of dishes received a single concentration of the test materials. After an exposure period of 20 hr, growth medium containing the test materials was removed. The cells were washed once in a phosphate buffered saline solution and reincubated in 3 mL of fresh growth medium. Exposed single cells were allowed to grow into colonies and were then fixed and stained after 7 days. The number of colonies for each exposure condition was calculated as a percent of the number of colonies in untreated control

plates, and expressed as the relative plating efficiency.

The results of the clonal toxicity assay are shown in Figure 11, where concentration-dependent survival curves have been plotted using the average of the data points from duplicate clonal toxicity experiments. The concentrations indicated represent dilutions of the samples being tested. Concentrations producing 50 percent lethality (LC_{50}) are shown in Table 7, along with the corresponding TOC concentrations. As indicated in Figure 11 and Table 7, V79 cytotoxicity decreases with increasing degree of wastewater treatment as measured by residence time.

It is interesting to note in Table 7 that while Reactor 1 provided an 87.5-percent reduction in TOC compared to the raw wastewater, the LC_{50} was reduced only three-fold. This suggests several possible explanations. Most of the easily degradable TOC may not be very cytotoxic. On the other hand, it is possible that a reduction in TOC below certain threshold levels, which occurs in the reactors with longer detention times, accounts for the observed changes in cytotoxicity. The 95-percent TOC

TABLE 7. SUMMARY OF MAMMALIAN CYTOTOXICITY DATA

<u>Sample</u>	<u>TOC, mg/l</u>	<u>LC_{50}, %</u>
Raw Wastewater	1600	1.0
No. 1 - 5 day residence time	200	3.0
No. 2 - 10 day residence time	80	23.5
No. 3 - 20 day residence time	45	80*
No. 4 - 20 day residence time	45	80*

*Reactors 3 and 4 did not produce 50% lethality at the highest concentrations tested (75%). The LC_{50} values shown are extrapolated from the plots in Figure 11.

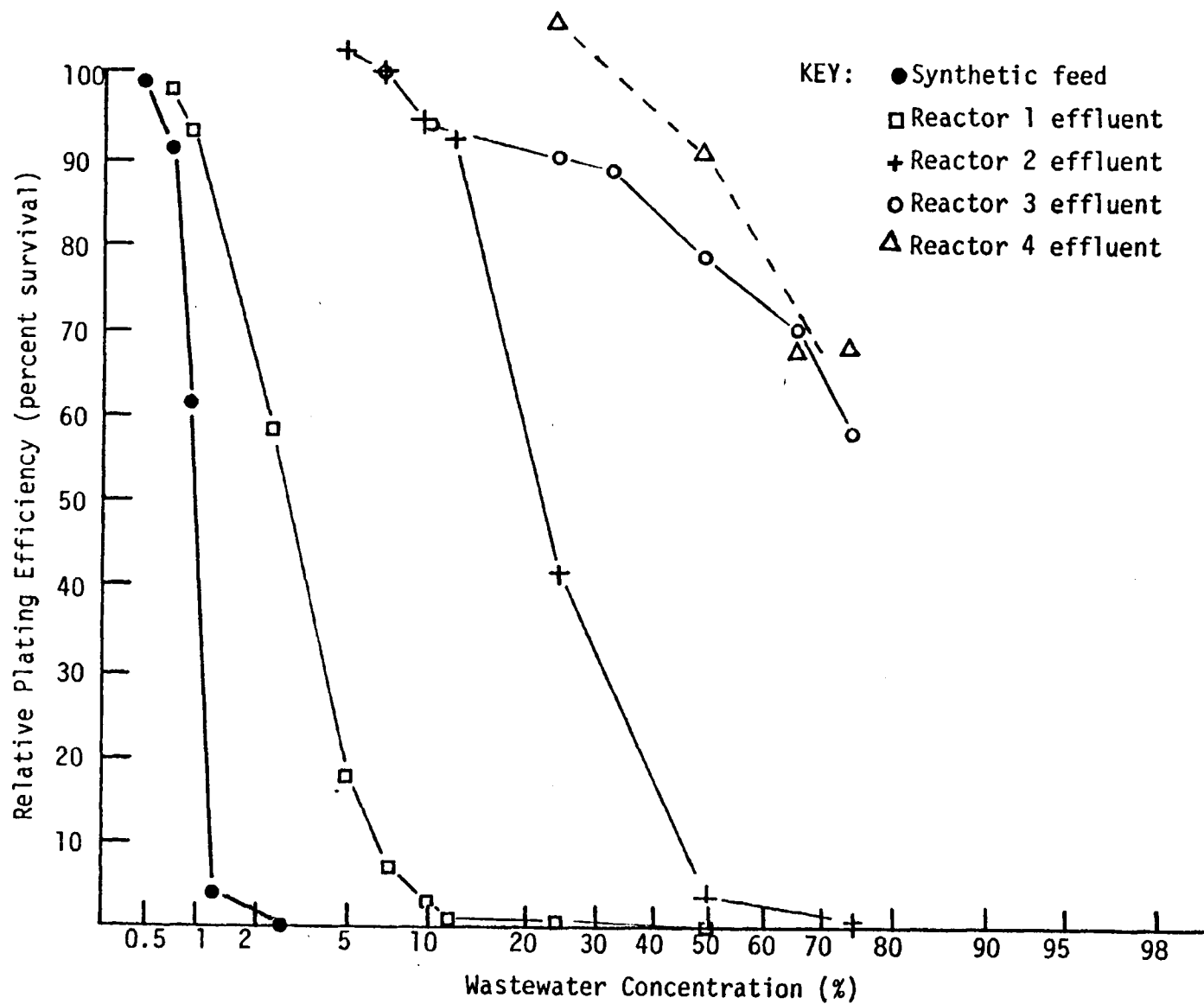


Figure 11. Results of 20-hr V79 Chinese hamster clonal toxicity assay.

reduction produced by the 10-day reactor corresponded to a 23-fold reduction in cytotoxicity, while the 97-percent reduction in TOC produced by the 20-day reactors corresponded to an 80-fold reduction in cytotoxicity compared to the raw wastewater.

CONCLUSIONS

A synthetic coal conversion wastewater, representative of wastewaters from coal gasification and liquefaction processes, has been prepared. The wastewater appears to be biologically treatable, but some degree of dilution may be necessary. Biological treatability, as measured by BOD, COD, and TOC removal, improves with increased solids residence time (sludge age), but it appears that a minimum sludge age of 10 days may be necessary to achieve a reasonable degree of treatment. A mammalian cytotoxicity assay, used as an indicator of potential human health effects associated with the wastewater, shows that cytotoxicity decreases with increasing degrees of biological wastewater treatment.

Due to continued difficulties with pH variations, recent changes in the character of the synthetic wastewater have been made to provide additional buffer capacity and to eliminate acetone in preparing the synthetic feed. It does not seem appropriate to develop more detailed conclusions at this interim point in the experi-

mental program. Continued operation of the reactors should lead to more stable performance in the near future, allowing detailed analysis of performance and operating parameters and more conclusive results.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Dean Smith and Dr. Thomas Petrie of the Industrial Environmental Research Laboratory (Research Triangle Park) of EPA for their assistance in the performance of this research, and to EPA for sponsoring this project.

REFERENCES

1. Singer, P. C., F. K. Pfaender, J. Chinchilli, A. F. Maciorowski, J. C. Lamb III, and R. Goodman. *Assessment of Coal Conversion Wastewaters: Characterization and Preliminary Biotreatability*. U.S. Environmental Protection Agency. Washington, D.C. EPA-600/7-78. 181. September 1978.
2. Metcalf and Eddy, Inc. *Wastewater Engineering*, McGraw Hill Book Co., 1972.
3. Luthy, R. G., and J. T. Tallon. *Biological Treatment of Hygas Coal Gasification Wastewater*. U.S. Department of Energy. Washington, D.C. FE-2496-43. December 1978.

CONTROL TECHNOLOGIES FOR PARTICULATE AND TAR EMISSIONS FROM COAL CONVERTERS

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Abstract

Raw product gases from coal converters generally contain particulates and tars that must be controlled to a level compatible with environmental regulations and process and equipment requirements. Alternate control technologies for removing particulates and tars from product gases were identified and evaluated.

Particulate and tar emissions in raw product gases from several types of coal gasifiers were characterized in terms of their total quantities, chemical composition, and size distribution. The emissions data were organized and summarized according to generic gasifier type, with fixed-, fluid-, and entrained-bed gasifiers being considered. The design and operating features of each identified alternate control technology were described, with emphasis on characterizing collection efficiencies as a function of particle size and other important parameters. These data were also organized into generic categories such as cyclones, wet scrubbers, electrostatic precipitators, fabric filters, and granular bed filters.

The applicability of each of the identified control technologies was assessed with respect to the generic gasifier types and various end uses. These assessments were based on existing and proposed environmental regulations and process requirements for product gas purity. End uses considered include combined cycles and gas-fired boilers. The fate of the particulate and tar emissions from the various gasifiers was assessed in terms of their presence in the puri-

fied product gases, liquid effluents, and solid wastes or sludges. In addition, gaps in the data base required for these assessments were identified.

INTRODUCTION

The energy supply problems of the United States and most of the major industrialized nations are well known and well documented. Current projections indicate that the world demand for petroleum and natural gas will exceed supply sometime during the 1980's. One obvious approach to increasing domestic fuel supplies, and, consequently, to reducing demand for imported gas and oil, is to utilize the vast coal resources of the United States to produce synthetic oil and gas.

In recent years, the electric utility and industrial sectors of the economy together accounted for about 55 percent of the energy consumption in the United States. Natural gas and petroleum supplied about 80 percent of the industrial energy consumption and 30 percent of the utility consumption. The use of coal-derived fuels to replace natural gas and petroleum in these areas could benefit the United States economically, in addition to reducing the nation's dependence on foreign, unreliable sources of energy. Such coal-derived products might be employed in a wide variety of end uses, such as industrial process heat, industrial and utility boilers, gas turbines, and reducing or synthesis gas for various industries.

In the case of product gases from coal gasifiers, each particular end use for the gases would have different environmental regulations and/or process requirements governing the

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allowable particulate and tar levels in the product gases. Thus, the use of coal-derived product gases to replace nature gas and oil on a large scale will require adequate control technology to remove tars and particulates from the product gases to levels compatible with the various possible end uses. The overall objective of this study was, therefore, to assess the applicability of alternate control technologies both commercially available and under development for the removal of particulates and tars from coal-converter product gases.

The first step in carrying out these control technology evaluations involved the identification and collection of pertinent sources of information. Computerized literature searches covering the *Chemical Abstracts*, *Engineering Index*, *Pollution Abstracts*, U.S. and foreign patents, government publications, and numerous journals were made to identify sources of information. These computerized searches were complemented by thorough library and patent searches. In addition, other U.S. Environmental Protection Agency (EPA) contractors, process developers, and equipment vendors were contacted for relevant data. When identified sources of information had been reviewed, appropriate data were employed to carry out the control technology evaluations, as discussed in the following sections.

This study was performed under EPA Contract Number 68-02-2601 for the Fuels Process Branch of the Environmental Assessment and Control Division of the Industrial Environmental Research Laboratory (IERL) at Research Triangle Park. The methodology and results summarized herein are described in detail in Reference 1.

CHARACTERISTICS OF PARTICULATE AND TAR EMISSIONS

As an initial step in the evaluation of technologies for the control of particulates and tars in gaseous streams originating from coal gasifiers, emissions and process data were obtained for a wide variety of gasifiers. The availability of pertinent data was generally found to be limited. The emissions data were organized and summarized according to generic gasifier type, with fixed-, fluid-, and entrained-bed gasifiers being considered. Because of the uncertainties in the emissions data for the dif-

ferent types of gasifiers, these results are presented in terms of best-case, worst-case, and average-case (or typical) analyses. The worst-case condition represents the estimated upper limit of particulate load, with a relatively high percentage of small particles, which are difficult to remove. The best-case condition represents the estimated lower limit of particulate load with a relatively low percentage of small particles. All available data on the characteristics of gasifier emissions were considered in estimating these upper and lower bounds.

Typical operating parameters and raw product gas stream characteristics are presented in Table 1 for several different fixed-bed, fluid-bed, and entrained-bed gasifiers. Several of the fixed-bed gasifiers are commercially available, whereas the Winkler and Koppers Totzek are the only commercial fluid-bed and entrained-bed gasifiers, respectively. It can be seen from Table 1 that the fixed-bed gasifiers produce tars, while the entrained-bed gasifiers do not. Most of the fluid-bed gasifiers produce tars, while the entrained-bed gasifiers do not. Most of the fluid-bed gasifiers also do not produce tars.

The particulate and tar loading data are summarized in Table 2. The best-, worst-, and average-case data for the particulate and tar loadings from each generic type of gasifier were estimated from the detailed data for the individual gasifier types in Table 1. It can be seen that fixed-bed gasifiers produce the smallest particulate loadings, while the entrained-bed gasifiers produce the highest loadings.

Particle size distribution data are presented in Figures 1, 2, and 3, and are summarized in Table 2. The particulate collection efficiency of most control devices is especially sensitive to particle size. Such data were generally found to be scarce and incomplete. More complete data over a broad, specified range of gasifier operating conditions are needed. In the case of fluid- and entrained-bed gasifiers, particle size data were not available below approximately 35 and 20 μm , respectively. Extrapolation of the existing data for large size particles down to the small size particle range was, therefore, required for these two types of gasifiers. Large particles are removed more easily than particles below approximately 5 μm ; therefore, future R&D programs should concentrate on the collection of particle size data down to the submicron size range.

TABLE 1. OPERATING AND RAW PRODUCT GAS STREAM CHARACTERISTICS

Gasifier	Coal Type	Temperature °C	Pressure MPa	Particulate Loading g/nm ³	Particulate Composition	Tar Loading g/nm ³	Tar Composition
Fixed Bed							
Wellman Galusha (2,3)	anthracite bituminous coke	430-920	0.10			10-50	
Lurgi (2,3,4,5)	"variety of coals"	370-590	2.07-3.21	0.5-6.0	C-75-80% ash-10-25%	tar-13 tar oil 79	tar S-0.77% tar oil S-0.29%
Woodall Duckham (2,3)	lignite bituminous	120-650	0.10			oil & tar 10.3	
Wilputte Chapman (2,3)	all types	540-650	0.10				
Piley Morgan (2)	anthracite bituminous coking bit. bituminous	570-620	0.10	2-4		tar 10-20 tar oil 10-20	
MERC (2,3,4,5,6)	all types	480-650	0.10-2.10	0.5-6.0	C-75-80% ash-10-25%	10	C-82.1 H-7.6 N+O-8.8
GFERC (2,4)	lignite lignite char bit. char	95-370	0.65-2.96			tar-10 tar oil-25	
Fluid Bed							
Winkler (2,3,4)	several coal types	590-730	0.10		C-30% ash-70%	None	
Synthane (3,4,5)	all types	760	6.90	4.8-12	C-80% ash-20%	2.4-17	
CO ₂ Acceptor (3,4,5)	lignite sub-bit.	815	1.03-2.06	26	C-82% ash-38%	None	
Hygas (3,4)	all coals	1100	6.90-10.3	120	C-55% ash-40% O ₂ -5%	None	
CoGas (3)	all types	870	0.21-0.41				
Hydrane (3)	all types	540-815	6.90			4.3	
Union Carbide (3)		870-990	0.69	0.1-1.2		None	
Westinghouse (3)	"variety of coals"		0.90-1.38	8		None	
U-Gas (3)	non-caking, caking req. pretreatmt.	840-1040	0.34-2.41			None	
BCR (3)			≤1.62			None	
Ignifluid (5)		590-715	0.10-0.50	84			
Entrained Bed							
Koppers Totzek (2,3,4)	all types	1480	0.10	30-60	C-10% ash-90%	None	
Bi-Gas (2,3)	lignite sub-bit. bitumin.	745-1180	1.62-10.3	230	char-96-99% ash-12-10% volatiles - 2-1%	None	
Texasco (2,3)	lignite	200-260	2.10-8.27			None	
Combustion Engineering (3)	all types	870	0.10				
B & W (3)	all types	990	0.10-2.10			None	
Coalex (2)	all types	925-950	0.10				
Foster Wheeler (2,3)	non-caking	upper stage 2.41 980-1150 lower stage 1370-1540				None	

**TABLE 2. SUMMARIZED PARTICULATE AND TAR LOADINGS AND
PARTICLE SIZE DISTRIBUTIONS**

	Particulate Loading (g/m ³)	Tar Loading (g/m ³)	Percent Particles (by weight) Less Than Specified Diameter (in Micrometers)				
<u>Fixed Bed</u>			<u>1</u>	<u>5</u>	<u>10</u>	<u>50</u>	<u>100</u>
Best Case	0.5	10.0	<0.1	0.1	1	23	50
Worst Case	6.0	50.0	<0.1	4.0	30	67	76
Average	3.0	18.0	<0.1	2.0	15	45	63
<u>Fluid Bed</u>							
Best Case	1.2	None	0.1	1.0	2	13	22
Worst Case	120.0	None	0.5	5.0	12	52	78
Average	26.0	None	0.3	3.0	7	33	50
<u>Entrained Bed</u>							
Best Case	30.0	None	<0.1	0.5	2	12	24
Worst Case	230.0	None	<0.1	0.5	4	66	90
Average	110.0	None	<0.1	0.5	3	39	57

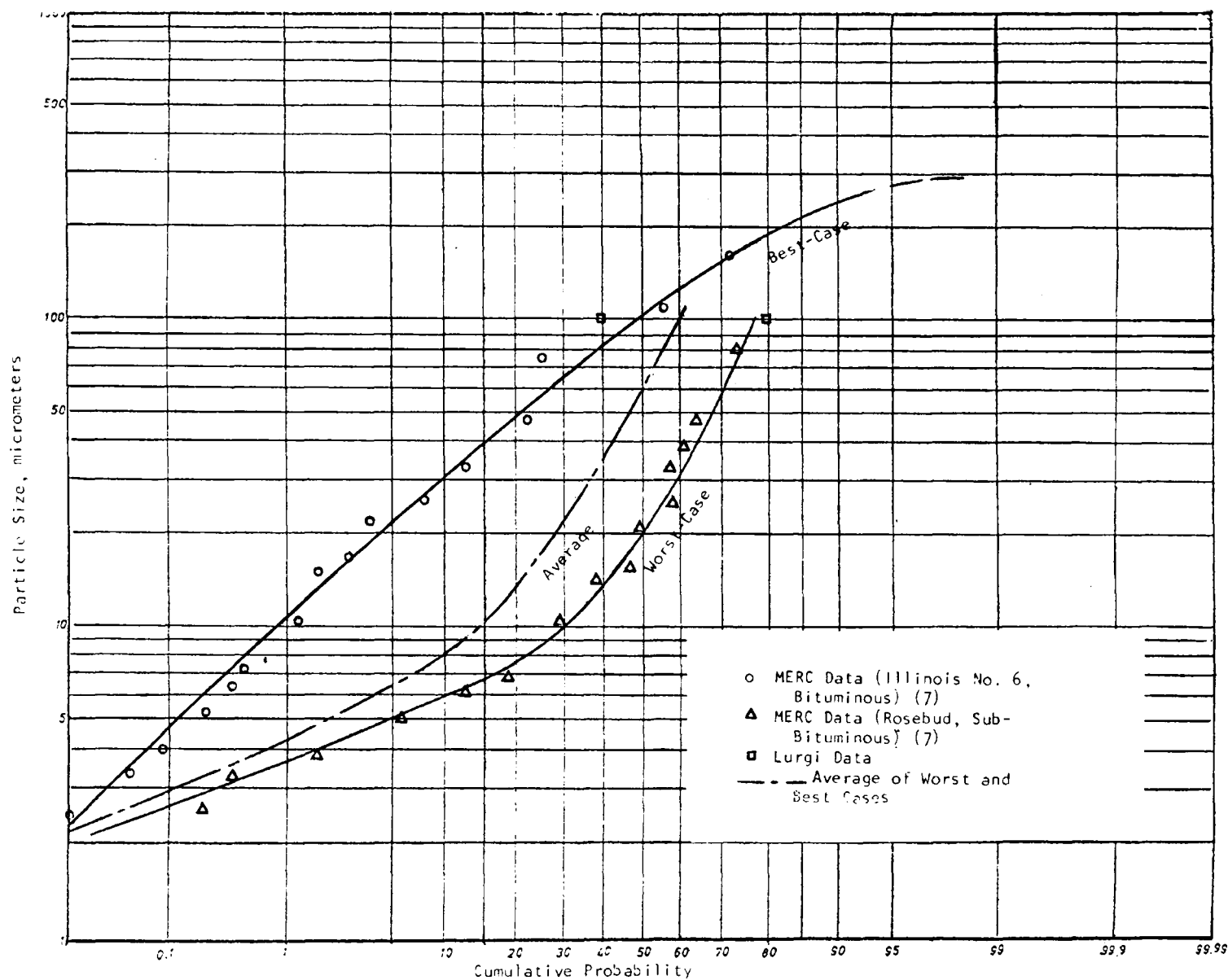


Figure 1. Particle size distribution for fixed-bed gasifiers.

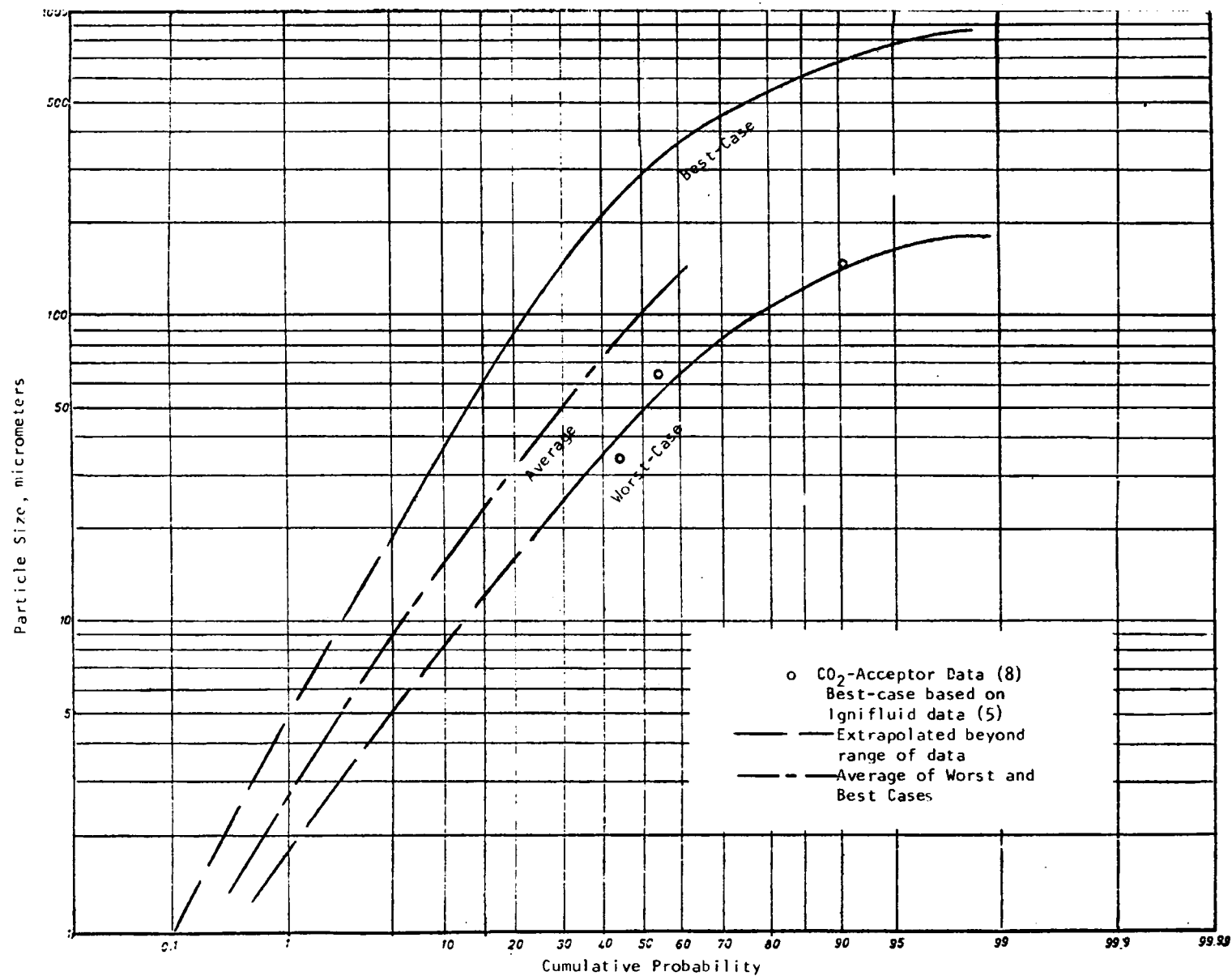


Figure 2. Particle size distribution for fluid-bed gasifiers.

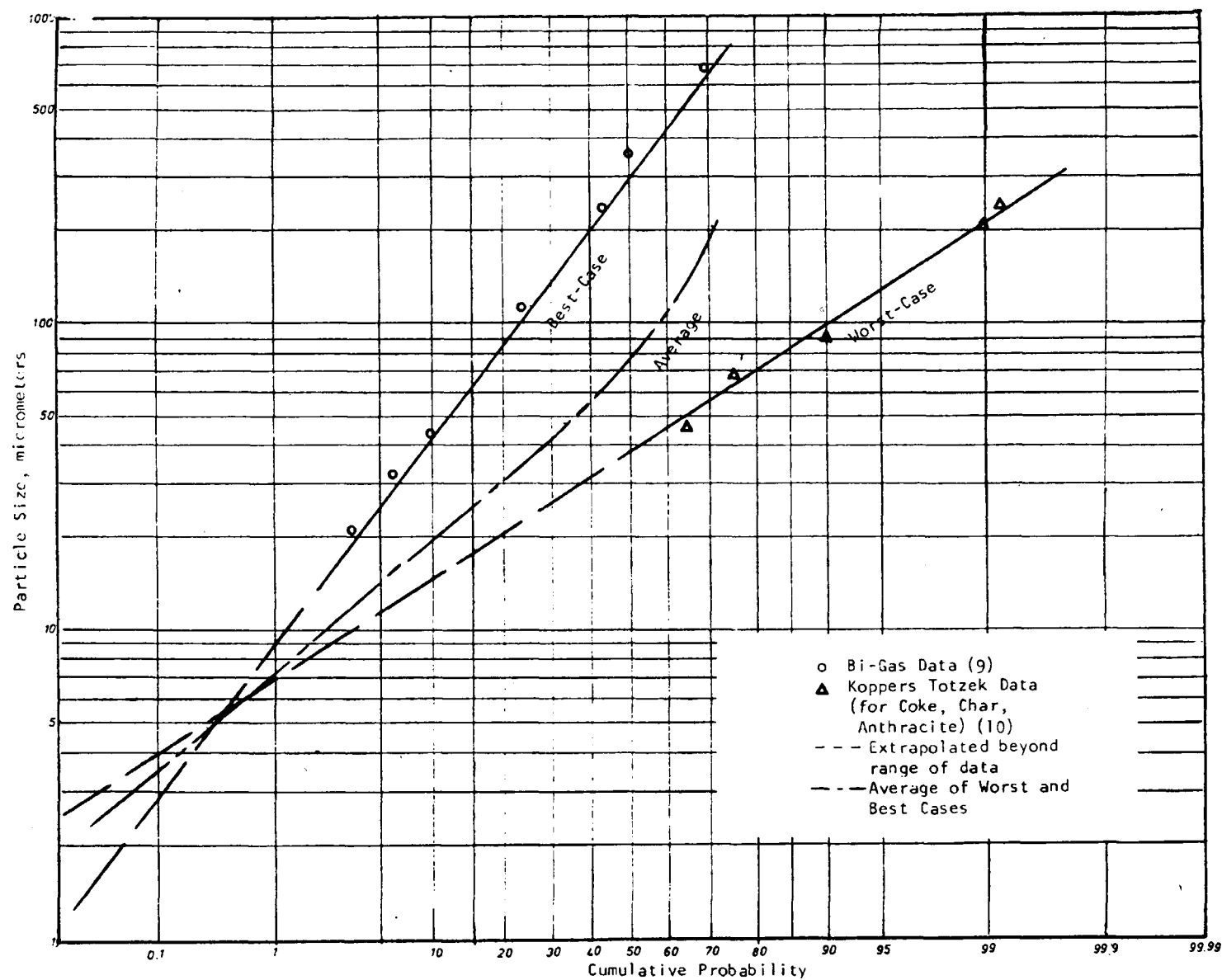


Figure 3. Particulate size distribution for entrained-bed gasifiers.

Particle size distribution measurements are usually based on either aerodynamic or optical properties of the particles. Measurements in the same gas stream by these two different techniques often yield inconsistent results. Particle sizes are especially difficult to measure at high-temperature and high-pressure (HTHP) conditions. The collection of reliable particle size distribution data for coal-gasifier product gases will require the development of improved methods and instrumentation suitable for HTHP conditions.

Additional data are also needed to accurately estimate particulate and tar loadings from the various types of gasifiers, particle and tar compositions, and other pertinent properties such as particle resistivity. It should be noted that complete data sets were not available for any of the gasifier types. For example, the particle size distribution might be available for a specific type of gasifier at a given or unspecified set of conditions, whereas particulate loadings and compositions might be available for another type of gasifier within the same generic class, but at a different set of conditions. There is, then, a need for R&D programs to provide complete data for all of the above parameters at the same specified gasifier operating conditions.

ALTERNATE CONTROL TECHNOLOGIES

Alternate control technologies (both commercially available and under development) for removing the particulates and tars from the raw product gases from coal converters were identified and evaluated. The performance characteristics of the commercial types of control devices are generally well known and well documented. Sufficient data were available for the following six generic control technologies to permit performance of detailed applicability assessments: conventional cyclones, rotary flow cyclones, venturi (wet) scrubbers, fabric filters, electrostatic precipitators (ESPs), and granular bed filters (GBFs). Typical collection efficiencies for each of these control technologies are presented as a function of particle size in Figure 4. The fabric filter and ESP are most efficient for small particle sizes; the fabric filter, venturi scrubber, and rotary flow cyclone are most efficient for the relatively large particles. Detailed descriptions of most of these control devices are readily available in the literature. Brief sum-

maries of important design and operating features are presented below.

Cyclones utilize the centrifugal force created by a spinning gas stream to separate particulates from the carrier gas. The advantages of the conventional cyclone are that it is a simple device—there are no moving parts—and it is a proven technology. However, cyclones suffer from the disadvantages of having low removal efficiencies for particulate sizes less than 5 μm . Because of their relatively low capital and operating costs, cyclones are commonly used as pre-cleaners to remove most of the large particles in a gas stream upstream of a more expensive control device (e.g., venturi scrubber or electrostatic precipitator) required to remove the smaller size particles. Particulate collection efficiency increases with an increase in particulate diameter, particulate density, inlet velocity, cyclone body length, ratio of cyclone body diameter to outlet diameter, and the smoothness of the inner wall. Efficiency decreases as the gas viscosity, gas density, body diameter, and gas outlet diameter increase. Because the gas viscosity is proportional to temperature, an increase in temperature results in a decrease in the collection efficiency.

Rotary flow cyclones are designed to augment the normal tangential swirl of the inlet gas by the addition of a secondary airflow. By doing so, the possibility of short-circuiting particulates from inlet to outlet is greatly reduced. In the Aerodyne rotary flow cyclone,¹⁴ particulate-laden gas enters the collection chamber and passes a stationary vane, which imparts a rotary motion to the flow. Particulate matter is thrown toward the outer wall by centrifugal force and then swept downward to the collection hopper by the secondary flow. The vendor data for the Aerodyne Series "S" rotary flow cyclone are presented in Figure 4. Westinghouse has also tested an Aerodyne Tornado Cyclone. The grade efficiency data obtained in these tests show a discrepancy with respect to the claimed performance by the manufacturer. This may result from the difficulty of holding design control specifications when small unit is tested. Thus, the fractional collection efficiency data presented in Figure 4 need to be verified.

Although wet scrubbers are available in a wide variety of designs, all operate on a common principle of contacting a pollutant-laden gas with a liquid (usually water) that captures

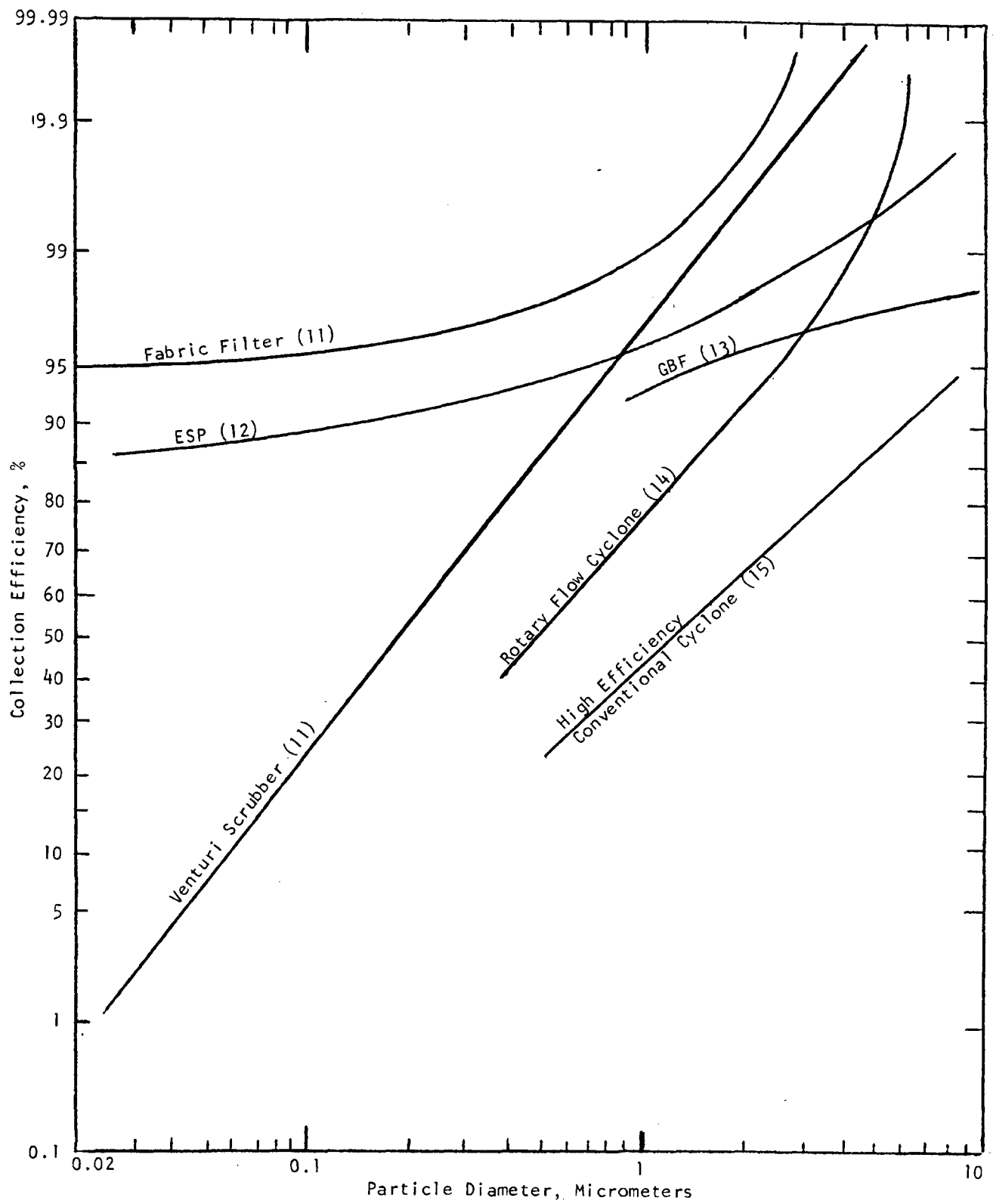


Figure 4. Typical collection efficiencies of control devices.

the pollutants. Wet scrubbers can be used to remove both particulates and tars. The objectives of good scrubber design are to provide good liquid-gas contact, minimize energy consumption and equipment size, and minimize water requirements. All wet scrubbers produce a liquid slurry for disposal or further treatment. Most modern applications attempt to concentrate the solids to simplify their ultimate disposal, and to recirculate as much of the scrubbing liquid as possible. The collection efficiency of wet scrubbers is strongly dependent on particle size. In order to achieve high collection efficiencies with small particles, a high-energy input is required. For particles above approximately 10 μm , simple wet scrubber designs are usually adequate, with a pressure drop of 0.25 kPa being typical. Fine particulates with diameters of 1 μm or less require more complex scrubbers with pressure drops usually well above 1.25 kPa. In exceptional circumstances, pressure drops up to 25 kPa have been employed. Wet scrubbers have been found to be very effective in removing tars from raw product gases. Commercially available gasification systems generally have employed various types of wet scrubbers to quench and cool the gases and knock out the tars, along with a portion of the particulates.

The venturi scrubber employs a venturi-shaped constriction and high throat velocities to atomize the scrubbing liquid. As with wet collectors in general, the collection efficiency increases with higher pressure drops. Different pressure drops are achieved by designing for varied gas velocities in the throat. Some venturi scrubbers are manufactured with adjustable throats, allowing a range of pressure drops for a given air volume. The collection efficiency of the venturi scrubber can generally be considered highest of the wet collectors.

Electrostatic precipitators (ESPs) for cleaning particulates from gases, which have been used by industry for over 70 years, have also been found to be an efficient means of detarring the gases. ESPs operate by using a high-voltage, direct current to create gas ions that impart an electrical charge to particulates by bombardment. The charged particles are collected by exposing them to an electric field, which causes them to migrate and deposit on electrodes of opposite polarity. The electrode cleaning system is dependent upon the type of pre-

cipitator. The conventional dry-type precipitator collects particulates on a dry electrode and removes them periodically by mechanical shaking or rapping. The new wet-type precipitator collects and removes particulates with a thin, continuous flowing film of water. The operating temperatures are generally less than 65° C.

The resistivity of particulates is a critical factor in the design and operation of a dry precipitator. Particulates with low resistivity (below 50 $\Omega\cdot\text{m}$) are difficult to collect efficiently because they tend to loosely adhere to the collector and are, therefore, easily reentrained in the gas stream. On the other hand, if the particulate resistivity is too high (above 0.2 G $\Omega\cdot\text{m}$), the voltage drop across the deposited particulate layer becomes so large that the discharge electrode electron emission rate drops, which leads to a decline in the overall collection performance. Hot-side precipitators, which operate at temperatures up to 540° C, were developed for certain applications involving high-resistivity particulates. Research Cottrell, under an EPA contract, has demonstrated the ability of an ESP to generate stable corona at temperatures up to 1,100° C and pressures up to 51 MPa.¹⁷ While their limited data are encouraging, more data are required at high temperatures.

One of the oldest and the most widely used techniques for removing particulates from a gas stream is the use of fabric filters. The baghouse design is very commonly used, and is highly effective even for small particulates. However, commercially available baghouses are not suitable for use at high temperatures. A number of high-temperature-resistant ceramic fabrics have become commercially available. Because of the lack of a suitable high-temperature, inorganic fiber lubricant needed for the fiber-to-fiber abrasions, many of these developed ceramic fabrics are presently unsuitable for filtration purposes. Still, ceramic fabric filters offer a potentially promising solution of the problem of controlling particulates in the high-temperature, high-pressure environment. The advantages of baghouse filters include high collection efficiencies, even for submicron particles, relatively low energy use and pressure drop (typically less than 7.5 kPa), and collection of particles in dry form, which simplifies ultimate waste disposal. Disadvantages include large form, which simplifies ultimate waste disposal. Disadvantages include large space require-

ments, high initial costs, and proven temperatures limited to about 290° C.

A granular bed filter (GBF) employs a stationary or moving bed of granules— sand, gravel, coke, or sintered material—as the filter medium. In order to maintain a steady operating performance, a granular bed filter needs to remove the collected particulates from the collecting surface. Several different designs are reported in the technical literature. In general, they may be classified as continuously moving, intermittently moving, or fixed-bed filters with respect to the cleaning methods. GBFs are a promising technique for high-temperature and high-pressure operation. They have the advantages of being able to use either inert or sulfur-absorbent material, and of accommodating high face velocities while incurring a moderate pressure drop. The collection mechanism is similar to that of fiber filters, with impaction predominating and particulates being collected in the interstices of the filter. After the initial collection at the filter surface produces a filter cake, further collection is accomplished essentially by cake sieving. Granular bed filters have received increased attention recently, and a number of research projects are underway to further develop these systems. The GBF developed by Combustion Power Company is the most advanced of this generic class of control devices. This GBF employs granular filter media between two vertical, louvered screens. To avoid particulate saturation, the medium is continuously recirculated and cleaned. Commercial devices, restricted to temperatures below 430° C and to near atmospheric pressures have been available for a few years.¹³

In contrast to the six generic classes of control devices discussed above, several other control devices are still in the developmental stage; data are insufficient to permit meaningful evaluations of their applicability to coal converters. Several of these newer, relatively advanced control devices are discussed below. Additional collection efficiency data and/or large-scale testing to determine operational reliability are required to evaluate these control devices.

Several advanced types of wet scrubbers are under development to improve the collection of fine, submicron particles. These newer types of scrubbers include foam, steam-assisted, and electrically augmented devices. At present,

their principal disadvantage appears to be high initial cost compared to other types of wet scrubbers. In addition, operating and performance experience with these devices is limited.

Porous ceramic filters appear to be especially promising for highly efficient collection of particles down to the submicron size range at high temperatures.¹⁸ Such devices can take the form of porous thick-walled filters or thin-walled (0.2-mm) monolithic honeycomb structures. While preliminary data at high temperatures are encouraging, additional testing with larger scale devices is required for confirmation.

Several novel devices are in the early stages of development, with only limited preliminary data available. Such devices include the A.P.T. dry scrubber,¹⁹ molten salt scrubber,²⁰ electrofluidized bed,²¹ and the Apitron charged filter.²² The latter appears to have especially high collection efficiencies down to submicron size particles, but operation is restricted to the same temperature range as a conventional bag-house filter.

APPLICABILITY OF CONTROL DEVICES

Applicability assessments were made for various combinations of particulate control devices and gasifier end use pairs. These assessments were made for the three major generic classes of coal gasifiers discussed previously (fixed-, fluid-, and entrained-bed).

Each potential end use for the product gases has different environmental regulations and process requirements governing the allowable particulate levels in the product gases. For the purposes of this study, two particular end uses were selected for consideration. These end uses were selected to cover a wide range of particulate removal requirements for the control devices under consideration. The use of product gases as a boiler fuel was selected to represent those end uses with low to moderate particulate cleanup requirements. On the other hand, the use of product gases as a fuel for gas turbines was selected to represent end uses with relatively restrictive cleanup requirements. The New Source Performance Standard established by EPA to limit particulate emissions from coal-fired steam generators (0.10 lb/10⁶ Btu heat input) was assumed to apply to boilers firing coal-derived fuel gases. This is equivalent to 0.24

g/m³ of particulates for low-Btu fuel gas with an average heating value of 0.56 MJ/m³ (150 Btu/scf).

Coal-derived product gases can be used as a fuel for gas turbines employed in combined-cycle power stations. The tolerance of a gas turbine to particulates is not known with a high degree of certainty. Stringent specifications for fuels to be burned in gas turbines have been established by various turbine manufacturers. Results obtained by the U.S. Department of Energy's High Temperature Turbine Technology Program⁵ suggest a maximum allowable particulate concentration of 0.0046 g/m³ of expansion gas, or 0.041 g/m³ of unburned fuel gas, with no particulates larger than 6 μ m in diameter. These results were used as the basis for the particulate control requirements for the gas turbine end use. It should be noted that there are presently no environmental regulations governing the emission of particulates from gas turbines.

Detailed applicability assessments were made for the six generic classes of control devices previously discussed. These assessments are based primarily on the capability of a control device to achieve the required degree of particulate removal for a specified gasifier end use pair. In some cases where obvious operating difficulties would be expected, such potential problems are also considered in evaluating the applicability of a control device.

As discussed previously, the removal efficiency of any particulate control technology is a strong function of particulate size. Thus, a meaningful applicability assessment of control technologies requires knowledge of the particulate size distribution in the gases to be treated, along with collection efficiencies of the control technologies as a function of particle diameter. The overall collection efficiency of each control device can then be obtained from the grade efficiency data of the control device and the particle size distribution data by means of graphical integration.²³ This graphical technique can be illustrated by the following example for determining the overall collection efficiency of a conventional cyclone operating on an effluent with the "best-case" particle size distribution of a fixed-bed gasifier, as shown in Figure 1. The particle size distribution data in Figure 1 and the fractional collection efficiency data in Figure 4 are presented in Table 3. Figure 5 was

then obtained by plotting these tabulated data. The overall collection efficiency for particulates in the size range from 0 to 6 μ m was determined by locating the point at which the areas above and below the curve are equal. An overall collection efficiency of 86 percent was thereby obtained. It should be noted that the accuracy of this graphical technique is limited by uncertainties in the particle size and grade efficiency data, as discussed previously. Errors introduced by the graphical procedure itself are negligible.

The graphical technique discussed above was employed for particulates less than 6 μ m in diameter for all control devices. For the particulates greater than 6 μ m, a representative value for removal efficiency could be selected for each generic control device, with the exception of the conventional cyclone. This is because of the fact that the collection efficiency of a conventional cyclone usually reaches a maximum at a much larger particle size than 6 μ m; for most other control devices the removal efficiencies are nearly constant for particles greater than 6 μ m. Thus, the same general graphical method was used to calculate the overall collection efficiencies of a cyclone for each gasifier effluent over the particulate size ranges below and above 6 μ m.

A compilation of the overall collection efficiencies for each combination of generic control device and gasifier effluent is presented in Table 4. With the overall removal efficiency of each generic control device thus determined, the applicability assessments were then carried out on the basis of the estimated particulate loadings from each gasifier, as presented in Table 2. The amount of particulates not removed was then calculated. The results for each generic control device under consideration are presented in Table 5. The applicability can then be determined by comparing the amount of particulates remaining in the product gases to the maximum allowable concentration of particulates for each end use.

The results of the applicability assessments are summarized in Table 6. Conclusions drawn from these results are discussed below separately for End Use 1 (combined-cycle fuel gas) and End Use 2 (conventional boiler fuel gas). As for End Use 1, the very restrictive requirement of removing all particles larger than 6 μ m has limited the potential control devices to fabric filters, a high-efficiency venturi scrubber, and

**TABLE 3. COLLECTION EFFICIENCY OF HIGH-EFFICIENCY CYCLONE
FOR PARTICULATES FROM FIXED-BED GASIFIER**

Particulate Size (D _p) micrometers	Amount $\leq$ D _p , * % by weight	Cyclone Efficiency, ** %
16	4	>99
15	3	99
14	2.5	99
13	2.0	98.5
12	1.5	98
11	1.3	97
10	1	96
9	0.7	95
8	0.4	94
7	0.3	92
6	0.25	90
5	0.11	87
4	0.07	83
3	0.02	77
2	0.01	68
1	0.001	53

* Cumulative size distribution data for fixed-bed gasifier (see Figure 1)

** Collection efficiency of conventional cyclone for particles with diameter of D_p (see Figure 4)

the Aerodyne rotary flow cyclone. Among these three control devices, the fabric filter was found to be the only device capable of achieving the required product gas purity (0.041 g/m³) for End Use 1 for all gasifier effluents. However, a fabric filter should not be employed for gases containing high levels of liquid or "sticky" particles. Thus, fixed-bed gasifiers, in particular, may not be compatible with fabric filters, because of the quenching operation commonly used to condense and remove tars and oils. The high-efficiency venturi scrubber is applicable for End Use 1 for all gasifier effluents, except for the worst-case fluid-bed gasifier. However, with a

high-efficiency cyclone upstream as a scalping device, the venturi scrubber is capable of achieving this requirement for the worst-case fluid bed, based on the assumption that the particulate size distribution for particulates less than 6 μ m remains unchanged after passing through the cyclone. The Aerodyne rotary flow cyclone is found to be inapplicable for the average and worst-case fluid-bed gasifier. It should be noted that the results presented herein for the rotary cyclone should be considered tentative until the vendor-supplied data employed in these assessments are confirmed.

Because the particulate removal requirement

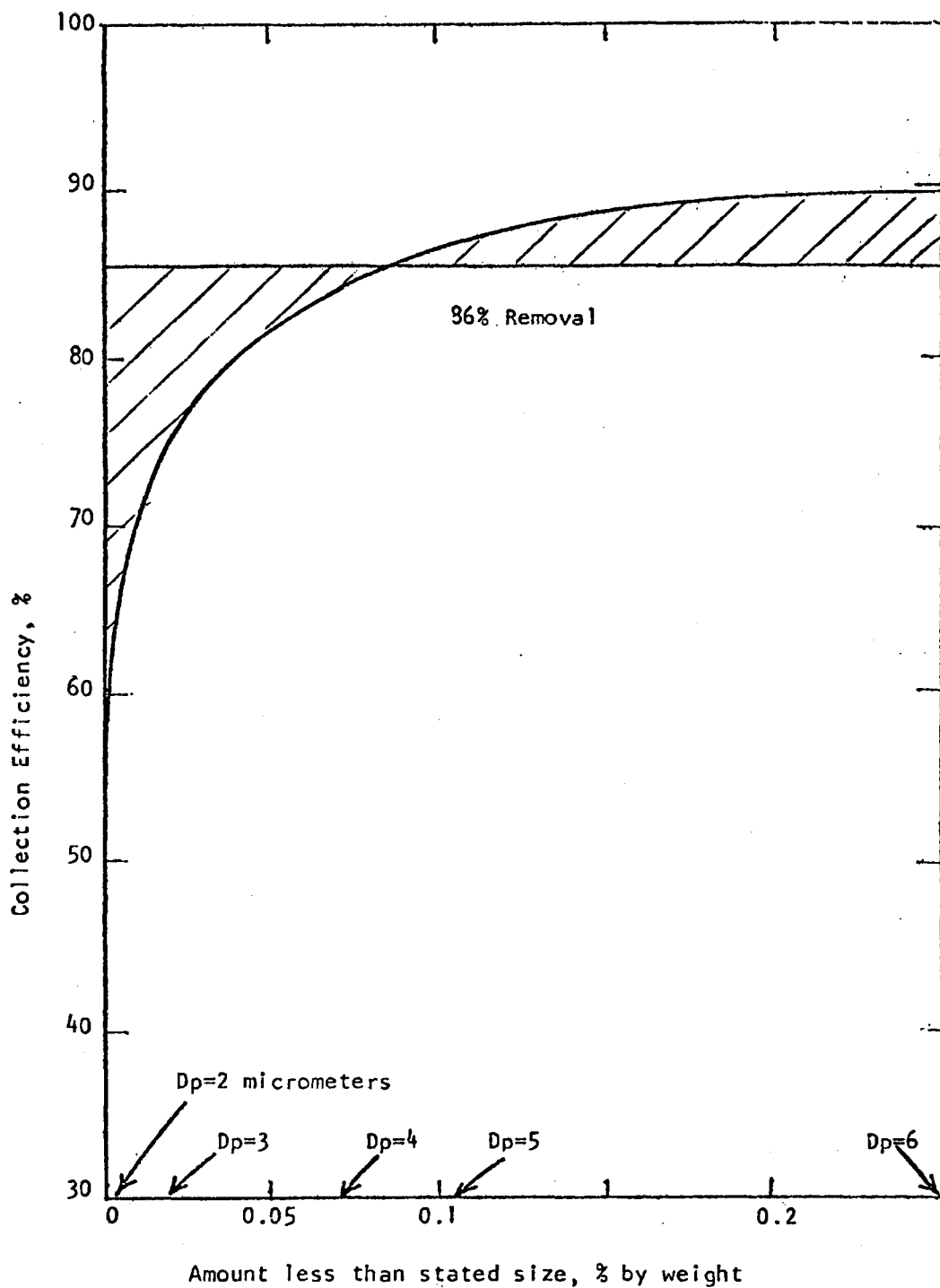


Figure 5. Graphical procedure for estimating overall collection efficiency for particulates up to 6 μm in diameter.

TABLE 4. OVERALL PARTICULATE REMOVAL EFFICIENCIES OF GENERIC CONTROL TECHNOLOGIES FOR TYPICAL GASIFIER OUTPUTS

Gasifiers		Particulate Size (μ m)	% Particulate Removal Vs. Particulate Size					
			Conventional Cyclone	Rotary Cyclone	Venturi Scrubber	Fabric Filter	E.S.P.	Granular Bed Filter
Fixed Bed	Best Case	<6 >6	86 99	98.5 100	99.93 100	99.99 100	N.A. N.A.	94.6 95
	Average Case	<6 >6	86 98	98.8 100	99.94 100	99.99 100	N.A. N.A.	94.7 95
	Worst Case	<6 >6	86 97	99 100	99.95 100	99.99 100	N.A. N.A.	94.7 95
Fluid Bed	Best Case	<6 >6	82 98.8	90 100	97 100	99.2 100	98 99.8	94.4 95
	Average Case	<6 >6	79 98.7	91.5 100	97.8 100	99.4 100	98.4 99.8	94.5 95
	Worst Case	<6 >6	76 98.5	93 100	98.5 100	99.6 100	98.8 99.8	94.5 95
Entrained Bed	Best Case	<6 >6	84 98.6	96.5 100	99.7 100	99.94 100	99 99.8	94.6 95
	Average Case	<6 >6	83 98.8	97.3 100	99.83 100	99.97 100	99.2 99.8	94.7 95
	Worst Case	<6 >6	82 98.9	98 100	99.95 100	99.99 100	99.4 99.8	94.7 95

**TABLE 5. EFFECTIVENESS OF PARTICULATE COLLECTION BY ALTERNATE
CONTROL DEVICES**

Gasifier Type		Percent Particulate Distribution		Particulates Remaining in Product Gases Downstream of Control Device, g/m ³ *					
		Size (μ m)	%	Conventional Cyclone	Rotary Flow Cyclone	Venturi Scrubber	ESP	Fabric Filter	GBF
Fixed Bed	Best Case	<6	0.3	0.003	0.00002	0	---	0	0.00003
		>6	99.7	0.0046	0	0	---	0	0.0229
	Average Case	<6	5.4	0.0023	0.0023	0.0001	---	0.00002	0.0085
		>6	94.6	0.0557	0	0	---	0	0.142
	Worst Case	<6	10.5	0.0869	0.0069	0.0002	---	0.00006	0.033
		>6	89.5	0.1603	0	0	---	0	0.269
Fluid Bed	Best Case	<6	1	0.0023	0.0012	0.005	0.0002	0.00009	0.00067
		>6	99	0.0137	0	0	0.0002	0	0.025
	Average Case	<6	3	0.1649	0.0664	0.017	0.013	0.0042	0.0419
		>6	97	0.3275	0	0	0.050	0	1.218
	Worst Case	<6	5	1.44	0.421	0.089	0.071	0.0024	0.318
		>6	95	1.65	0	0	0.227	0	5.422
Entrained Bed	Best Case	<6	0.5	0.023	0.0051	0.0005	0.002	0.00009	0.0077
		>6	99.5	0.419	0	0	0.060	0	1.972
	Average Case	<6	0.7	0.131	0.021	0.0014	0.006	0.00023	0.0397
		>6	99.3	1.312	0	0	0.210	0	5.281
	Worst Case	<6	0.8	0.339	0.036	0.0009	0.011	0.00019	0.095
		>6	99.2	2.512	0	0	0.456	0	10.95

* To be compared to maximum allowable particulate loads of:
0.041 g/m³ for combined cycles and 0.24 g/m³ for boiler fuel.

TABLE 6. SUMMARY OF APPLICABILITY ASSESSMENTS

End Use/Control Device	Applicability of Control Devices for Gasifier Types**								
	Fixed Bed			Fluid Bed			Entrained Bed		
	B	W	A	B	W	A	B	W	A
COMBINED-CYCLE									
conventional cyclone	-	-	-	-	-	-	-	-	-
rotary cyclone	X	X	X	X	-	-	X	X	X
venturi scrubber	X	X	X	X	-	X	X	X	X
fabric filter	P	P	P	X	X	X	X	X	X
E.S.P.	-	-	-	-	-	-	-	-	-
granular bed filter	-	-	-	-	-	-	-	-	-
rotary cyclone*	X	X	X	X	-	X	X	X	X
venturi scrubber*	X	X	X	X	X	X	X	X	X
fabric filter*	P	P	P	X	X	X	X	X	X
E.S.P.*	-	-	-	-	-	-	-	-	-
granular bed filter*	-	-	-	-	-	-	-	-	-
BOILER FUEL									
conventional cyclone	X	-	X	X	-	-	-	-	-
rotary cyclone	X	X	X	X	-	X	X	X	X
venturi scrubber	X	X	X	X	X	X	X	X	X
fabric filter	P	P	P	X	X	X	X	X	X
E.S.P.#	-	-	-	X	-	X	X	-	X
granular bed filter	X	-	X	X	-	-	-	-	-
rotary cyclone*	X	X	X	X	X	X	X	X	X
venturi scrubber*	X	X	X	X	X	X	X	X	X
fabric filter*	P	P	P	X	X	X	X	X	X
E.S.P.*	-	-	-	X	X	X	X	X	X
granular bed filter*	X	-	X	X	-	X	X	-	-

* A conventional cyclone is assumed to be employed as a scalping device upstream of the indicated primary control device.

** B - Best Case

W - Worst Case

A - Average Case

P - Designates probable inapplicability due to operating problems, although particulate removal is adequate.

X - Designates control device is applicable.

ESP is not applicable to a fixed bed gasifier due to high carbon content and low resistivity of particles.

of End Use 2 is not as restrictive as End Use 1, the number of control devices applicable to End Use 2 is increased considerably as compared to End Use 1. Both the fabric filter and the venturi scrubber are capable of achieving the requirements of End Use 2 for all gasifier effluents. The Aerodyne rotary flow cyclone was found to be applicable to all the gasifier effluents except for the worst-case fluid-bed gasifier. However, with a conventional cyclone upstream as a scalping device, it would be applicable to this worst case as well. A conventional high-efficiency cyclone by itself would be applicable to the best and average cases of the fixed-bed gasifier, and the best case of the fluid-bed gasifier. The CPC granular bed filter is found to have the same applicability as the high-efficiency cyclone mentioned above. Two cyclones in series are capable of achieving the same efficiency as an Aerodyne rotary flow cyclone. A cyclone followed by a CPC granular bed filter would be applicable to two more cases than the CPC filter by itself—the average case of the fluid-bed gasifier and the best case of the entrained-bed gasifier. It was found that a dry-type electrostatic precipitator is not applicable to fixed-bed gasifier effluents because the particles in these effluents have very high carbon contents (55 to 80 percent) which result in low resistivity of the particles and inefficient collection. The electrostatic precipitator was found to be applicable to the best and average cases of the fluid- and entrained-bed gasifiers for End Use 2. With a cyclone upstream as a scalping device, the electrostatic precipitator would also be able to achieve the required removal efficiency for the worst cases of the fluid- and entrained-bed gasifiers.

FATE OF POLLUTANTS

In the previous sections, technologies for controlling the particulate and tar levels of the converter product gases have been discussed and evaluated. Each control device, in turn, generates solid, liquid, and/or gaseous wastes that also must be disposed of in an environmentally acceptable manner. By identifying those streams in which certain pollutants tend to concentrate, proper disposal and control technologies can be selected to minimize environmental degradation.

Data on the fate of the particulates and tars

emitted in the product gases, in terms of their ultimate presence and concentrations in solid, liquid, and gaseous discharge streams, are preliminary and limited for all gasifier types. The distribution of these particulates and tars in the various discharge streams is dictated both by the removal technology and the physical and chemical characteristics of the contaminants. The conclusions summarized below should, therefore, be considered tentative until confirmed by additional data. The data on which these conclusions are based are presented in detail in Reference 1.

In the case of fixed-bed gasifiers, the quench liquor employed to condense and remove the tars contains high concentrations of phenolic compounds. These compounds, together with ammonia and dissolved acid gases, must be removed from the quench liquor. Mercury tends to concentrate in the tar, while most other volatile elements tend to become concentrated on the particulates. Selenium concentrations in the quench liquor are very high.

In the case of fluid-bed gasifiers, most of the available data on the fates of the various contaminants were obtained with the Synthane unit, which also produces tars. Since most other fluid-bed gasifiers do not produce tars, these data may not be representative of this generic type. The available data indicate that many of the trace elements tend to concentrate in the particulates and char. Some of the more volatile elements such as As, Pb, and Hg are also found in potentially harmful concentrations in the tar.

In the case of entrained-bed gasifiers, organics tend to concentrate on the particulate matter rather than the scrubber water. Volatile elements such as Hg, Se, and As are not absorbed in the scrubber water. Tars are not produced by entrained-bed gasifiers, so they do not present a disposal problem.

Of the six generic control technologies previously assessed, the venturi scrubber is the only wet process. The other five processes generally produce a dry, granular, or powdery solid waste. In the case of a venturi or other wet scrubber, the collected fly ash will be wet, complicating disposal of the ash and necessitating wastewater treatment. Liquid waste streams from scrubbing or quenching operations must be treated prior to final disposal or discharge to surface waters or groundwaters. Present and proposed regulations for liquid discharges gen-

erally require a high degree of water recycle and reuse within the plant, thereby minimizing the amounts of liquid to be released from the plant. The collected ash, whether wet or dry, must be disposed of in a landfill or in any other environmentally acceptable manner. Undesirable elements can sometimes be leached from the collected particulate matter. Even if a dry collection system is used, the solid wastes will ultimately be exposed to leaching by groundwater if they are disposed of as landfill or returned to the mine. Use of liners and entrapment of runoff and drainage water will minimize the likelihood of ecological degradation.

Additional sampling is required for all gasifier types to identify and determine the concentrations of contaminants in quench water, solid wastes, tars, and scrubber water under better defined conditions. Laboratory analyses should include trace metals and identification of the chemical forms in which they appear, as well as other inorganic and organic compounds. Studies to determine the leachability of trace elements from captured particulates and tars into quench and scrubber water and into groundwater after ultimate disposal would be very helpful.

REFERENCES

1. Chen, C., C. Koralek, and L. Breitstein. *Control Technologies for Particulate and Tar Emissions from Coal Converters* (draft). Dynalectron Corporation. (Prepared for U.S. Environmental Protection Agency.) January 1979.
2. Cavanaugh, E. C., W. E. Corbett, and G. C. Page. *Environmental Assessment Data Base for Low/Medium-Btu Gasification Technology, Volume II, Appendices A-F*. EPA-600/7-77-1256. November 1977.
3. Dravo Corporation. *Handbook of Gasifiers and Gas Treatment Systems*. FE-1772-11. February 1976.
4. Becker, D. F., and B. N. Murthy. *Feasibility of Reducing Fuel Gas Clean-up Needs*. FE 1236-15. June 1976.
5. Meyer, J. P., and M. S. Edwards. *A Survey of Processes for High Temperature-High Pressure Gas Purification*. ORNL/TM-6178. November 1978.
6. Sinor, J. E. *Evaluation of Background Data Relating to New Source Performance Standards for Lurgi Gasification*. EPA-600/7-77-057. June 1977.
7. Moore, A. S., Jr. *Cleaning Producer Gas from MERC Gasifier*. U.S. Energy Research and Development Administration. May 1977.
8. *Commercial Plant Conceptual Design and Cost Estimate—CO₂ Acceptor Process Gasification Pilot Plant*. Conoco Coal Development Corp. and Stearns-Roger Engineering Co. Vol. 10, FE/1734-43. August 1976-December 1977.
9. Parker, R., and S. Calvert. *High-Temperature and High-Pressure Particulate Control Requirements*. EPA-600/7-77-071. July 1977.
10. Whiteacre, R. W. Personal Communication with Koppers-Totzek. August 1978.
11. Shannon, L. J., P. G. Gorman, and M. Reichel. *Particulate Pollutant System Study, Vol. 11: Fine Particulate Emissions*. Midwest Research Institute. (Prepared for U.S. Environmental Protection Agency.) NTIS PB-203 521. 1971.
12. Shannon, L. J. *Control Technology for Fine Particulate Emissions*. Midwest Research Institute. (Prepared for U.S. Environmental Protection Agency.) NTIS PB-236 646. 1974.
13. Wade, G. L. Performance and Modeling of Moving Granular Bed Filters. In: *Proceedings of EPA/DOE Symposium on High Temperature High Pressure Particulate Control*. Acurex Corp. EPA-600/9-78-004. 1977. p. 133-192.
14. Gordon, M. *Aerodyne Series "SV" Dust Collector*. Aerodyne Development Corp. Cleveland, Ohio. Bulletin Number 1275-SV. 1978.
15. Calvert, S., and R. Parker. *Effect of Temperature and Pressure on Particle Collection Mechanisms: Theoretical Review*. A.P.T., Inc. Prepared for U.S. Environmental Protection Agency.) NTIS PB-264 203 1977.
16. Klett, M. G., W. Szwab, and J. P. Clark. *Particulate Control for Pressurized Fluidized-Bed Combustion*. Gilbert/Commonwealth, R&D Division. (Prepared for U.S. Energy Research and Development Administration.) FE-2220-16. January 1977.
17. Bush, J., P. Feldman, and M. Robinson.

- Development of a High-Temperature/High-Pressure Electrostatic Precipitator.* Research Cottrell, Inc. (Prepared for U.S. Environmental Protection Agency.) EPA-600/7-77-132. 1977.
18. Drehmel, D. C., and D. F. Ciliberti. *High Temperature Fine Particle Control Using Ceramic Filters.* Westinghouse Research Labs. (Prepared for U.S. Environmental Protection Agency.) EPA-600/72-77-207. NTIS PB 274485. 1977.
 19. Calvert, S., R. G. Patterson, and D. C. Drehmel. Fine Particle Collection Efficiency in the A.P.T. Dry Scrubber. In: *Proceedings of EPA/DOE Symposium on High Temperature High Pressure Particulate Control.* Acurex Corp. EPA-600/9-78-004. 1977. p. 399-414.
 20. Moore, R. H., G. F. Schiefelbein, G. E. Stegen, and D. G. Ham. Molten Salt Scrubbing For Removal of Particles and Sulfur From Producer Gas. In: *Proceedings of EPA/DOE Symposium on High Temperature High Pressure Particulate Control.* Acurex Corp. EPA-600/9-78-004. 1977. p. 430-463.
 21. Zahedi, K., and J. R. Melcher. Electrofluidized Beds in the Filtration of A Sub-micron Aerosol. *Journal of APCA.* 26(4):345-352. 1976.
 22. Kirsten, L. Private Communication with Apitron Divison, American Precision Industries, Inc. September 1978.
 23. Peters, J. M. Predicting Efficiency of Fine-Particle Collectors. In: *Calculation and Shortcut Deskbook.* Chemical Engineering. New York, McGraw Hill, Inc.

A COAL GASIFICATION-GAS CLEANING PILOT PLANT: OPERATING EXPERIENCE AND INITIAL RESULTS

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Abstract

An integrated computer-controlled coal gasification-gas cleaning pilot plant at North Carolina State University is currently in preliminary stages of testing. The gasifier is a 6-in diameter fluidized-bed unit, with a coal feed capacity of 23 kg/hr (50 lb/hr). The gas cleaning system contains a cyclone, a venturi scrubber, and an absorber-flash tank-stripper system for acid gas removal. This paper describes the plant and associated facilities for data acquisition, data logging, and process control; summarizes procedures for chemical analysis of all solid, liquid, and gas feed and effluent streams; reviews results of recent runs; and outlines plans for future tests.

INTRODUCTION

Many of the factors currently limiting the large-scale development of coal conversion technology are environmental in nature. Many processes exist to gasify coal, some of which are available commercially, but the technology of synthesis gas cleanup is less developed and the total environmental impact of the implementation of gasification technology is not yet understood.

Recognizing this problem, the U.S. Environmental Protection Agency (EPA) in 1977 contracted for the design and construction of a pilot-plant coal gasification-gas cleaning test facility at North Carolina State University (NCSU), to be operated by faculty and staff of the Department of Chemical Engineering. Construction was begun in January 1978, and the plant was completed and turned over to the University the following summer.

The principal components of the pilot plant are a continuous fluidized-bed gasifier; a cyclone separator and a venturi scrubber for removing particulates, condensables, and water-soluble

species from the raw synthesis gas; and absorption and stripping towers and a flash tank for acid-gas removal and solvent regeneration. The gasifier operates at pressures up to 100 psig (791 kPa), has a capacity of 50 lb coal/hr (23 kg/hr), and runs with either steam-air or steam-O₂ feed mixtures. The acid-gas removal system is modular in design, so alternative absorption processes may be evaluated. Associated with the plant are facilities for direct digital control of process systems and on-line data acquisition, logging, and graphical display. Facilities for sampling and exhaustive chemical analysis of all solid, liquid, and gaseous feed and effluent streams are also available.

The overall objective of the project is to characterize completely the gaseous and condensed-phase emissions from the gasification-gas cleaning process, and to determine how emission rates of various pollutants and methanation catalyst poisons depend on adjustable process parameters. Specific tasks to be performed are to:

- Identify and measure the gross and trace species concentrations in the gasifier product, including concentrations of sulfur gases (H₂S, COS), condensable organics (e.g., BTX and polynuclear aromatic hydrocarbons), water-soluble species (e.g., ammonia, cyanates, cyanides, halides, phenols, sulfates, sulfides, sulfites, and thiocyanates), and trace metals (e.g., antimony, arsenic, beryllium, bismuth, cadmium, lead, mercury, selenium, and vanadium).
- Correlate measured emission levels with coal composition and gasifier operating variables, particularly temperature, pressure, and solid and gas phase residence time distributions.
- Perform material balances around the gasifier, the raw gas cleanup system, and the acid-gas removal system, and determine the extent to which selected species are removed from the synthesis gas in each of the components.
- Correlate measured extents of conversion

*Speaker.

and removal efficiencies for various species with system-operating variables, including temperatures, pressures, holdup times, and solvent circulation rates.

- Evaluate and compare the performance characteristics of alternative acid gas removal processes, considering both CO₂ and H₂S removal capabilities and the degrees to which the processes remove trace pollutant species from the sour synthesis gas. Evaluate the buildup of contaminants in the various acid-gas removal solvents.
- Use the results obtained in the above studies to develop models for the gasification and the gas cleanup processes. The models will take as input variables the composition and feed rate of the coal, bed depth, steam and air (or oxygen) feed rates and inlet temperatures, gasifier pressure, and operating conditions (temperatures, pressures, solvent flow rates, etc.) for the gas-cleaning systems, and will predict the coal conversion and the product gas flow rate and composition, including trace pollutant levels. The model will be used as a basis for perfecting the pilot-plant operating conditions, and for estimating emission levels for scaled up versions of the processes investigated.

The sections that follow briefly describe the plant and its operation, provide illustrative results obtained in test runs, and outline future test plans.

DESCRIPTION OF PLANT FACILITY

The pilot-plant facility consists of six subsystems:

- Gasifier, coal feed, and char removal system;
- Particulates, condensables, and solubles removal (raw gas-cleaning) system;
- Acid-gas removal system;
- Utilities system;
- Instrumentation and process control systems;
- Data acquisition and display system.

These subsystems are represented schematically in Figures 1 through 4.

Gasifier

The gasifier (Figures 1 and 2) is a 6-in (15.2-cm)

I.D. Schedule 40 pipe (316 SS) enclosed in several layers of insulation and contained in a 24-in (61-cm) I.D. Schedule 80 carbon steel pipe. The overall height of the unit is roughly 12 ft (3.7 m). Thermocouples are mounted in the center of the bed at positions 10, 20, 30, 40, 50, and 60 in above the gasifier feed cones to monitor the bed temperature profile. Differential pressure taps are set at 15 and 35 in above the feed cones, and the pressure drop between these taps is used as an operating parameter. The cones are three 1/2-in (12.7-mm) diameter tubes arranged triangularly, with each tube tapering out to 1 in (2.54 cm) for better flow distribution.

Coal is fed and removed by screw conveyers from pressurized hoppers at either end of the vertical reactor. The bed height may be as low as 8 ft (1 m) and as high as 5.5 ft (1.7 m). The level of the fluidized bed is monitored with a nuclear level gauge and kept constant by adjustment of the char removal screw rotation rate. The coal feed and removal systems contain nitrogen purges to prevent back-flushing of any reactants. The insulation section around the gasifier is also equipped with a nitrogen purge flow for safety considerations. The gasifier typically operates at 100 psig (791 kPa) and between 1,600° and 1,800° F (1,150-1,250 K). Steam and carbon react to form CO and H₂; carbon combustion also occurs. Carbon conversions on the order of 30 to 50 percent have been obtained in preliminary runs.

Particulates, Condensables, and Solubles Removal (PCS) System

The raw gas produced in the gasifier is fed to the PCS subsystem (Figure 2). A cyclone separator removes most particulates, and a venturi scrubber quenches the gas stream, removing water-soluble and condensable compounds at the same time. The quenched gas stream is fed through a shell and tube heat exchanger to a condensate-receiving tank. The heat exchanger was added after excessive temperature increases in the receiving tank and consequent losses of volatile condensate components were observed in initial runs.

Water in the receiving tank can be used on a once-through basis or recirculated to the venturi scrubber. The gas leaving the tank goes through a second heat exchanger, to a mist eliminator, and then through either a coalescing or a

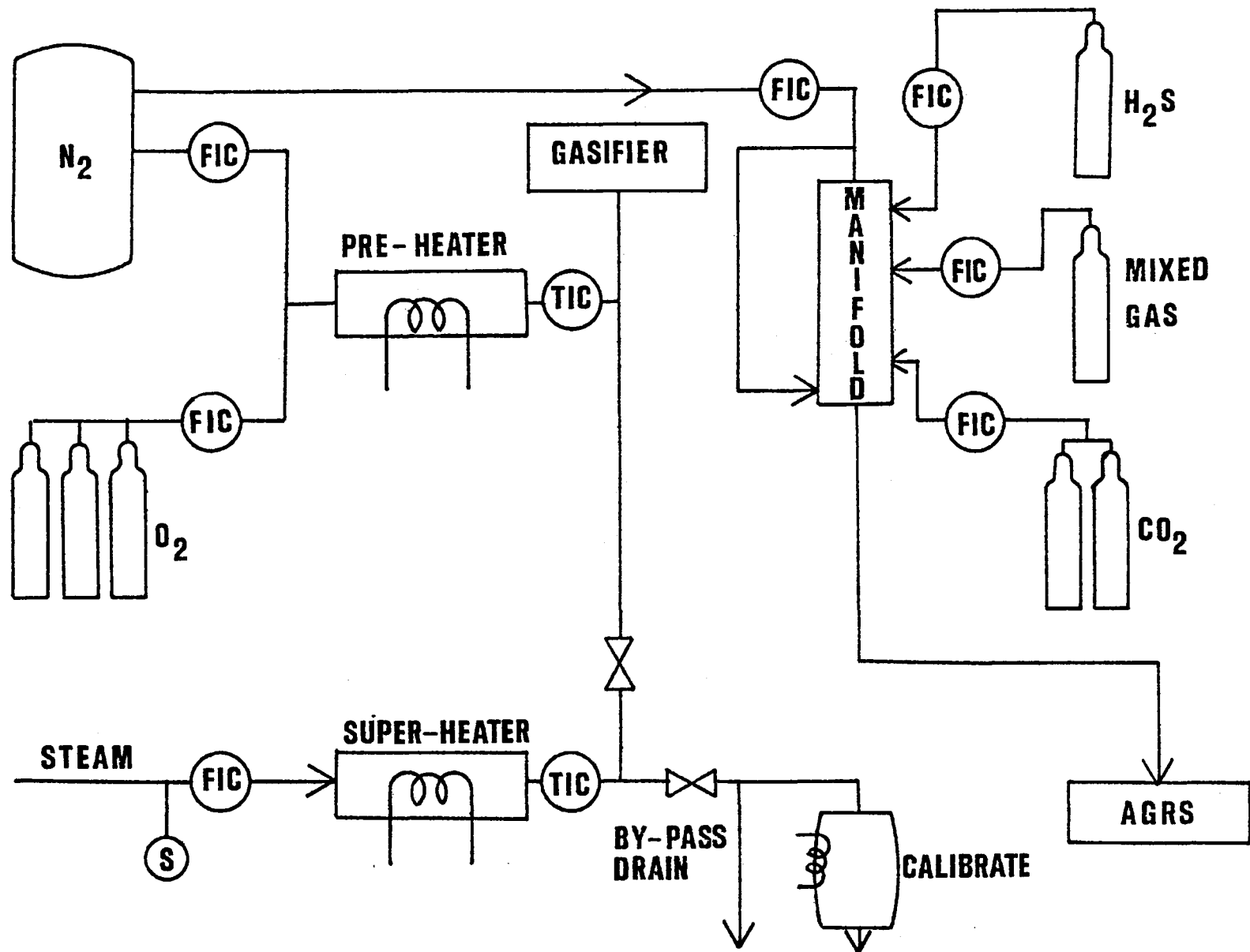


Figure 1. Utilities system.

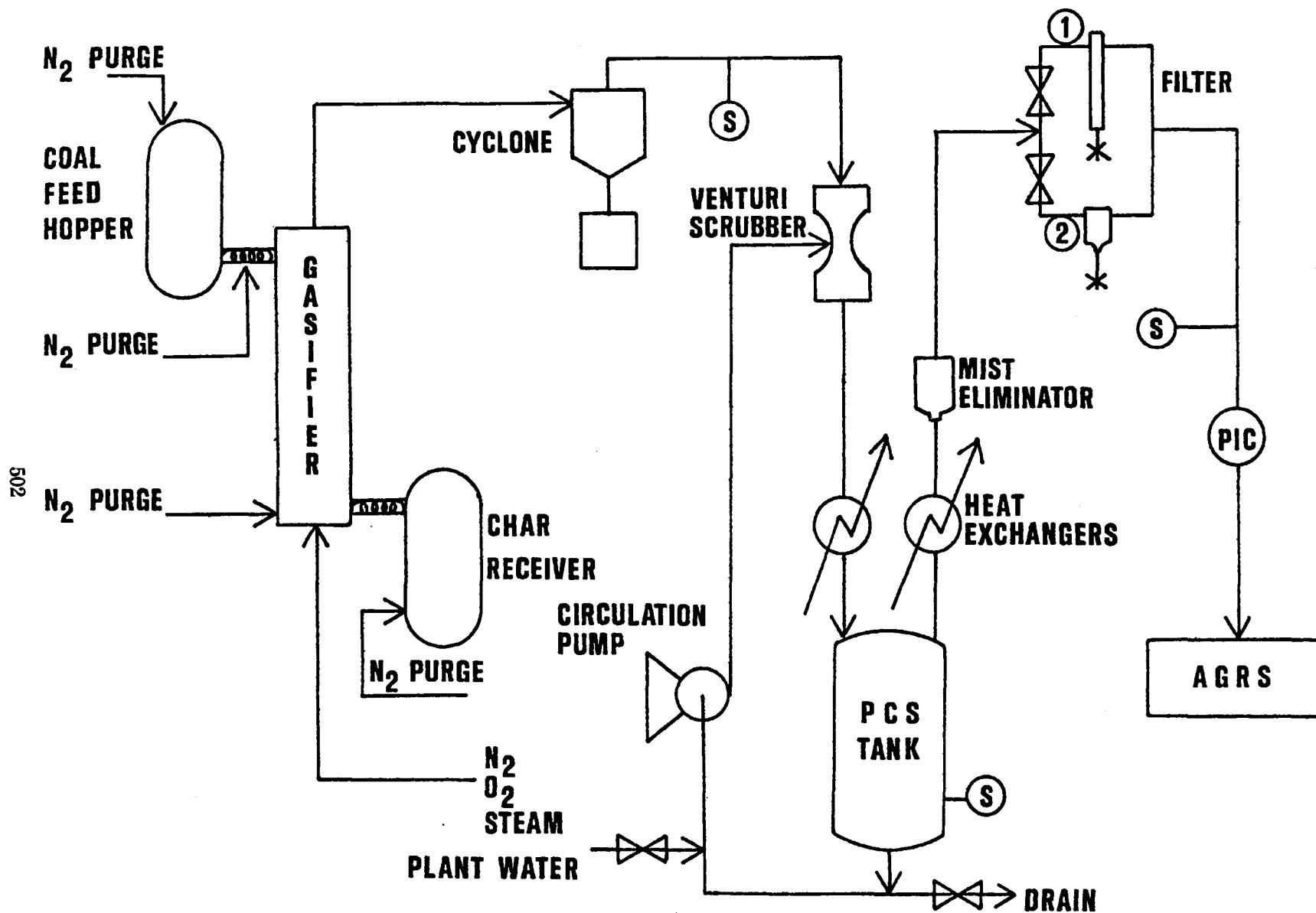


Figure 2. Gasifier-PCS system.

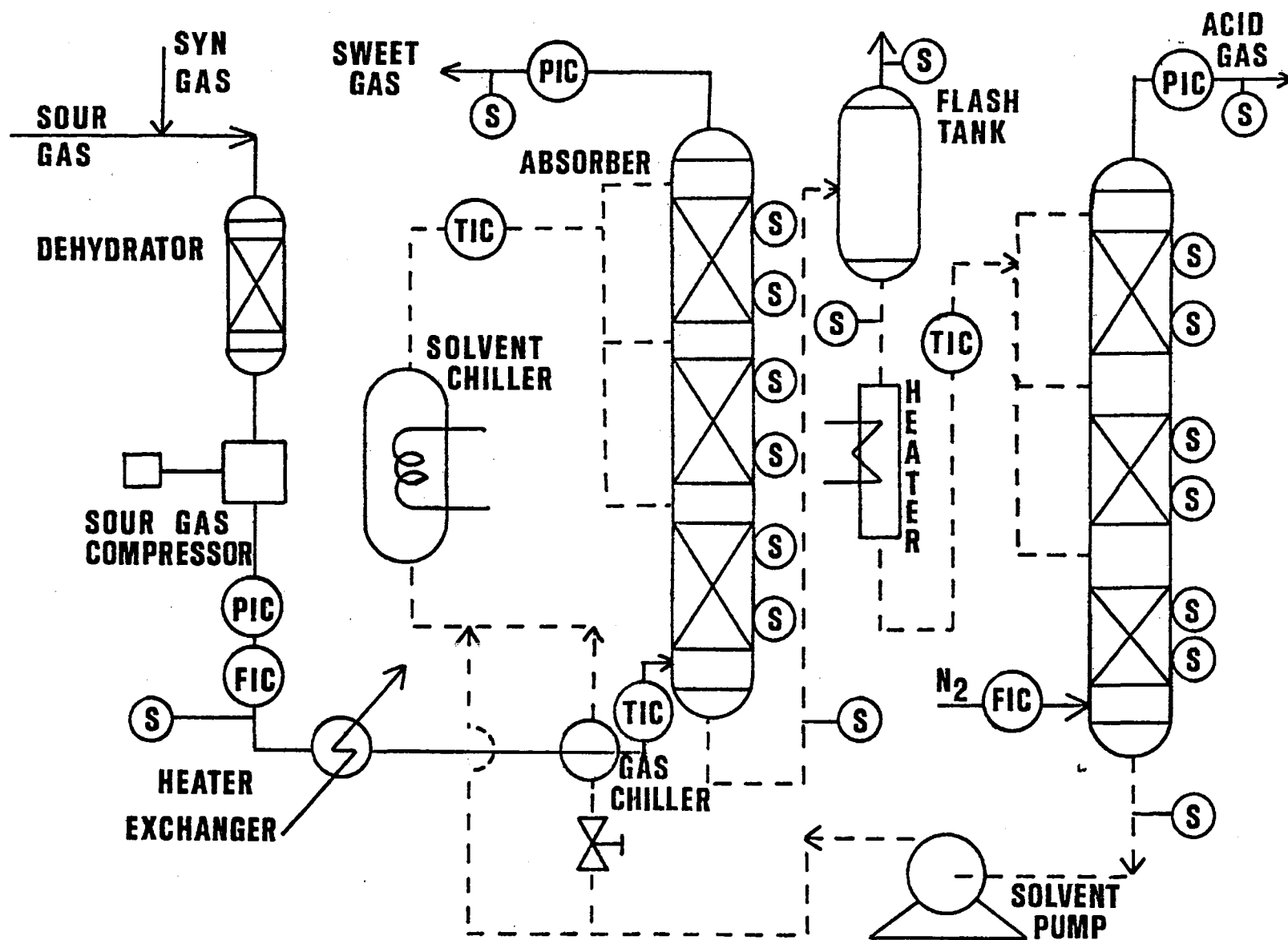


Figure 3. Acid-gas removal system.

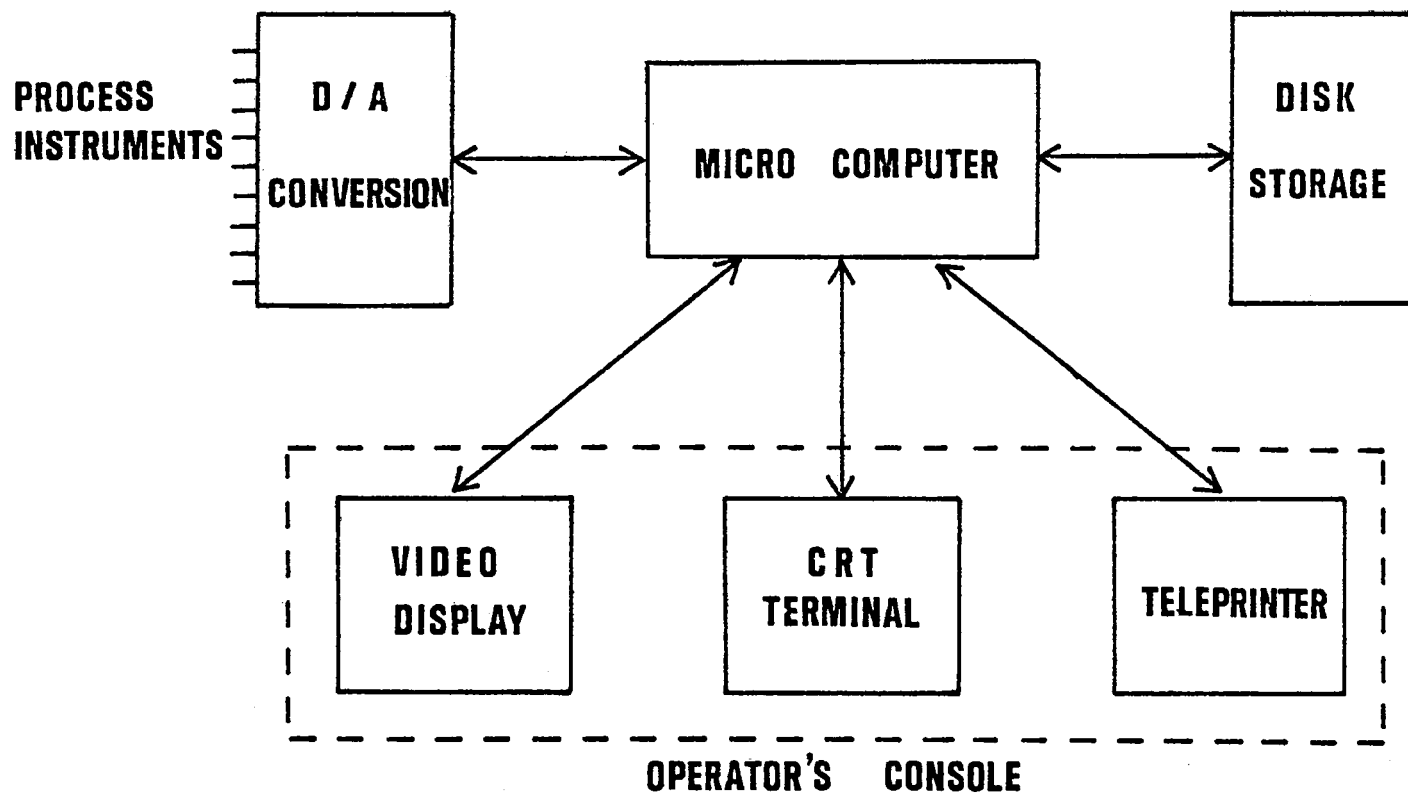


Figure 4. Data acquisition system.

cartridge filter. The pressure drop around the filter is monitored; if plugging is observed, the flow is directed to a parallel filter while the first filter is cleaned or replaced. After leaving the filter, the sour gas is either burned in a shielded flare located on the roof or fed to the acid-gas removal system.

Acid-Gas Removal System (AGRS)

The acid-gas removal system (Figure 3) is designed to operate in four different modes—with refrigerated methanol, with hot potassium carbonate, with monoethanolamine, or with dimethyl ether of polyethylene glycol. All experience to date has been with methanol, and only this mode of operation will be described in the remainder of the paper.

The AGRS can accept either a sour gas feed stream from the gasifier or a synthetic gas (Syngas) feed stream. The feed gas is first passed through a dehydrator, then compressed to 500 psig (3.54 mPa), cooled, and fed to an absorption column. The absorber contains approximately 21.5 ft (6.5 m) of 1/4-in ceramic Intalox saddles. The 5-in (12.7-cm) diameter column can accept solvent feed at any of three locations, which provides flexibility for mass transfer studies. The sweet gas (whatever remains after CO₂, H₂S, and other sulfur gases are absorbed) is then burned in the shielded flare.

The recirculating methanol is refrigerated to about -30° F (239 K) before being routed to the absorber. After passing through the absorber, the methanol is sent to a flash tank to reduce its pressure to about 100 psig (791 kPa). It is then sent to a trim heater before being fed to the stripping column. The 6-in (15.2-cm) diameter stripping column containing 22.5 ft (6.9 m) of 1/4-in ceramic Intalox saddles is operated at about 10 psig (170 kPa), with nitrogen used as the stripping gas. The column feed temperature can be regulated by a trim heater. The solvent is regenerated and sent through a gas chiller (to further cool the entering sour gas) before being sent to the refrigeration unit to undergo another cycle.

Utilities System

Both the gasifier and AGRS are linked to the utilities subsystem (Figure 1), which provides the feed streams to both systems. Nitrogen,

oxygen (or air), and steam are all regulated through flow control loops to the gasifier, while a prepared mixture of N₂, CO₂, H₂S, or other gas mixtures can be fed to the AGRS in place of gasifier make gas. The feed stream to the gasifier is first preheated (N₂, O₂/air) or superheated (steam). The Syngas feed to the AGRS is mixed and regulated through a flow control valve on the sour gas compressor outlet.

Data Acquisition and Process Control Systems

Plant operation is monitored and regulated from a control room. Signals from 96 sensors (temperature, pressure, flow rate, etc.) are sent to a control panel, where they are processed and sent to a video display terminal and/or a Honeywell TDC 2000 process control computer and/or a microprocessor-based plant data acquisition system. The TDC 2000 regulates 16 different control loops in the plant. An alarm panel superimposed on a process schematic provides visual and auditory indications of potentially hazardous conditions.

The data acquisition system has two main objectives: to provide rapid, easily read information to the operator during plant operation, and to provide a permanent record of run data. A block diagram of the system hardware is shown in Figure 4. Each process instrument is wired to a channel of an L.F.E. Model 6100 Remote Terminal Unit. The LFE 6100, a 96-channel analog-to-digital converter, digitizes the 1- to 5-V transmitter signals to 12-bit resolution and transmits the results to the computer through a serial communication line. The conversion takes place every 15 s upon command from the microcomputer.

The microcomputer used in the acquisition system is an INTEL 8080A-based system. The system includes two 8-in floppy disk drives and 32 kbytes of read/write memory. Another 4 kbytes of video display memory are directly addressable by the processor. The operator communicates with the system through a standard CRT-type terminal, and hard-copy output is available on a Decwriter II teleprinter.

Once every 15 s the remote terminal unit transmits signals proportional to all 96 process variables to the microcomputer. The information is translated to engineering units with a stored calibration function for each channel.

Several calculated variables, such as the superficial gas velocity within the fluidized bed, are also displayed. Running sums are kept to allow interval averaging of data.

The operator, through the use of commands entered at the CRT terminal, controls subsequent data processing. By entering a "Display" command, the operator selects one of eight schematic representations of the plant shown on the video display. Process information is superimposed on these displays to provide an easily readable display of information. The display information is updated after every 15-s scan.

Using the "print-on" and print-off" commands, the operator can control hard-copy output during a run. The interval average of selected channels is printed out at the end of a designated interval. Similarly, the "save" and "no-save" commands are used to control the storage of data on disk. Data are written in blocks including all channels and calculated variables. This interval is also specified by the "Interval" command. One 8-in disk holds all information collected during a 12-hr run.

In the initial runs of the pilot plant it became apparent that the acquisition system could be useful for more than simple information collection. A capability of displaying trends of particular variables vs. time would greatly facilitate plant operation, for example, and the implementation of a "snapshot" function to record the sequence of events preceding an alarm-oriented shutdown of the plant might provide enough information to prevent a second similar occurrence. To provide the computing capability needed to implement such data management functions, a Digital Equipment Company PDP 11/34 minicomputer and a color graphics terminal have been ordered to replace the present microcomputer facility.

ANALYTICAL LABORATORY FACILITIES

Solid, liquid, and gas samples from the pilot plant are analyzed in four analytical laboratories. Compounds and major, minor, and trace elements that are analyzed are listed in Table 1. Brief descriptions of the laboratory facilities are given in the sections that follow.

Main Laboratory

The main laboratory is a general purpose

laboratory, in which ultimate and proximate analyses of coals and chars are carried out. Equipment available for these analyses includes furnaces, ovens, and combustion trains constructed and installed following American Society for Testing and Materials (ASTM) guidelines.

The main laboratory also houses a water purification system consisting of a deionizer and a water still; several macrobalances, semimicrobalances, and microbalances; glassware; reagents; and four instruments for analysis of selected pollutants in the plant wastewater. These instruments are a Dionex System 10 ion chromatograph, an Orion Model 901 selective ion-analyzer, a Dohrmann Model DC-50 carbon analyzer, and a Bausch & Lomb-Shimadzu Spectronic 210 UV-Visible spectrophotometer.

Trace Analysis Laboratory

This laboratory is devoted to the analysis of trace elements by atomic absorption spectrophotometry. Instruments housed in the laboratory include a Perkin-Elmer Model 603 atomic absorption spectrophotometer with a deuterium arc and various types of flames, a Perkin-Elmer HGA-2200 graphite furnace, a Perkin-Elmer mercury analysis system, an LFE Model LTA-504 low-temperature plasma asher, and a Barnstead water deionizer.

Coal Research and Analysis Laboratory

This laboratory is equipped for the study of coal pyrolysis and the analysis of sulfur, nitrogen, and free-swelling index in coals and chars. The instruments housed in the laboratory include a Fisher Scientific Model 470 sulfur analyzer, an Antek Model 707 nitrogen analyzer, and a laminar flow furnace reactor capable of operation at temperatures up to 1,273 K with particle residence times as low as 50 ms.

Gas Chromatography Laboratory

The chromatography laboratory is equipped for analysis of fixed and condensable species in gas samples, and for analysis of BTX and phenolics in wastewater samples. Instruments in this laboratory include two Tracor 550 gas chromatographs equipped with flame ionization and thermal conductivity detectors, a Varian 3700

TABLE 1. SUMMARY OF COAL GASIFICATION ANALYTICAL PROGRAM

Sample Type	Analysis	Analyte
coal/char	-	Sieve analysis, density, free swelling Index
	Proximate	Moisture, ash, volatile matter, fixed carbon
	Ultimate	C, H, N, O, S
	Trace Element	As, Be, Cd, Cr, Hg, Ni, Pb, Sb, V
Gas/solvents	Compounds	N ₂ , CO, CO ₂ , H ₂ , H ₂ O, CH ₃ OH, CH ₄ , H ₂ S, COS, CS ₂
	Trace Elements	As, Be, Cd, Cr, Hg, Ni, Pb, Sb, V
Wastewater	Major Elements	C, N, S
	Compounds	Ammonia, total organic carbon, chloride, COD, cyanate, cyanide, pH, phenolics, residue, sulfate, sulfide, sulfite, thiocyanate, benzene, toluene, xylene.
	Trace Elements	As, Be, Cd, Cr, Hg, Ni, Pb, Sb, V

gas chromatograph equipped with thermal conductivity and dual-flame photometric detectors, and a Perkin-Elmer Sigma X chromatograph data station.

PLANT OPERATIONS

Gasifier Operation

The gasifier and PCS system are pressurized by starting a flow of process nitrogen through the gas feed preheater. The preheater and gasifier pressure controllers are set at 1,000° F (811 K) and 100 psig (791 kPa), respectively. Coal feed is commenced when the reactor temperature reaches about 450° F (506 K), with the nitrogen flow maintained at a level sufficient to fluidize the bed as it forms. During this time, steam flow is started through the steam superheater, also set at 1,000° F (811 K), and the reactor bypass duct.

When the bed temperature has reached 700° F (644 K) with the bed height between 20 and 30 in (50 and 76 cm), a small flow of oxygen

is started. At this temperature, the bed almost always ignites. After ignition, the bed temperature is brought to about 1,450° F (1,061 K) by a slow increase of oxygen flow, and a small flow of superheated steam is diverted into the reactor from the bypass. To achieve the desired steady-state conditions, nitrogen flow is gradually decreased, steam flow is increased, and oxygen flow is adjusted to maintain the reactor temperature at the desired value. All of the above changes must be made smoothly; good results are usually obtained if sudden large changes in the superficial gas velocity can be avoided.

The steady-state coal feed rate is established through control of the speed of the coal feed screw to maintain the desired feed rate and adjustment of the removal screw speed to maintain the desired bed height as indicated by the nuclear bed level gauge. During startup, the bed height can be monitored if signals are observed from the temperature sensors located in the bed, the bed differential pressure sensor, and the nuclear bed level gauge.

When the bed is well fluidized from the outset, the process described works well, and reactor startup is fast and smooth. For a number of reasons, the bed is often not well fluidized during the startup period, and a variety of difficulties occur. The probable causes are hot spots because of poor mixing in the bed and bed agglomeration, which result in the bed being lifted to the top of the reactor.

Figure 5 shows a history of a startup of the gasifier. Shown plotted vs. time are the reactor bed temperature at 10 in above the gas feed cones, the pressure drop measured across 20 in of the bed, and the calculated superficial gas velocity in the bed. Noted on the figure is the time when coal feed and oxygen feed were started. Apparently, one or more of the upset conditions noted above occurred after oxygen feed was started, and a steady operating condition was obtained only after several hours of erratic behavior.

Once a good steady state has been obtained, the operation is stable and cannot be easily upset. We believe that one reason for the difficulty of operation during startup and ease of operation during steady state is the difference in the manner in which the fluidizing gas is dispersed. During startup, with no reaction in the bed, all of the fluidizing gas emerges in jets from the three feed cones and is not well distributed. During steady-state operation, the carbon-steam reaction causes a progressive increase in the gas flow rate, and the carbon-oxygen reaction increases the gas temperature in a zone just above the cones. Both of these factors act to increase the gas turbulence and to improve the distribution across the bed.

Researchers carry out the startup procedures by using the TDC 2000 controller, making set point changes to effect changes in process variables. During startup, the reactor temperature is controlled manually by adjustment of the coal and gas feed rates. When the desired steady-state values of bed level, and coal, steam, and nitrogen feed rates have been established, the reactor temperature and oxygen flow control loops are cascaded so the temperature is controlled by the oxygen flow rate.

The steady-state operation of the gasifier-PCS system is illustrated by plots of selected process variable vs. time in Figures 5, 6, and 7. Figure 5 shows three different steady-state conditions. The first of these, designated Run

GO-5, used a coal feed rate of 50 lb/hr (22.7 kg/hr), a bed height of 52 in (132 cm), a steam feed rate of 25 lb/hr (11.4 kg/hr), and flows of nitrogen and oxygen adjusted to give a bed temperature of 1,800° F. For the second steady state, GO-6, the steam feed rate was increased to 30 lb/hr (13.6 kg/hr) while the partial pressure of steam in the feed gas and the reactor temperature was held constant. The gas residence time in the reactor was thus decreased. For GO-7, the steam rate was reduced to 20 lb/hr (9.0 kg/hr), and the velocity and gas residence time were made the same as those of GO-5.

As noted, when the bed is well fluidized a good steady state can be achieved, as indicated by the constancy of the feed flow rates, bed temperatures, reactor pressure, etc. An example of a poorly fluidized bed and poor steady state is shown in Figure 6 for Run GO-13, and an example of operation with a well-fluidized bed is shown in Figure 7 for Run GO-14. During the early part of Run GO-13 the bed was obviously not well fluidized, as evidenced by the erratic behavior of most of the process variables shown in Figure 6. The data indicate that while the upper portion of the bed may have been well fluidized, the region in the vicinity of the 10-in thermocouple was not. A zone nearly devoid of solids probably exited at this point, suggesting that the bed had agglomerated and lifted. At approximately 13:30 the bed temperature was raised to 1,250 K for a time and then returned to its former set point. As can be seen, this upset resulted in an improved operation.

Also shown on Figures 6 and 7 are the times when samples were drawn for analysis at the sample point locations shown on the plant schematics (Figures 2 and 3). All gas samples are taken in heated 1-L sample cylinders. Raw gas samples at 100 psig are drawn from the cyclone and PCS system exits. Also available are high- and low-pressure samples of cleaned and cooled gas drawn from a sampling train at the cyclone exit (Figure 8). In addition to providing a clean gas sample, the sampling train allows for a gravimetric determination of the water content of the gasifier effluent and provides liquid samples that may be analyzed for condensable and soluble species in the effluent. Integrated liquid samples can also be taken from the receiving tank following the venturi scrubber. Wherever they are obtained, liquid samples are im-

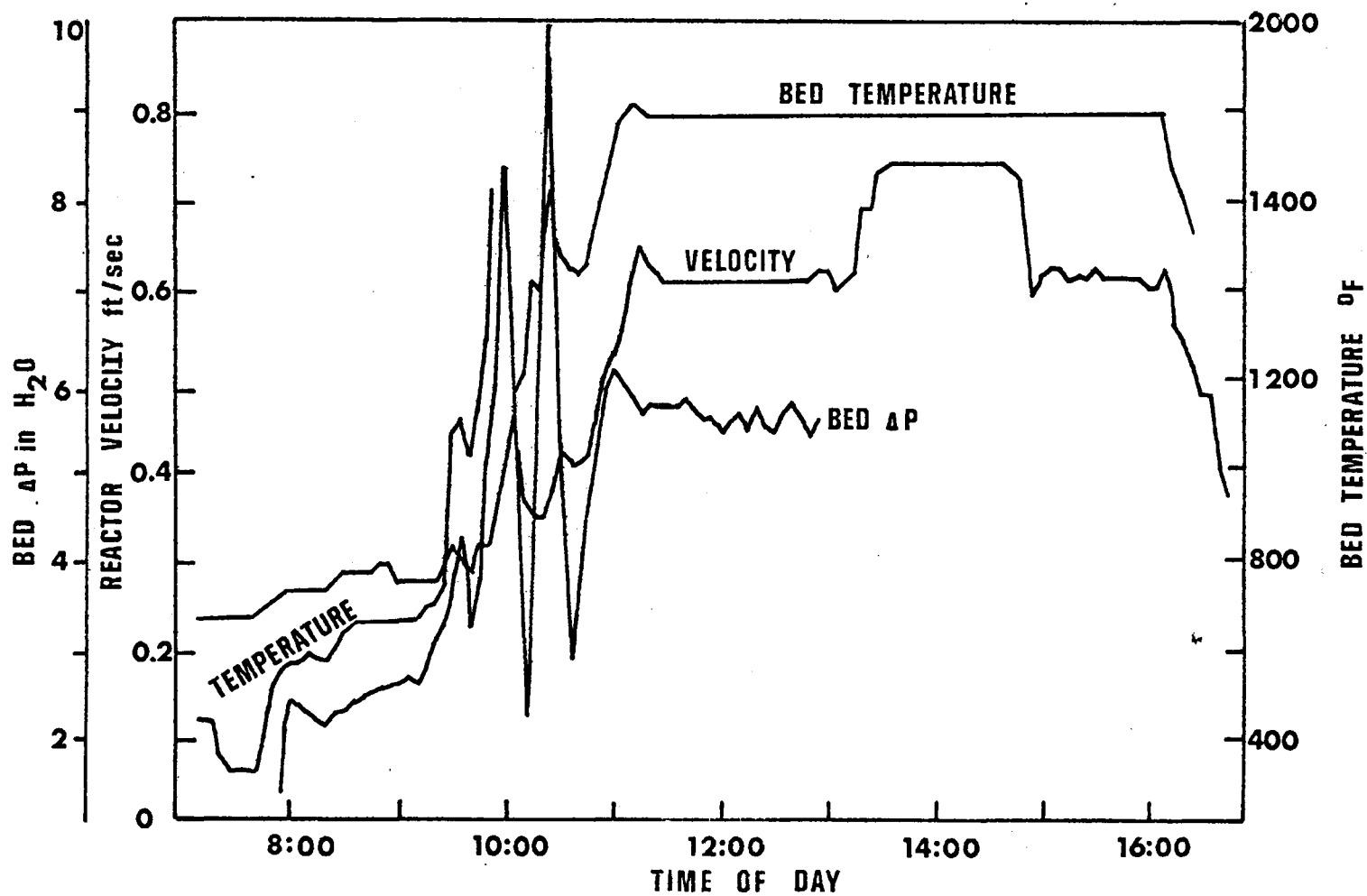


Figure 5. Startup and steady-state data for runs GO-5, GO-6, GO-7.

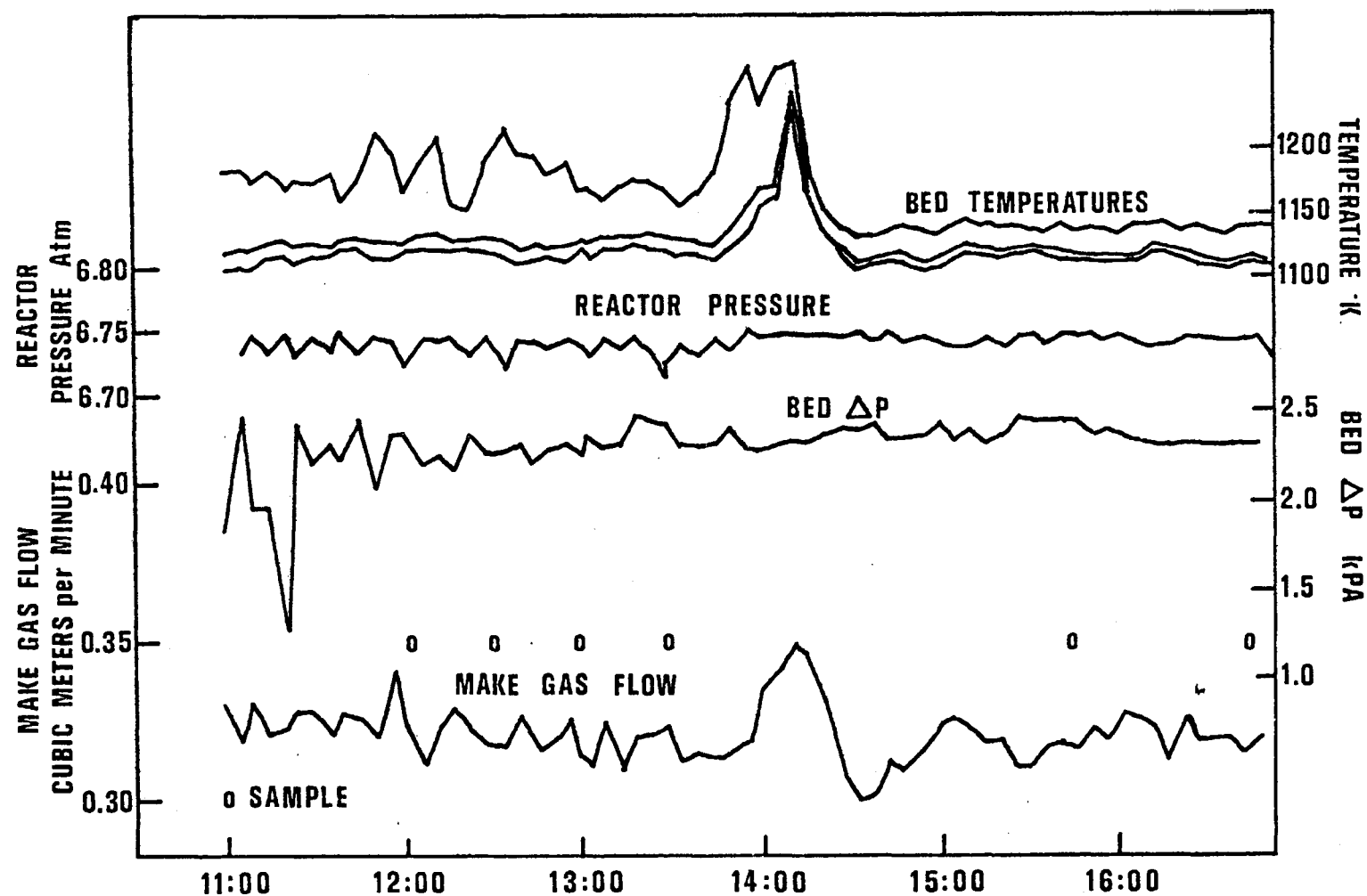


Figure 6. Run GO-13 steady state.

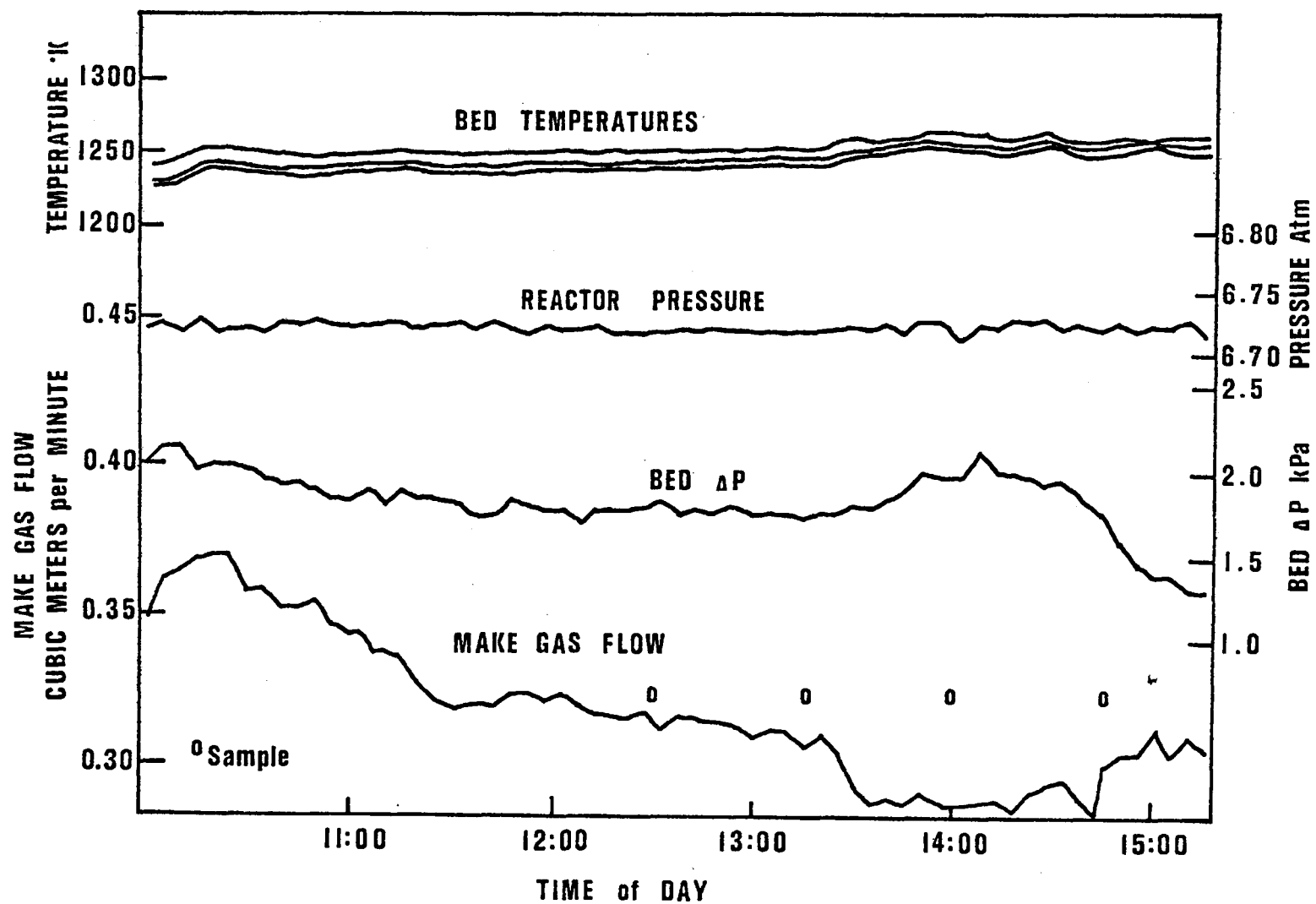


Figure 7. Run GO-14 steady state.

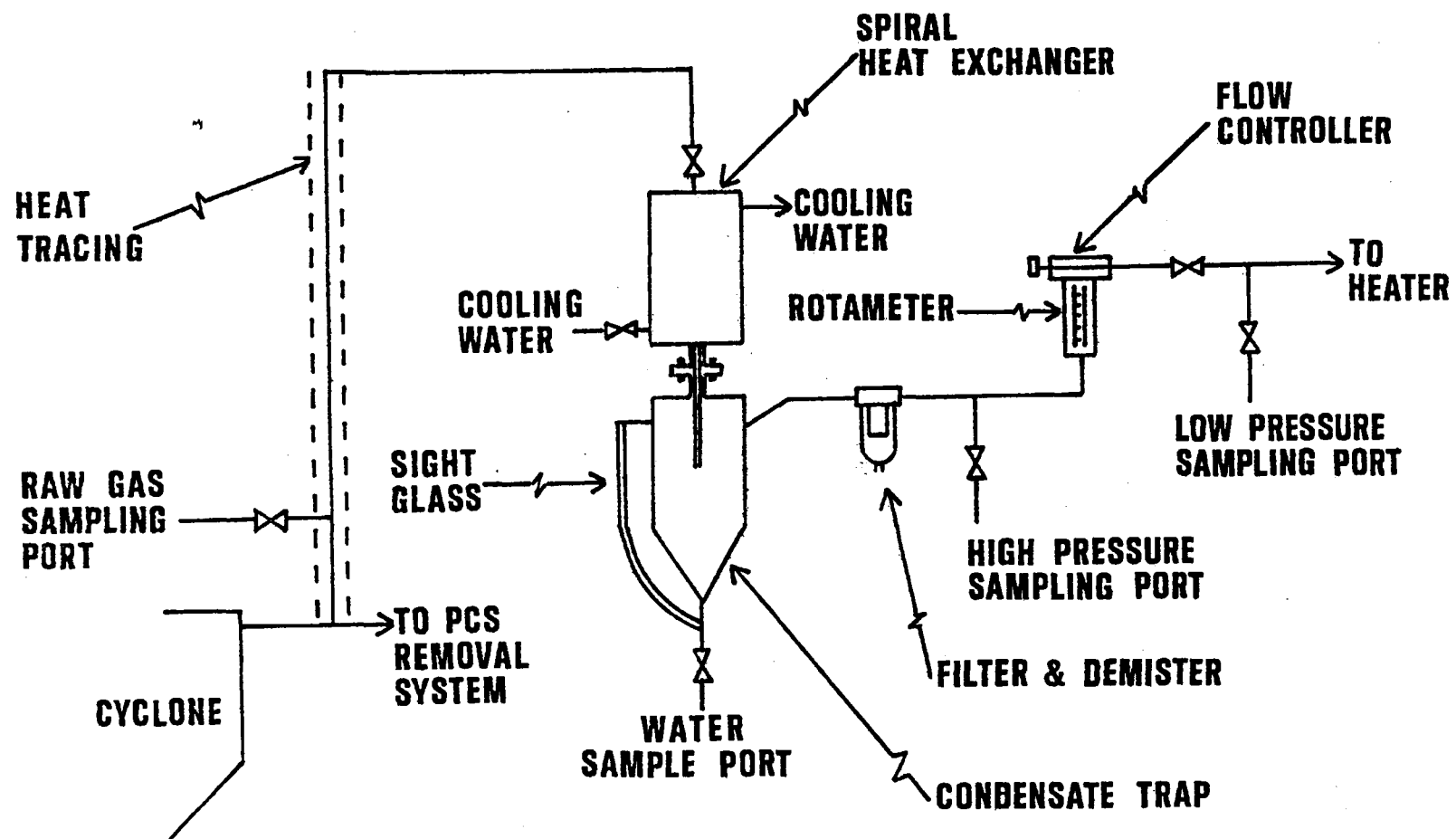


Figure 8. Sample system located at cyclone exit.

mediately subjected to appropriate preservation steps and are stored to await subsequent analysis.

AGRS Operation

The absorber is pressurized to 95 psig (756 kPa) using Syngas nitrogen bypassed around the sour gas compressor. The flash tank is pressurized to 30 psig (308 kPa) with process nitrogen, and the stripper is pressurized to 10 psig (170 kPa) with stripping nitrogen. After these pressures are achieved, solvent flow is begun at 1.5 g/min (5.7 L/min) and the solvent chiller is started and set at -30°F (239 K). After the solvent flow is well established, the absorber is pressurized to 500 psig (3.5 MPa) with Syngas nitrogen using the sour compressor, and the flash tank is brought to 70 psig (584 kPa) using process nitrogen. These pressures and flows are maintained during the remainder of the cool-down period. During this period, the gas flow rate to the absorber is kept as low as possible to help increase the cooling rate.

When the absorber and stripper are near their final temperatures, the solvent and sour gas flow rates are set at their steady-state values and the desired flow rates of Syngas and stripping nitrogen are also set. The composition of the gas leaving the flash tank is monitored, and when acid gas is detected in appreciable quantities, the process nitrogen is turned off and the flashing gas is used to maintain the desired pressure.

The approach to steady state is monitored using an on-line carbon dioxide analyzer. In the near future an on-line analyzer that will monitor both hydrogen sulfide and total sulfur will also be used to define the approach to steady state.

Figures 9 and 10 show the transient and steady-state values of selected process variables for a typical AGRS run. Shown plotted vs. time are feed gas temperature, two temperatures in the stripper, and three temperatures in the absorber. The results will be discussed in more detail in a later section.

After steady-state conditions have been achieved, samples are taken of the feed gas, sweet gas from the top of the absorber, flash tank gas, and acid gas from the stripper. Attempts to sample gas at various points in the columns have been complicated by liquid entrainment. Liquid sampling, especially at var-

ious points in the columns, has also proven difficult. Both problems are currently being worked on, with different sampling port designs considered.

ILLUSTRATIVE RESULTS: GASIFIER OPERATION

Shown on Figure 7 are process conditions for Run GO-14, carried out February 2, 1979. The long residence time of solids in the bed (roughly 30 min) probably accounts for the long time required for the make gas flow rate to reach steady state.

The raw plant operating and gas analysis data for Run GO-14A were processed to generate input for a data logging and material balance program. (The designation 14A refers to the period between 12:30 and 13:30, after which conditions changed in the plant.) The output from this program is shown in Figures 11a and 11b. The paragraphs that follow summarize the calculated results and the calculations used to generate them, more or less in the order in which the results appear on the computer print-out.

Reactor Specifications

The reactor pressure and average bed temperature were 103 psig (811 kPa) and $1,792^{\circ}\text{F}$ (1,251 K). The reactor diameter is a fixed 6 in (15.2 cm), and the bed height was controlled at 38 in (97 cm).

The pressure drop in the bed over a fixed length was measured and used to calculate an apparent density of the expanded bed. From this quantity and the known densities of the solid and gas phases, the bed voidage was determined to be $0.79\text{ ft}^3\text{ void/ft}^3\text{ reactor}$. The expansion factor is then calculated from this value and the known settled bed density is $1.95\text{ ft}^3\text{ expanded bed/ft}^3\text{ settled bed}$.

It has so far not been possible to eliminate leakage from the reactor, particularly around the feed and char removal screw conveyors. The magnitude of this leakage is estimated before each run in both static and dynamic tests, and the result is incorporated into material balance calculations. In Run GO-14A, the leakage rate was estimated to be $0.55\text{ stdft}^3/\text{min}$ (16 L [STP]/min), roughly 3 percent of the product gas flow rate.

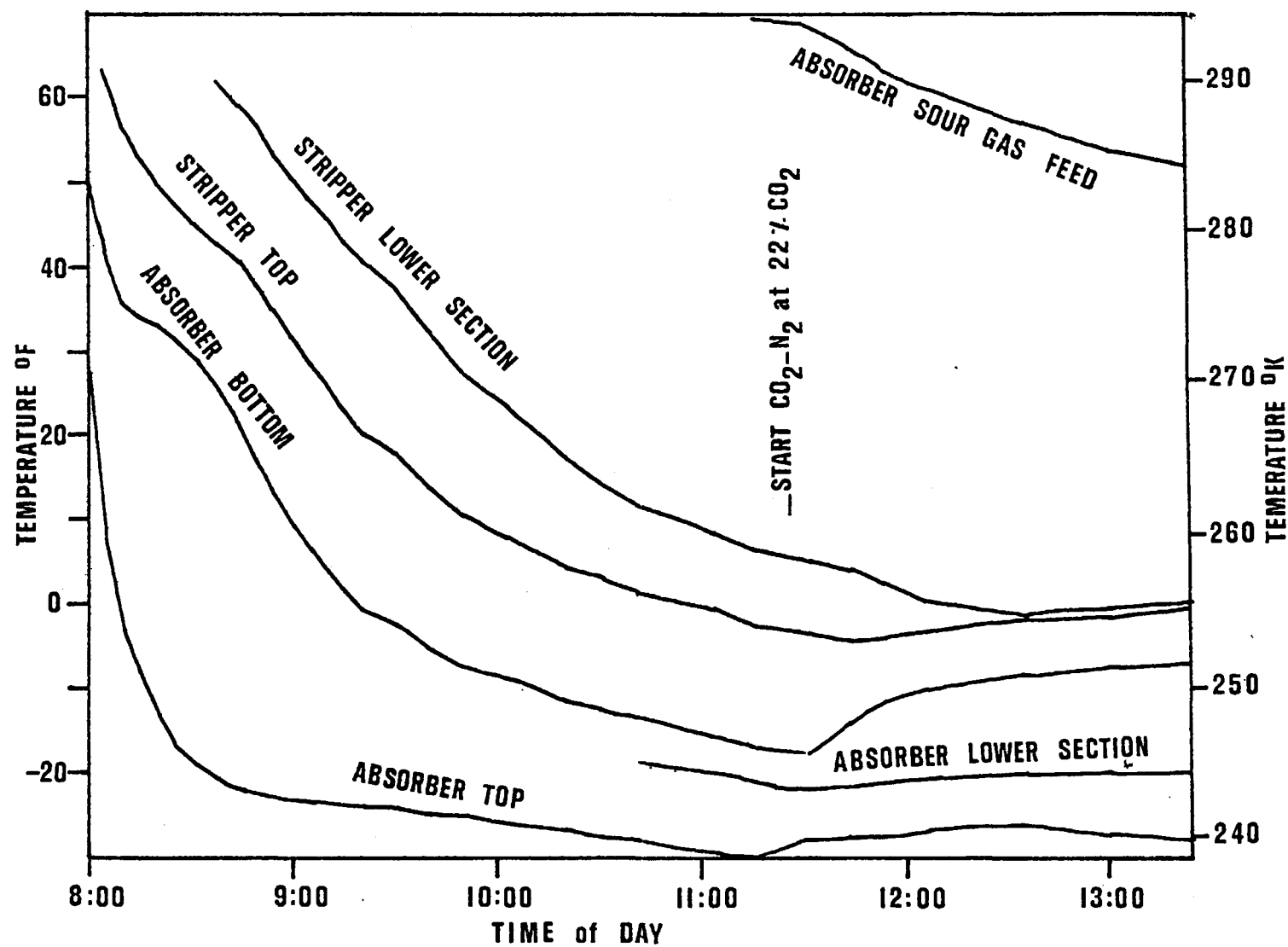


Figure 9. Run AM-4 startup temperature data.

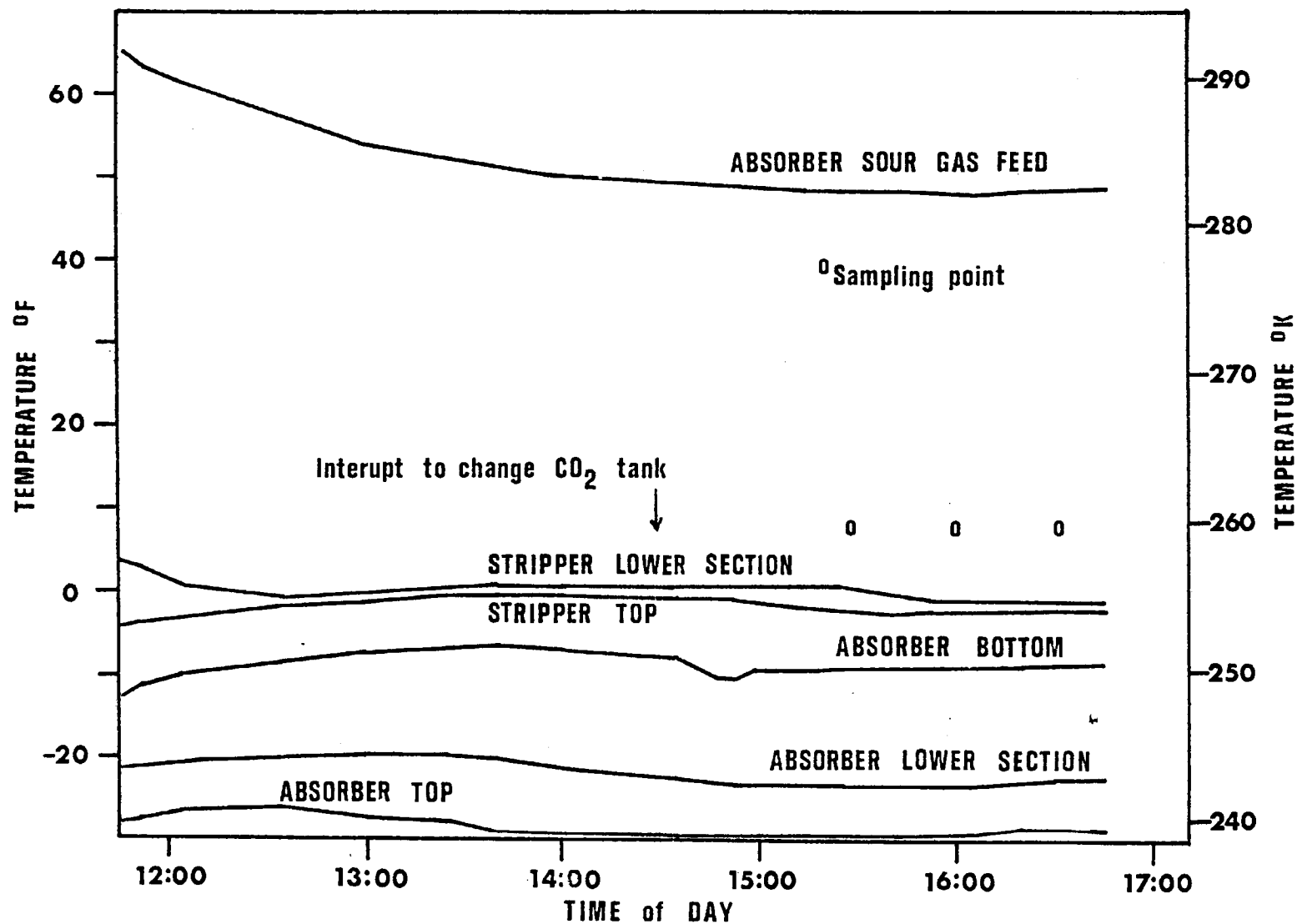


Figure 10. Run AM-4 steady-state temperature data.

 * NCSU DEPARTMENT OF CHEMICAL ENGINEERING *
 * FLUIDIZED BED COAL GASIFICATION REACTOR *

RUN GO-14A 2/20/79, 12:30-1:15 RUN #4 ON EXPERIMENTAL PLAN

REACTOR SPECIFICATIONS

PRESSURE = 103.0 PSIG (8.01 ATM , 611.5 KPA)
 TEMPERATURE = 1792.0 DEG.F (977.8 DEG.C)
 BED HEIGHT = 36.0 IN. (0.91 METERS)
 BED DIAMETER = 6.0 IN. (0.152 METERS)
 ESTIMATED BED VOIDAGE = 0.79
 BED EXPANSION FACTOR = 1.95
 ESTIMATED LEAK RATE = 0.55 SCFM

SOLID FEED PROPERTIES

WESTERN KENTUCKY #11 COAL CHAR, 10X80 MESH
 PARTICLE DENSITY = 112.2 LB/FT**3 (1.797 G/CM**3)
 SETTLED BED DENSITY = 46.2 LB/FT**3 (0.740 G/CM**3)
 AVERAGE PARTICLE DIAMETER = 651.01 MICRONS
 A-R MOISTURE CONTENT = 0.0063

PROXIMATE ANALYSIS OF COAL FEED

FIXED CARBON = 0.856
 VOLATILE MATTER = 0.022
 MOISTURE = 0.006
 ASH = 0.115

ULTIMATE ANALYSES(ESTIMATED)

COAL FEED SPENT CHAR CYCLONE DUST

CARBON	0.844	0.836	0.639
HYDROGEN	0.005	0.001	0.017
OXYGEN	0.004	0.017	0.180
NITROGEN	0.003	0.005	0.001
SULFUR	0.029	0.021	0.037
ASH	0.115	0.120	0.125

FEED RATES

COAL = 31.20 LB/HR AT 70.0 DEG.F
 = 14.15 KG/HR AT 21.1 DEG.C
 STEAM = 24.90 LB/HR AT 365.3 DEG.F
 = 11.29 KG/HR AT 185.2 DEG.C
 OXYGEN = 9.51 LB/HR AT 74.5 DEG.F
 = 4.32 KG/HR AT 23.6 DEG.C
 = 1.78 SCFM

FEED RATIOS AND CONDITIONS

STEAM/COAL = 0.91 LB STEAM/LB COAL(MAF)
 = 0.95 LB STEAM/LB CARBON
 O2/COAL = 0.35 LB O2/LB COAL(MAF)
 = 0.36 LB O2/LB CARBON

N2/O2 = 1.26 MOLES N2/MOLE O2

COMBINED GAS FEED TEMPERATURE = 1000.0 DEG.F
 = 537.8 DEG.C

NITROGEN = 10.51 LB/HR AT 73.8 DEG.F
 = 4.77 KG/HR AT 23.2 DEG.C
 = 2.25 SCFM

SUPERFICIAL GAS VELOCITY IN REACTOR = 0.60 FT/S
 = 0.18 M/S

PURGE N2 = 8.83 LB/HR (4.01 KG/HR , 1.89 SCFM)

VS/V(MIN,FLUIDIZATION) = 1.8 (VMF = 0.325 FT/S)

Figure 11a. Run GO-14A data output.

RUN GO-14A 2/20/79, 12:30-1:15 RUN #4 ON EXPERIMENTAL PLAN

CONTROL VARIABLES

OUTPUT VARIABLES

TEMPERATURE	= 1792.0 DEG.F	PRESSURE DROP OVER 20 IN.	= 7.6 IN.H ₂ O (0.275 PSI)
N ₂ /O ₂ MOLAR FEED RATIO	= 1.26	PCS GAS FLOW RATE	= 1.9 KPA
STEAM PARTIAL PRESSURE	= 14.16 PSI		= 2.02 LB-MOLE/HR (12.08 SCFH)
BED HEIGHT	= 3.17 FT		= 2.01 LB-MOLE/HR (DRY BASIS)
SOLID SPACE TIME	= 28.3 MIN	CYCLONE GAS FLOW RATE	= 2.86 LB-MOLE/HR (17.11 SCFH)
GAS SPACE TIME	= 5.31 S		= 2.01 LB-MOLE/HR (DRY BASIS)
		SOLID HOLDUP	= 1.30 KMOL/HR
			= 14.7 LB (6.7 KG)

PRODUCT FUEL PROPERTIES

CONVERSION VARIABLES

CO	= 22.1% (MOLAR BASIS)	CARBON CONVERSION	= 33.7%
H ₂	= 0.363 LB CO PRODUCED/LB COAL(MAF)	STEAM CONVERSION	= 39.0%
CH ₄	= 0.047 LB H ₂ PRODUCED/LB COAL(MAF)		
	= 1.1% (MOLAR BASIS)		
	= 0.011 LB CH ₄ PRODUCED/LB COAL(MAF)		

SOLID MATERIAL BALANCE

HEATING VALUE OF MAKE GAS	= 3599.6 BTU/LB	COAL FED	= 233.2 LB
	= 214.2 BTU/SCF	SPENT CHAR COLLECTED	= 145.1 LB = 62.2% OF FEED
	= 8365.6 KJ/KG	CYCLONE DUST COLLECTED	= 6.5 LB = 2.8% OF FEED
HEATING VALUE OF SWEET GAS	= 6124.1 BTU/LB	COAL GASIFIED	= 81.6 LB = 35.0% OF FEED
	= 268.2 BTU/SCF	SPENT CHAR REMOVAL RATE	= 20.8 LB/HR
	= 14232.7 KJ/KG	CHAR RATE FOR MASS BALANCE	= 23.6 LB/HR

CYCLONE EXIT GAS ANALYSIS

PCS EXIT GAS ANALYSIS

ELEMENTAL MATERIAL BALANCES : FLOWS IN LB/HR

	WET	DRY	LB-MOL/HR	WET	DRY	LB-MOL/HR		MASS	C	H	O	N
CO	13.11	18.61	0.375	17.98	18.03	0.363	COAL	31.2	26.33	0.16	0.12	0.11
H ₂	22.16	31.45	0.833	31.77	31.85	0.842	GASES	53.0	0.0	2.79	31.63	19.34
CH ₄	0.86	0.94	0.019	1.00	1.00	0.020	TOTAL INPUT	85.0	26.33	2.95	31.74	19.44
N ₂	11.91	16.90	0.340	16.63	16.68	0.336	CHAR	20.8	17.38	0.03	0.36	0.10
H ₂ O	22.62	32.10	0.647	32.37	32.45	0.654	DUST	0.9	0.60	0.02	0.17	0.00
	29.54		0.845	0.24		0.005	GASES	60.4	8.82	3.06	30.41	18.11
							WASTEWATER	0.0	0.0	0.0	0.0	0.0
							TOTAL OUTPUT	82.1	26.79	3.10	30.94	18.21
							% DIFFERENCE	-3.3%	1.7%	5.2%	-2.5%	-6.3%

Figure 11b. Run GO-14A data output.

Solid Feed

The feed to the reactor was a devolatilized Western Kentucky #11 coal, pretreated at 2,000° F (1,100° C) and pulverized and screened to 10 × 80 mesh. The proximate and ultimate analyses of the feed coal are shown on the output page, along with ultimate analyses of the spent char and dust collected in the cyclone. The term "estimated" above the ultimate analyses signifies that the given number was obtained in a previous run under similar conditions; time and manpower limitations prohibit analysis of solid samples following every run.

Feed Specifications

Coal was fed at a rate of 31.2 lb/hr (14.15 kg/hr). Steam was fed at a rate corresponding to 0.95 lb H₂O/lb coal (moisture- and ash-free basis), and oxygen was fed in a ratio of 0.35 lb O₂/lb coal (MAF). To prevent the feed nozzles from being burned, nitrogen was fed at a rate corresponding to 1.3 mol N₂/mol O₂. Therefore, the reactor could not be considered strictly oxygen fired or air fired but was much closer to the former.

In the operation of the gasifier, a separate stream of nitrogen (purge nitrogen) is fed through the insulating shell and the feed and char removal screws, eventually combining with the reactor effluent gas stream. The flow rate of this stream was 1.9 stdft³/min (4 kg/hr).

The superficial gas velocity in the reactor is evaluated by assuming a molar gas flow rate equal to that of the feed gas (steam + O₂ + N₂), converting to a volumetric flow rate at the mean reactor temperature and pressure, and dividing by the total reactor cross-sectional area. The calculated velocity in Run GO-14A was 0.60 ft/s (0.18 m/s).

The minimum fluidization velocity was calculated from a correlation of Babu et al.,¹ after the feed gas viscosity at the reactor temperature and pressure was determined using correlations of Rohsenow and Hartnett.² The actual superficial velocity was found to be 1.8 times the estimated minimum fluidization velocity.

Control and Output Variables

Several parameters to be used for subsequent correlation analysis are summarized in

the output sheet. They include the solid holdup (14.7 lb, 6.7 kg), estimated as the apparent solids density in the bed times the bed volume; the solid space time (28.3 min, solids holdup/coal feed rate), and the gas space time (5.31 s, bed height/superficial gas velocity). Also shown are the measured pressure drop in the bed, the gas flow rate (corrected for leakage) measured following the PCS removal system, and the gas flow rate at the cyclone outlet, calculated from the PCS gas flow rate by assuming that the molar flow rate of dry gas is the same at the two points.

Product Fuel Properties, Conversion Variables, and Solid Material Balance

Most of the remaining quantities shown in Figure 11 are derived from a chromatographic analysis of the cyclone exit gas. As of the date of the run shown, reliable measurements of sulfur gases could not be obtained, so values shown on the output page referring to sulfur have no significance.

The fuel properties of the make gas are first summarized: these include the molar percentages of carbon monoxide (22 percent), hydrogen (37 percent), and methane (1 percent), and the heating values of the make gas and sweet gas. The make gas is defined as the cyclone effluent gas with water and purge nitrogen subtracted, and the sweet gas is the make gas with CO₂ and sulfur gases removed.

The carbon conversion in the gasifier is calculated as the mass flow rate of carbon in the product gases divided by the feed rate of carbon in the coal. A 34-percent carbon conversion was obtained in Run GO-14A. The steam conversion was 39 percent.

A solid material balance for the total time period of the run was obtained by weighing the total amounts of coal feed and spent char and cyclone dust collected, and determining the coal gasified by difference. The value of 35 percent gasified is consistent with the previously cited 34 percent carbon conversion.

The rate at which spent char is removed during the steady-state period (21 lb/hr, 9.5 kg/hr) is determined from the known rotational speed of the screw conveyor and the total mass of spent char collected. Also shown on the output page is the char removal rate that would close the total mass balance on the gasifier.

Gas Analyses and Elemental Material Balances

Chromatographic analyses of the gases at the cyclone and PCS system exits are shown next on the output page. The measurement of water in the cyclone gas was subject to considerable error in this run, and the estimated value of 29.5 percent may be off by as much as 5 percent.

The mass flows in and out of the unit of C, H, O, N, and total mass are listed, and the percentage differences between input and output are shown. Better closures in the material balances are anticipated as sampling and analysis procedures become more refined.

ILLUSTRATIVE RESULTS: AGRS OPERATION

The acid-gas removal system functioned well mechanically during three initial runs with a pure nitrogen gas feed. The objects of these runs were to check the mechanical operation of the system, to obtain column hydraulic data for pressure drop and flooding calculations, and to calibrate and tune all instrumentation and control loops.

Thus far, only one run (AM-4) has been conducted using a synthetic acid gas (CO_2 and N_2) feed. The objectives of Run AM-4 were to eval-

uate system performance and on-line sampling and analysis techniques, observe system performance over an extended period of operation, provide operating experience for project personnel, and obtain qualitative information for the development of an experimental plan. Other sulfur gases, including H_2S , were not used but will be used in future runs. The results of the gas analysis for this run appear in Table 2. All gas compositions are reported on a methanol-free basis; only trace quantities of methanol were detected in gas analyses.

A temperature-time plot of several system parameters for Run AM-4 is shown in Figure 9 (transient period) and Figure 10 (steady-state period). As can be seen from these plots, approximately 3.5 hr were required for the system to cool down to its desired value of -30°F (239 K), with solvent flow set at 1.5 g/min (5.7 L/min). All three packed tower sections were used for mass transfer. Gas was fed to the absorber at approximately 7.5 stdft³/min (212 L [STP]/min). The feed rate of N_2 to the stripping tower was 1.1 stdft³/min (31 L [STP]/min). Quantitative measurement of all outlet flows and compositions for mass balance purposes was not possible at the time of the run. The temperature of the solvent feed to the stripper was not controlled but was fixed by the absorber bottom temperature.

TABLE 2. DATA FOR AGRS RUN AM-4

Time	Location	Composition Mole %	
		N_2	CO_2
15:30	Feed gas	76.8	23.2
	Absorber top	100.0	-
	Flash tank	72.3	27.7
	Stripper exit	35.1	64.9
16:00	Feed gas	76.9	23.1
	Absorber top	100.0	-
	Flash tank	73.2	26.8
	Stripper exit	32.5	67.5

After the system was started with N_2 flow, CO_2 was added to the feed gas. A substantial solution exotherm quickly became apparent in the absorber. While the top section in the absorber showed only a slight effect, the temperature in the absorber bottom reservoir rose considerably. The temperature measured in the lower section of the column packing also reflected a milder exotherm than that observed for the absorber bottom. These observations suggest that for these solvent and gas flows, a significant amount of the mass transfer takes place in a small fraction of the packed tower. This is further substantiated by the fact that all the CO_2 was absorbed in the column. In future runs, information will be obtained using only the bottom section of packing for mass transfer with higher inlet CO_2 concentrations and lower solvent rates. Also, additional temperature measurement capability will be installed in the lower section.

The temperature profile in the stripper also varied. The stripper inlet temperature rose as a result of the absorber bottoms temperature increase, while temperature in the lower section of the stripper fell as a result of the desorption endotherm. The thermal effects were not confined to a particular column section, as they were in the absorber.

FUTURE PLANS

The gasifier will be run with devolatilized bituminous coal feed through the summer of 1979. The precision of the analyses and the mass balance closures associated with the gasifier operation are nearly at a satisfactory level, but some refinement in procedures is still required. Once these refinements have been implemented, a designed series of experiments will

be carried out to study the effects of operating temperature, solid and gas phase residence times, and feed gas composition on carbon conversion and sulfur gas and trace pollutant emission levels.

The acid-gas removal system will be subjected to a series of tests with Syngas feeds—mixtures of CO_2 , H_2S , CO , and H_2 in nitrogen with refrigerated methanol as the solvent. Mass transfer parameters will be determined and correlated with the absorber and stripper temperature and pressure and the gas and solvent flow rates. During this period, test runs of the integrated gasifier-gas cleaning facility will be performed, with the PCS system effluent gas serving as the AGRS feed gas. This will eventually be the normal mode of operation of the plant; Syngas runs will only be performed in the initial stages of the test program for each new solvent. The development of mathematical models to correlate the performance of both the gasifier and AGRS systems will be carried out in parallel with all experimentation.

Beginning in the fall of 1979, a nondevolatilized lignite or subbituminous coal will be used as the feedstock to the gasifier, with refrigerated methanol still being used as the AGRS solvent. After several months of integrated plant operation, a new absorption process will be implemented and tested. A decision concerning process has not yet been made.

REFERENCES

1. Babu et al. Institute of Gas Technology, *Report No. E(49-18)-1930*. Chicago, Ill. 1976.
2. Rohsenow, Warren, and J. P. Hartnett. *Handbook of Heat Transfer*. New York, McGraw-Hill, 1972.

CHEMICAL ANALYSIS AND LEACHING OF COAL CONVERSION SOLID WASTES

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Abstract

Five solid wastes from coal conversion processes were characterized chemically and mineralogically. The wastes included three Lurgi gasification ashes and mineral residues from the SRC-I and H-Coal liquefaction processes. Chemical analyses of the solid wastes were performed for 60 constituents. Mineralogical characterization of the solid wastes was carried out using X-ray diffraction, Mössbauer spectroscopy, scanning electron microscopy, and optical techniques.

Leachates generated from the solid wastes at eight pH levels and under two different gas atmospheres were analyzed for over 40 chemical constituents. Thermodynamic speciation of inorganic ions and complexes in solution were modeled. There were 115 aqueous species considered in the model, and saturation data were computed for over 100 minerals.

Results of the mineralogical characterization and leachate analyses showed a wide range in constituent concentration and in the minerals present in the solid wastes. However, thermochemical modeling demonstrated that similar mineral phases controlled the aqueous solubility of the major ionic species for all five solid wastes.

INTRODUCTION

Although the fuels produced by coal gasification and liquefaction processes are free of certain pollution hazards (e.g., sulfur), accessory elements from the coal may be present in these fuels or concentrated in the waste streams. These waste products must be characterized before environmentally acceptable methods for their disposal can be developed.

Until recently, primary emphasis had been on characterizing airborne contaminants from coal conversion processes. However, several investi-

gators, including Cavanaugh and Thomas,¹ Cavanaugh et al.,² and Somerville and Elder,³ have recently characterized the waste streams from low/medium-Btu gasifiers. Filby et al.,⁴ have characterized the trace elements in the solid wastes from the SRC-I liquefaction process. These waste characterizations are important, as demonstrated by the work of Sinor,⁵ who determined that the flow rate of Ni, As, Cd, and Pb from a Lurgi gasification plant may be environmentally significant. Because of the large quantities of raw materials consumed, potentially hazardous accessory elements may be discharged, even though these elements may be present in the waste in low concentrations.

Because the quantity of solid wastes produced from coal conversion processes can be large and variable (Griffin et al.⁶), the wastes must be characterized in detail. However, characterization alone is insufficient for evaluating acceptable waste disposal methods. Therefore, it is necessary to determine which elements can be leached from the wastes and under what circumstances.

The solubility of the accessory elements in coal conversion ashes and residues has not been thoroughly investigated. Some gasification ashes and liquefaction residues are produced under relatively severe conditions, namely, at high temperatures and/or pressures. Liquefaction residues are produced under a reducing atmosphere. Such conditions can alter the mineralogy and subsequent solubility of accessory elements in the feed coals, thus affecting potential release of pollutants.

The application of equilibrium solubility models can provide useful insights into the chemistry of aqueous systems. Equilibrium models provide, at a minimum, boundary conditions within which questions may be framed. For example, a typical environmental problem solved by equilibrium models is one of predicting the highest concentration of a given constituent that can be achieved in solution before precipitation occurs with a given solid phase.

*Speaker.

Solutions to such problems can be useful in developing a "worst case" scenario for a given pollutant leaching from a solid waste. Such solutions set the upper boundary for concentrations of the pollutant that will have to be dealt with under a given set of conditions.

Applications of solubility models to environmental problems must be interpreted with care. For example, it is not uncommon to find large discrepancies in literature values for the solubility products of some mineral phases. The value of the solubility product may depend on the approach to equilibrium, using well-defined crystals vs. precipitation, and phenomena such as phase transitions, aging, colloid formation, and differences in particle size. These factors, along with slow attainment of equilibrium and the presence of impure minerals in nature as opposed to the pure minerals used to determine solubility constants, may obscure solubility relationships and their application to practical environmental problems.

Important factors controlling the solubility of mineral phases include pH, redox environment of the system, oxidation state of the mineral components, concentration and speciation of individual inorganic and organic ions and complexes in solution, and ionic strength (total soluble ions). Application of results from solubility models to real environmental conditions requires considerable caution. Nevertheless, assuming that the activities are calculated correctly and that the equilibrium constants are numerically factual, the models should accurately predict the solubility of an ion under a given set of conditions for an exhaustive list of solid phases.

Purpose

The purpose of this study was to investigate the potential pollution hazards of selected coal conversion solid wastes. The project is part of ongoing research by the Illinois State Geological Survey into the characterization of coal and coal residues (Ruch et al.,⁷ Ruch et al.,⁸ Ruch et al.,⁹ Gluskoter,¹⁰ and Gluskoter et al.¹¹). The five wastes chosen for this study included three Lurgi gasification ashes from runs employing three different feed coals and two liquefaction residues—an SRC-I dry mineral residue and an H-Coal vacuum still bottoms mineral residue. It

is beyond the scope of this study to describe the three coal conversion process technologies, which are available elsewhere (e.g., Braunstein et al.,¹² and Parker and Dykstra¹³).

To assess the solubility of the accessory elements contained in the solid wastes, this study was developed in four stages:

- Chemical characterization of the solid wastes,
- Mineralogical characterization of the solid wastes,
- Determination of the soluble constituents from the solid wastes, and
- Application of thermochemical equilibrium modeling to determine the mineral phases controlling the solubilities of accessory elements in the solid wastes.

CURRENT STUDIES OF THE SOLUBILITY OF COAL GASIFICATION AND LIQUEFACTION SOLID WASTES

Sources of Gasification Ashes and Liquefaction Residues

During 1973 and 1974, the American Gas Association and the Office of Coal Research studied the performance and suitability of various American coals for gasification by the Lurgi process. Four different coals were sent to Scotland, where they were gasified in the Lurgi plant at Westfield. Among these four coals were 5,000 tons each of Illinois No. 6 and No. 5 (seam) coals and a Rosebud (seam) coal from Montana that was gasified. The unquenched waste ash was then sent back to the United States, where it has been used in several studies. The samples of Illinois No. 5 and No. 6, and Rosebud Lurgi ash, for which data are reported here, were supplied to us by Peabody Coal Company's Central Laboratory at Freeburg, Illinois.

The H-Coal liquefaction residue was obtained from Hydrocarbon Research, Inc., Trenton, New Jersey. The residue was the vacuum still bottoms generated during production of a fuel oil product using an Illinois No. 6 (seam) coal and the H-Coal® pilot development unit at the HRI Trenton Lab May 3, 1976.

The SRC-I liquefaction dry mineral residue was obtained in September 1976 from the Pittsburgh and Midway Coal Mining Company solvent-refined coal pilot plant at Fort Lewis, Washing-

ton. A Kentucky No. 9 (seam) coal was being processed at the time the sample was obtained.

Chemical Characterization

The chemical composition of the five solid wastes has been characterized for over 60 chemical constituents including major, minor, trace, and rare earth elements using the methods described by Gluskoter et al.¹¹ The results of these analyses have been reported previously by Griffin et al.,⁶ Schuller et al.,¹⁴ and Griffin et al.¹⁵ Nine elements were generally found in concentrations greater than 1,000 mg/kg of the solid wastes: Al, Ca, Fe, K, Mg, Na, S, Si, and Ti. An additional group of elements was found in concentrations generally between 100 mg/kg and 1,000 mg/kg. These included B, Ba, Ce, Cl, Cr, F, Mn, Sr, V, Zn, and Zr. Another 20 elements were found in detectable concentrations less than 100 mg/kg.

The most noteworthy differences in chemical composition between the wastes were the high levels of Ca and Mn in the ashes from the Lurgi process and the high levels of S and Cl in the two liquefaction residues. The wastes from the Rosebud and Kentucky No. 9 coals contained higher levels of P and F than did the wastes from the Illinois coals. Trace element composition was highly variable, and no clear pattern could be distinguished. Concentrations of Zn varied over the widest range (13 to 1,500 ppm), presumably in response to the presence or absence of ZnS in the feed coals. Correlation between the chemical characterization of the wastes from this study and other investigations is quite difficult. The difficulty arises from the variability within the feed coals employed and the process parameters used. Changes in temperatures and pressures affect the fate of constituents and the nature of the various coal conversion process waste streams.

Mineralogical Characterization

Samples of the five solid wastes were analyzed by X-ray diffraction, Mössbauer spectroscopy, scanning electron microscopy, and optical techniques. The minerals identified are listed in Table 1. Comparison of the mineralogy of the samples from gasification and liquefaction processes is instructive from the standpoint of the mineral transformations occurring during coal

conversion. For example, pyrite (FeS_2) is the dominant form of iron in the feed coals but is not detected in any of the solid wastes. The pyrite has been converted to hematite and magnetite during the Lurgi gasification process. In contrast, the pyrite has been converted to pyrrhotite and troilite during the liquefaction processes. Another interesting contrast occurs in the clay minerals present in the feed coals. They remain unaltered during the liquefaction processes but are converted to feldspar and mullite during the Lurgi gasification process.

Aqueous Solubility

To determine the soluble constituents of the five solid wastes, large-volume, static leaching tests were used. This involved making 10 percent (weight to volume) slurries of solid waste with distilled water in large glass carboys. The slurries were made in a series of four and adjusted to pH values over the range 2 to 11. The pH values of the slurries were monitored and readjusted to the specified values when necessary. Chemical equilibrium was assumed when the pH remained constant. The period for achieving equilibrium lasted 3 to 6 mo. However, studies conducted with the Lurgi ashes indicated that they had reached over 90 percent of their equilibrium concentrations within 1 week. Duplicate sets of the slurries were made; one set was equilibrated under an argon (oxygen- and CO_2 -free) atmosphere and the other under an air atmosphere.

The leachates from the wastes were analyzed for 43 constituents, and these concentrations were compared to recommended water quality levels (EPA¹⁶). The results of the actual leachate analyses have been reported previously by Griffin et al.⁶ and Griffin et al.¹⁵ Table 2 lists constituents found to exceed the recommended levels over the pH range studied and under the laboratory conditions described above. Although many constituents exceed the recommended levels under acid conditions, those that exceed the recommended levels over the entire pH range or at their natural pH were felt to represent the highest potential for pollution. These constituents are listed under the "Natural pH" column in Table 2. Also given in Table 2 are the pH ranges of the leachates used and the pH values of the two natural pH solutions for each aerobic (air) and anaerobic (argon) set of slurries

TABLE 1. MINERALS IDENTIFIED IN COAL CONVERSION SOLID WASTES

Minerals Identified	Lurgi IL 5	Lurgi IL 6	Lurgi Rose- bud	H-Coal IL 6	SRC KY 9
Hematite (Fe ₂ O ₃)	X	X	X		
Magnetite (Fe ₃ O ₄)	X	X	X		
Goethite (FeOOH)	X	X	X		
Pyrrhotite (Fe _{1-x} S)				X	X
Troilite (FeS)				X	X
Sphalerite (ZnS)				X	
Quartz (SiO ₂)	X	X	X	X	X
Gypsum-Anhydrite (CaSO ₄)	X	X	X		X
Calcite-Dolomite (CaCO ₃ -CaMg(CO ₃) ₂)			X	X	
Wollastonite (CaSiO ₃)				X	
Plagioclase Feldspar Na(Ca)AlSi ₃ O ₈	X	X	X		
Mullite (3Al ₂ O ₃ •2SiO ₂)	X	X	X		
Clay Minerals				X	X

for each waste. The natural pH slurries are slurries that were allowed to equilibrate without pH adjustment by addition of either nitric acid or sodium hydroxide. Table 2 indicates that there is a strong similarity between the soluble constituents found in a solid waste and the treatment it undergoes; i.e., the three Lurgi ashes yielded nearly the same major soluble constituents for all three feed coals employed. The same was true for the two liquefaction wastes. The Illinois No. 6 coal was used in both the Lurgi and H-Coal processes but resulted in

the derivation of different soluble constituents from their wastes. The levels of Cd, K, Mn, Na, Pb, and Sb found in the Lurgi ash leachates were higher than those found in the leachates from the H-Coal and SRC residues under the conditions employed.

In addition to constituents listed under the "Natural pH" column in Table 2, Al, Be, Cr, Co, Cu, F, Fe, Mg, Ni, P, V, and Zn were found in the leachates at concentration levels exceeding the recommended levels in water under certain pH conditions, generally when the pH was acidic.

TABLE 2. CONSTITUENTS WITH CONCENTRATIONS EXCEEDING RECOMMENDED WATER QUALITY LEVELS UNDER THE LABORATORY TEST CONDITIONS

Sample	Natural pH			Range	Adjusted pH
	Air	Argon	Constituents		Additional constituents leached
Lurgi Ash Illinois #6 Coal	7.6	8.9	B, Ca, Cd, K, Mn, NH ₄ , Pb, SO ₄ , Sb	8.9-2.7	Al, Cr, Co, Cu, Fe, Zn
Lurgi Ash Illinois #5 Coal	8.3	10.9	B, Ca, K, Mn, NH ₄ , Pb, SO ₄ , Sb	10.9-3.1	Al, Cd, Cr, Co, Cu, Fe, Ni, Zn
Lurgi Ash Rosebud Coal	8.5	11.1	B, Ca, Cd, F, K, Mo, NH ₄ , Pb, SO ₄ , Sb	11.1-3.1	Al, Cr, Co, Cu, Fe, Mg, Mn, P, Zn
SRC-I Kentucky #9 Coal	6.4	7.5	B, Ca, Fe, Mn, NH ₄ , SO ₄	10.2-2.9	Al, Be, Cd, Cr, Co, K, Ni, Pb, P, V, Zn
H-Coal Illinois #6 Coal	8.8	11.3	Al, B, Ca, NH ₄	11.3-2.3	F, Fe, Mn, Pb, Zn

Discharges of the constituents listed in Table 2 at the levels found in this study could cause some environmental degradation and require wastewater treatment.

Equilibrium Solubility Model

It is difficult to explain the aqueous chemistry of a complex system such as the leachates from coal conversion solid wastes. Possible complexation, ion pair formation, and the effects of organic components on the formation of organo-metallic complexes hinder the description of these systems. On the other hand, it is still of interest to examine these systems in an effort to account for their soluble components, and we progress if we prepare diagrams showing the relations of the known aqueous species to the mineral solid phases.

The solubility and mineral stability diagrams were prepared as described by Garrels and

Christ.¹⁷ The thermodynamic solubility model used in this study (WATEQF) considered the speciation of 115 aqueous inorganic ions and complexes and computed saturation data for over 100 minerals. The theory of the model and its computer implementation have been discussed previously by Truesdell and Jones,^{18, 19} and by Plummer, Jones, and Truesdell.²⁰

The stability relations of the iron oxides and sulfides in water are shown in Figure 1 plotted as a function of Eh and pH. The data from the leachates of the five wastes and a pyrite standard, equilibrated under the same conditions as the solid wastes, are shown plotted on the diagram.

Some explanation of the diagram may aid in interpreting the data. The upper and lower limits of water stability are shown on the diagram and mark the upper and lower boundaries of Eh and pH of concern. That is, at Eh and pH values above the upper boundary shown,

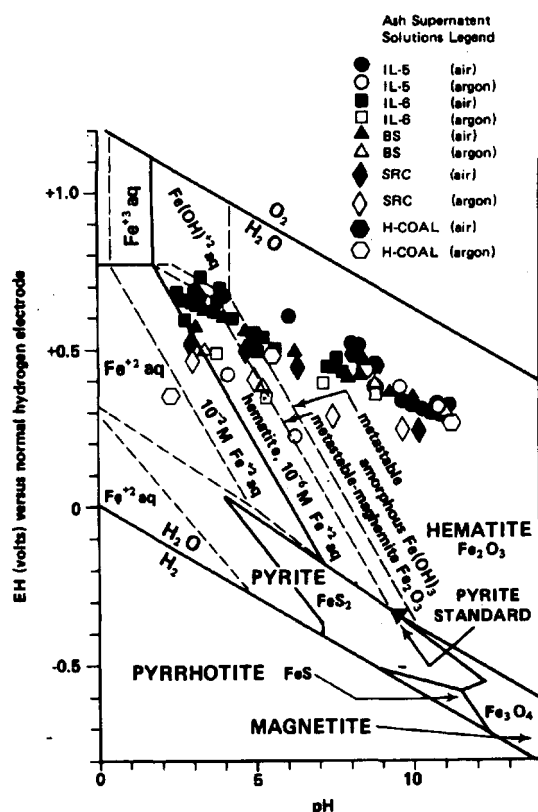


Figure 1. Stability relations of iron oxides and sulfides in water at 25° C when the sum of $S = 10^{-3}M$ and $Fe^{+2}_{aq} = 10^{-6}M$

water decomposes into oxygen gas and at the lower boundary decomposes into hydrogen gas. Thus, Eh and pH values outside this range are not normally of concern when the aqueous chemistry of natural systems is interpreted.

The solid lines between solid phases such as hematite and magnetite mark the boundaries of mineral stabilities. Data points falling within these regions indicate that the samples are within the stability field of the particular mineral. Most of the data points shown in Figure 1 fall within the hematite stability field. This is reasonable because hematite was identified by X-ray diffraction as being present in most of the samples. However, magnetite and pyrrhotite were also identified as minerals present in the solid wastes. These diagrams illustrate that these two minerals are unstable in these systems and, given sufficient time, will decompose to other mineral phases.

Data points that fall on or near a boundary line, such as the pyrite standard plotted in Figure 1, illustrate a solution in simultaneous equilibrium with the various solid phases described by the boundary. The pyrite used in this study was a technical grade material that contained both hematite and magnetite as impurities. Thus, it is reasonable that the solution would be in equilibrium with these three mineral phases and serves to illustrate that the electrodes used in the measurements were operating properly.

The boundaries between solid phases and aqueous species such as between hematite and the aqueous Fe^{+2} ion serve as true "solubility" boundaries; as such, they are a function of the activity of the ion in solution. Two boundaries are shown in Figure 1, one for $10^{-6}M$ and another for $10^{-2}M$ Fe^{+2}_{aq} . The $10^{-6}M$ boundary is chosen by convention, on the premise that if the activity of an ion in equilibrium with a solid phase is less than $10^{-6}M$, the solid will be immobile in the particular environment. This convention was developed largely from experience but seems to correlate well with natural geologic systems. The $10^{-2}M$ boundary was chosen because it corresponds to the upper limit of Fe^{+2} concentrations measured in the leachates from the solid wastes.

The boundary between two aqueous species such as Fe^{+2} and Fe^{+3} ion is drawn where the concentration of each ion is equal. Thus, the labeled areas are areas where the particular ion dominates but where small concentrations of other ions may also be present.

The $10^{-6}M$ boundaries of the metastable minerals maghemite and freshly precipitated ferric hydroxide are shown as dashed lines on the diagram. It is certain that these two minerals are unstable with respect to hematite, pyrite, and magnetite, and that, given sufficient time, will convert to the thermodynamically stable minerals. However, these minerals are clearly of more than transitory existence in natural environments and warrant consideration as mineral phases likely to control iron concentrations during the initial leaching of solid wastes, which may be the environmentally critical period.

The data plotted in Figure 1 indicate that amorphous ferric hydroxide is a likely control on iron concentrations in the leachates at pH values less than 7. Indeed, computations of ion

activity products for the leachates yield good agreement with the solubility constant for the amorphous ferric hydroxide in the acid solutions. The iron concentrations tend to drop below detectable levels in the alkaline solutions.

It is clear from the plot of the data in Figure 1 that the Eh-pH relations of the alkaline leachates are not controlled by equilibria between minerals shown on the diagram. Figure 2 shows the aqueous stability relations of the manganese oxide-carbonate system. The data indicate that the manganese oxides and carbonate are in equilibrium in the alkaline leachates, while the data points for the acid leachates fall in the aqueous Mn^{+2} ion field. This conclusion is supported by the computations of the ion activity products for the manganese minerals. These computations showed that the alkaline solutions were generally in equilibrium with the manganese oxides or carbonate on which boundary the particular data points shown in the diagram fell. The acid leachates were undersaturated with respect to the various manganese minerals, as deduced from Figure 2. Thus, it appears that manganese oxides control the Eh-pH relations

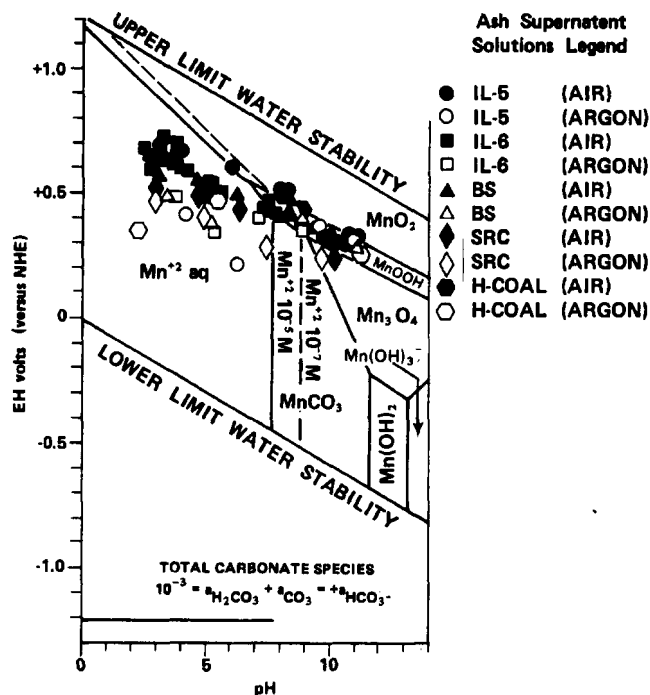


Figure 2. Stability relations of manganese oxides in water at 25° C.

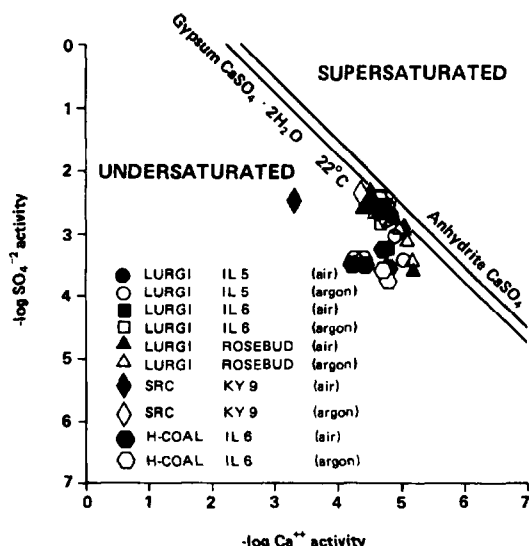


Figure 3. Calcium sulfate equilibria of leachates from five coal conversion solid wastes.

of the alkaline leachates and metastable freshly precipitated ferric hydroxide in the acid leachates.

The solubility relations of anhydrite and gypsum are shown in Figure 3. Here, the solubility of gypsum exerts a dominant influence over calcium and sulfate concentrations in the leachates at all pH levels, with the exception of the H-Coal leachates. The H-Coal leachates are all undersaturated with respect to gypsum, but gypsum still provides the upper boundary for prediction of calcium and sulfate concentrations. This is noteworthy because the H-Coal residue contained the highest concentrations of sulfur but had the lowest water-soluble sulfur levels, including all sulfur species considered. This underscores the need for information on mineral forms in the solid waste in addition to chemical analysis of the waste.

The calcium and magnesium carbonate equilibria of alkaline (pH > 7.6) leachates from the five solid wastes in contact with air are shown in Figure 4. Calcium concentrations of the acid leachates were controlled by gypsum equilibria, but it is expected that calcium concentrations in alkaline solutions in contact with atmospheric carbon dioxide would be controlled by calcite solubility. However, the data plotted in Figure 4 indicate that the solutions are supersaturated

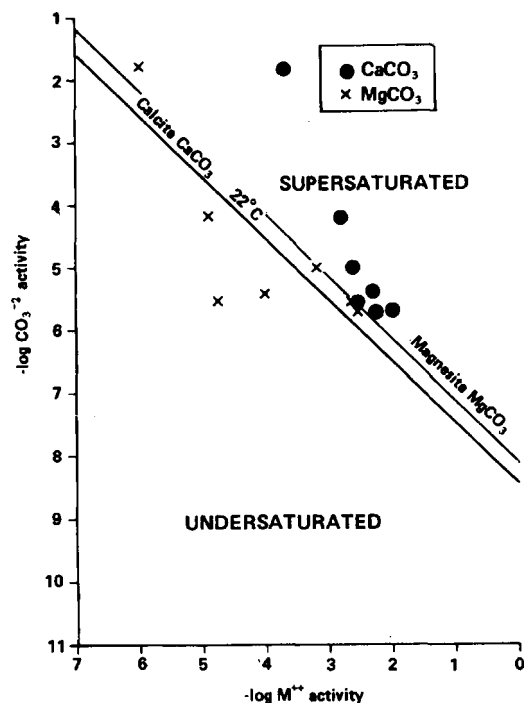


Figure 4. Calcium and magnesium carbonate equilibria of alkaline ($\text{pH} > 7.6$) leachates from five coal conversion solid wastes in contact with air.

with respect to calcite while some samples are either in equilibrium with or undersaturated with respect to magnesite. Other workers have also noted higher solubility of calcite in the presence of Mg. Hassett and Jurinak²¹ found that calcites with low levels of Mg showed an increase in solubility. Likewise, Berner²² showed incorporation of Mg within the calcite to be considerably more soluble than pure calcite. Further, the presence of Mg and SO_4 have been shown by Aken and Lagerwerff²³ to enhance the solubility of calcite. Thus, it appears that magnesite equilibria in alkaline leachates can be used to predict the upper bounds on Mg concentrations but that problems with supersaturation preclude the use of calcite to make similar predictions of Ca concentrations.

The silicon dioxide and aluminum hydroxide solubility equilibria are shown in Figure 5. Most samples were found to fall within the range of Si solubilities expected from amorphous glass and quartz. This is consistent with the experimental design, which employed glass carboys as the

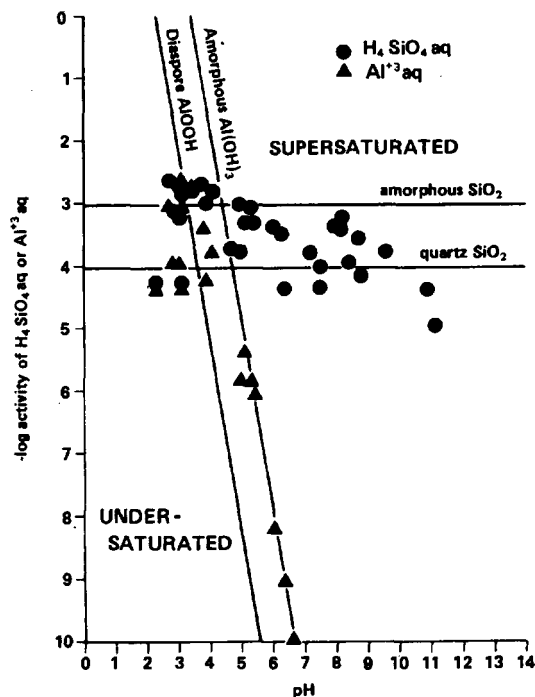


Figure 5. Silicon dioxide and aluminum hydroxide solubility equilibria of leachates from five coal conversion solid wastes.

equilibration vessel and in which quartz was identified as being present in all the solid wastes. Amorphous SiO_2 is clearly not the most stable phase, and silica concentrations, after long time periods, would be expected to be controlled by aluminosilicate minerals or quartz.

The Al equilibria in the mid-acid and alkaline (not shown) pH range were dominated by the amorphous hydroxide. Similar to the Fe and Si equilibria, a metastable mineral phase was apparently controlling the solubility. It is clear that these metastable mineral phases must be considered when the environmental impact is predicted during the initial leaching of coal conversion solid wastes.

The aqueous chemistry of some other potential contaminants was examined. For example, computation of ion activity products for BaSO_4 indicated that Ba concentrations in the leachates would never exceed 0.1 ppm, even in very acid solutions. Fluoride concentrations in the leachates were predicted to be controlled by precipitation of fluorite (CaF_2) and fluorapatite

($\text{Ca}_5(\text{PO}_4)_3\text{F}$). Phosphate levels in the alkaline leachates would never exceed 1 ppb; this was predicted from the ion activity product calculations for fluorapatite and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$). In the acid leachates, phosphate levels are predicted to be controlled by precipitation of insoluble iron and manganese phosphates.

The data from this study strongly suggest that removal of trace metals such as Cd, Co, Cr, Cu, Ni, Pb, and Zn from slurry pond leachates may be controlled by adsorption on or coprecipitation with iron, manganese, and aluminum oxides and hydroxides. The removal of trace metals by this mechanism would be operative for long time periods because the adsorptive capacity of the solid phase would be continually replenished by formation of new metal oxides in the leachates. In any case, the partitioning between trace metals and solid phases must be considered when trace metal mobility is evaluated in these systems. Further, these studies show that hydroxide, sulfate, and carbonate are the major inorganic ligands that must be considered.

Thus, application of thermochemical solubility models to the coal solid waste leachates examined in this study has yielded valuable insight into the potential pollution hazards of these wastes. It has shown that, while the concentrations of chemical constituents in the solid wastes and leachates varied over a wide range, similar mineral phases controlled the aqueous solubility of many major, minor, and trace ionic species for all five of the solid wastes.

ACKNOWLEDGMENTS

We gratefully acknowledge the U.S. Environmental Protection Agency, Fuel Process Branch, Research Triangle Park, North Carolina, for partial support of this work under Contract 68-02-2130, Characterization of Coal and Coal Residues. We also are indebted to the Peabody Coal Company, Freeburg, Illinois; to Hydrocarbon Research, Inc., Trenton, New Jersey; and to Pittsburg and Midway Coal Mining Co., Fort Lewis, Washington, for supplying us with samples.

The authors are indebted to G. V. Smith, C. C. Hinkley, and M. Saporoschenko of Southern Illinois University, Carbondale, for Mössbauer

Spectroscopic Analysis of the samples. The authors also wish to thank the Analytical Chemistry Section of the Illinois State Geological Survey under the direction of Dr. R. R. Ruch, and to thank Dr. H. D. Glass and T. M. Johnson for assistance in portions of this research.

REFERENCES

1. Cavanaugh, E. C., and W. C. Thomas. *Environmental Assessment of Low/Medium Btu Gasification: Annual Report*. U.S. Environmental Protection Agency. Publication Number EPA-600/7-77-142. Washington, D.C. 1977.
2. Cavanaugh, E. C., W. E. Corbett, and G. C. Page. *Environmental Assessment Data Base for Low/Medium Btu Gasification Technology*. U.S. Environmental Protection Agency. Publication Number EPA-600/7-77-125a. Washington, D.C. 1977.
3. Somerville, M. H., and J. L. Elder. A Comparison of Trace Metal Analyses of North Dakota Lignite Laboratory Ash with Lurgi Gasifier Ash and Their Use in Environmental Analysis. In: *Environmental Aspects of Fuel Conversion Technology III*, Ayer, F. A. (ed.). Research Triangle Park, U.S. Environmental Protection Agency, 1978.
4. Filby, R. H., K. R. Shah, and C. A. Sautter. Trace elements in the Solvent Refined Coal Process. In: *Environmental Aspects of Fuel Conversion Technology III*, Ayer, F. A. (ed.). Research Triangle Park, U.S. Environmental Protection Agency, 1978.
5. Sinor, J. E. *Evaluation of Background Data Relating to New Source Performance Standards for Lurgi Gasification*. U.S. Environmental Protection Agency. Publication Number EPA-600/7-77-057. Washington, D.C. 1977.
6. Griffin, R. A., R. M. Schuller, J. J. Suloway, S. J. Russell, W. F. Childers, and N. F. Shimp. Solubility and Toxicity of Potential Pollutants in Solid Coal Wastes. In: *Environmental Aspects of Fuel Conversion Technology III*, Ayer, F. A., (ed.). Research Triangle Park, U.S. Environmental Protection Agency, 1978.
7. Ruch, R. R., H. J. Gluskoter, and J. E. Kennedy. *Mercury Content of Illinois coals*. Il-

- Illinois State Geological Survey. Environmental Geology Note 43. 1971. 15 p.
8. Ruch, R. R., H. J. Gluskoter, and N. F. Shimp. *Occurrence and Distribution of Potentially Volatile Trace Elements in Coal: An Interim Report*. Illinois State Geological Survey Environmental Geology. Note 61. 1973. 43 p.
9. Ruch, R. R., H. J. Gluskoter, and N. F. Shimp. *Occurrence and Distribution of Potentially Volatile Trace Elements in Coal: A Final Report*. Illinois State Geological Survey Environmental Geology. Note 72. 1974. 96 p.
10. Gluskoter, H. J. Mineral Matter and Trace Elements in Coal. In: *Trace Elements in Fuel* (Advances in Chemistry Series 141), Babu (ed.). American Chem Soc. p. 1-22.
11. Gluskoter, H. J., R. R. Ruch, W. G. Miller, R. A. Cahill, G. B. Dreher, and J. K. Kuhn. *Trace Elements in Coal: Occurrence and Distribution*. Illinois State Geological Survey. Circular 499. 1977.
12. Braunstein, H. M., E. D. Copenhaver, and H. A. Pfudere. *Environmental Health, and Control Aspects of Coal Conversion: An Information Overview*. Oak Ridge National Laboratory. ORNL/EIS-94 and 95, Volumes 1 and 2. 1977.
13. Parker, Leon C., and Dewey L. Dykstra. *Environmental Assessment Data Base for Coal Liquefaction Technology*. U.S. Environmental Protection Agency. EPA-600/7-78-184a and 184b. September 1978.
14. Schuller, R. M., J. J. Suloway, R. A. Griffin, S. J. Russell, and W. F. Childers. Identification of Potential Pollutants from Coal Conversion Wastes. In: *Proceedings of the Society of Mining Engineers—American Institute of Mining Engineers Annual Meeting, New Orleans, February 18-22, 1979*.
15. Griffin, R. A., R. M. Schuller, J. J. Suloway, N. F. Shimp, and W. F. Childers. U.S. Environmental Protection Agency. *Final Report for Contract 68-02-2130, Task D*. Research Triangle Park, N.C. 1979.
16. *1972 Water Quality Criteria*. U.S. Environmental Protection Agency. R3-73-033. Washington, D.C.
17. Garrells, R. M., and C. L. Christ. *Solutions, Minerals, and Equilibria*, New York, Harper and Row, 1965.
18. Truesdell, A. H., and B. F. Jones. *WATEQ, a Computer Program for Calculating Chemical Equilibria on Natural Waters*. National Technical Information Service. P.B. 220464. 1973.
19. Truesdell, A. H., and B. F. Jones. *WATEQ, a Computer Program for Calculating Chemical Equilibria on Natural Waters*. *U.S. Geol Survey J. Research*. 2:233-248. 1974.
20. Plummer, N. L., B. F. Jones, and A. H. Truesdell. *WATEQF—A Fortran IV Version of WATEQ, a Computer Program for Calculating Chemical Equilibrium of Natural Waters*. U.S. Geological Survey Water-Resources Investigations 76-13. NTIS No. PB-261-027. 1976.
21. Hassett, J. J., and J. J. Jurinak. Effect of Mg^{+2} ion on the Solubility of Solid Carbonates. *Soil Sci Soc Am Proc*. 35:403-406. 1971.
22. Berner, R. A. The Role of Magnesium in the Crystal Growth of Calcite and Aragonite From Sea Water. *Geochimica et Cosmochimica Acta*. 39:489-504. 1975.
23. Akin, G. W., and J. V. Lagerwerff. Calcium Carbonate Equilibria in Solutions Open to the Air. II. Enhanced solubility of $CaCO_3$ in the presence of Mg^{+2} and SO_4^{-2} . *Geochimica et Cosmochimica Acta*. 29:253-260. 1965.

HAZARDOUS WASTE—DEFINITION AND REGULATION

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Abstract

The Resource Conservation and Recovery Act of 1976 (RCRA), in amending the Solid Waste Disposal Act, created a regulatory framework in which to control waste materials disposal. The Act further requires the U.S. Environmental Protection Agency (EPA) to set and enforce standards for managing hazardous wastes. This paper summarizes the development of the definition of hazardous waste, based on the requirements of RCRA and the other standards mandated by RCRA. These regulations, proposed in the Federal Register on December 18, 1978, are briefly reviewed.

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA), which substantially amends the Solid Waste Disposal Act, creates a regulatory framework in which to control the disposal of wastes defined as hazardous. Subtitle C of RCRA requires the U.S. Environmental Protection Agency (EPA), in consultation with State governments, to develop national standards to define hazardous wastes; generators and transporters of hazardous waste; performance, design, and operating requirements for hazardous waste treatment, storage, and disposal facilities; a permit system for such facilities; and guidelines describing conditions under which State governments will be authorized to carry out the hazardous waste control program.

This "cradle-to-grave" concept is somewhat unique but necessary to ensure that wastes requiring special management are handled only at facilities with proper permits. All stages of the hazardous waste management cycle are controlled, whether the waste is managed "onsite," at the point of generation, or transported to an "offsite" waste management facility.

The national standards mentioned previously have been proposed for public comment and are to be finalized no later than December 31, 1979. RCRA provides that these standards will go into effect 6 mo after final promulgation, or in early summer of 1980.

The proposed regulatory strategy uses a pathways approach wherein the path and destination of any hazardous waste are controlled without particular attention to the source of the waste. This approach is basically different from the approach used to regulate air and water pollution, where specific standards are written for and tailored to each industrial category. The pathways approach was chosen because hazardous wastes are mobile and can be disposed of at locations far from the generating sources, whereas industrial, air and water pollution sources are fixed and relatively easy to identify.

I will briefly review the regulations within the proposed hazardous waste program and provide additional detail on the proposed definition of hazardous waste.

HAZARDOUS WASTE DEFINITION

RCRA requires hazardous waste to be defined by inherent characteristics (e.g., flammability and corrosiveness) and by listing of particular hazardous wastes.

HAZARDOUS WASTE GENERATORS

The proposed standards for hazardous waste generators require recordkeeping, annual reports, proper containing and labeling of hazardous waste shipped offsite for disposal, and a transport manifest document for each shipment. Retailers, farmers, and generators of small amounts of waste (less than 100 kg/mo) are excluded from these requirements provided they dispose of waste in State-approved facilities. Generators do not need permits.

*Speaker.

HAZARDOUS WASTE TRANSPORTERS

Hazardous waste transporters are required to take the hazardous waste shipments only to the permitted facility designated by the generator, to keep appropriate records, and to report spills enroute. Transporters (as in the case with generators) do not need permits in the Federal system, but some States require hazardous waste transporters to be registered.

HAZARDOUS WASTE FACILITY STANDARDS AND PERMITS

National standards for hazardous waste treatment, storage, and disposal facilities not only establish acceptable levels of performance that such facilities must achieve but also are the criteria against which regulatory officials will measure applications for permits. In setting facility standards, EPA has relied primarily on specific design and operating standards (as opposed to general ambient or source emission standards) because they are more easily understood and enforced than other types of standards.

STATE HAZARDOUS WASTE PROGRAMS

Congress intended that EPA establish national standards for hazardous waste management but that the individual States implement and enforce this new regulatory program. EPA has developed a guideline that describes the elements a State hazardous waste program must have in order for that State to have authority to carry out the national program. Among other things, States must have legislation and regulations for hazardous waste management that are no less stringent than in the Federal analogs and must demonstrate that they have adequate resources to administer and enforce the program.

DEVELOPMENT OF THE PROPOSED DEFINITION

I would like to highlight the development of the definition of hazardous waste in the December 18, 1978 *Federal Register*. Before a material can be defined as a hazardous waste, it must first be established that the material is a solid

waste. RCRA defines "solid waste" as "any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant, or air pollution control facility and *other discarded material*, including solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations and from community activities. The term does not include solid or dissolved material in domestic sewage or solid or dissolved materials in irrigation return flows or industrial discharges that are point sources subject to permits under Section 402 of the Federal Water Pollution Control Act, as amended, or source, special nuclear, or byproduct material as defined by the Atomic Energy Act of 1954; as amended." There are three noteworthy aspects of a solid waste definition. The term encompasses not only solids, but liquids, semisolids, and contained gases; it explicitly excludes certain materials; and it includes "other discarded material." EPA has grappled with the meaning of "other discarded material" for over a year because it is one of the more ambiguous yet important parts of the definition. For example, are byproducts of manufacturing processes "discarded materials"? Sometimes they are, and sometimes they aren't. Are materials sent to recycling or reprocessing centers "discarded materials"?

After substantial discussion and comment inside and outside the Agency, EPA has judged this phrase to mean any material that is abandoned or committed to final disposition; reused, if such use constitutes land disposal; and a waste oil, if it is incinerated or burned as a fuel.

Under this definition, for example, used solvents sent to a reclaiming facility would not be considered a discarded material and, therefore, would not be considered a solid or a hazardous waste. Similarly, materials being transferred between industrial facilities, perhaps via a waste exchange, would not be subject to hazardous waste controls. On the other hand, materials reused in a way involving land application (i.e., soil conditioners, fill materials, dust suppressants, etc.) would be considered discarded materials because reuse of materials in this manner could result in serious adverse impacts from uncontrolled release and dispersion of contaminants into the environment. Similarly, EPA has singled out *waste oils* for special control

because they are ubiquitous and there are documented health and environmental problems associated with their reuse.

Criteria of Identification and Listing

In defining a hazardous waste as mandated in Section 3001 of RCRA, EPA is required to develop and promulgate criteria for identifying the characteristics of hazardous waste and for listing hazardous waste, and to identify the characteristic of hazardous waste and list particular hazardous wastes. As a first step in this definition process, EPA has developed a set of criteria in defining the characteristics of a hazardous waste and for listing these wastes. These criteria are identified in Section 250.12 of the proposed rule and are:

- *Criteria for Identifying Characteristics of a Hazardous Waste*
 - Damage cases: certain wastes are known to have caused substantial public health or environmental damage in documented cases.
 - Availability of economical sampling and analysis procedures for a particular property of the waste.
- *Criteria for Listing Hazardous Wastes*
 - The waste is known to meet, or strongly suspected of meeting, one of the defined general characteristics.
 - The waste meets the statutory definition of a hazardous waste.

Based on these criteria, EPA has elected to define the general characteristics of ignitability, corrosivity, reactivity, and certain aspects of toxicity to identify hazardous wastes. It should be noted that EPA also attempted to define characteristics of infectious and radioactive waste and other aspects of toxicity such as genetic change potential and bioaccumulation. However, in developing this regulation, EPA encountered difficulty in describing these properties and elected to deal with potentially infectious, radioactive, and certain toxic wastes by listing known sources of these wastes or processes likely to produce them. EPA does intend to explore the appropriateness of additional characteristics to further define toxicity and radioactivity. To this end, it has published an advanced notice of proposed rulemaking seeking additional data related to these concepts. It should also be emphasized that neither the char-

acteristics nor the listing is static. Both may be added to or changed, after opportunity for public comment, as new information develops.

Hazardous Waste Characteristics

In order to provide specific descriptions of wastes meeting these characteristics, each characteristic was defined in terms of specific definable properties. The following is a brief description of each characteristic and its properties.

- *Ignitability.* The objective of the ignitability characteristic is to identify wastes that may present a fire hazard under routine waste disposal and storage conditions. The resulting fires at disposal and storage facilities present not only the immediate danger of heat and smoke but can initiate explosions, generate toxic vapors, and provide a pathway by which toxic particulates can spread to the surrounding area. (The term ignitable was chosen to avoid confusion with the U.S. Department of Transportation's (DOT) category of "flammable" in its hazardous materials transportation regulations).

Several methods can be used to identify ignitable wastes, depending on the physical state. For liquid wastes, flash point was selected as the property to use because testing methods are available and are the most reproducible. The flash point proposed for identifying ignitable wastes is 140° F (60° C); this value was selected after consideration of ambient temperatures to which wastes may be exposed during management.

For solid wastes, a prose definition was selected because test methods are not available for ignitable solids that simulate the field conditions to which a waste is subject during handling and management. For waste gases, EPA proposes to use the DOT identification for flammable compressed gases because the major hazard from ignitable gases would arise during transport.

- *Corrosivity.* A corrosivity characteristic has been included to identify wastes that must be segregated from others because of ability to extract and solubilize toxic contaminants (especially heavy metals) that might otherwise not migrate, and to identify wastes requiring special containers during transportation and storage.

While heavy metal solubilization is an extremely complex phenomenon, pH has been found to be its most important indicator. The pH limits chosen in these proposed regulations were based upon skin corrosion limits and heavy metal solubilization data. The metal corrosion limits were taken from DOT hazardous materials regulations because EPA's concern about container damage is identical to that of DOT's in this case.

- **Reactivity.** The object of the reactive waste characteristic is to identify wastes that under routine management present a hazard because of instability or extreme reactivity. Reactivity includes the tendency to auto-polymerize, to create a vigorous reaction with air or water, to exhibit shock and thermal instability, to generate toxic gases, and to explode.

In their proposed regulation, EPA included a descriptive definition of a reactive waste, together with test methods for thermal and shock instability, because of the problem in developing general test methods for identifying reactive wastes. While there are many inputs of energy that may cause a waste to react or exhibit hazardous properties, there is no one stress that can cause all reactive waste to do so. To compound the problem, reactivity is not just a function of the composition, temperature, and availability of initiating agents. It is also affected by the mass and geometry of the waste. Thus, the reactivity of a tested waste sample may not necessarily correspond to the reactivity of the waste as a whole.

Because reactive waste is dangerous to the generator's own operations (as well as being hazardous for long-term disposal), generators of reactive waste tend to be aware that their waste has that characteristic. For this reason, EPA considers the proposed descriptive definition an adequate identification method when it is used in conjunction with the test methods identifying thermal and shock instability.

- **Toxicity.** The toxicity characteristic is intended to identify waste which, if improperly disposed of, may release toxicants in sufficient quantity to pose a substantial hazard to human health or the environment. The RCRA definition of hazardous waste re-

quires EPA to judge the hazard posed by a waste "when improperly treated, stored, transported, or disposed of, or otherwise managed." For waste containing toxic constituents, the hazard depends on two factors: the intrinsic hazard of the constituents of the waste, and the release of the constituents to the environment under conditions of improper management.

To assess the intrinsic hazard posed by the constituents, a series of toxicity indicators were initially considered: acute and chronic toxicity to humans, animals, and plants; potential for bioaccumulation in tissue; oncogenicity; mutagenicity; and teratogenicity.

However, the toxicity definition proposed December 18, 1978, has been limited as noted earlier to include only toxicants for which National Interim Primary Drinking Water Standards (NIPDWS) have been developed.

To determine whether toxic constituents in the waste might migrate in the disposal environment, a procedure has been developed to measure the tendency of the constituents of a waste to leak or leach out and become available to the environment under poor management conditions.

Numerous studies and reports indicate that damage to ground- and surface water frequently results from migration of toxic chemicals from a disposal site. Groundwater contamination is a particularly important concern because groundwater provides drinking water to almost one-half of the population. In addition, once contaminated, an aquifer's usefulness as a source of drinking water may be impaired for years. It was thus decided that use of a groundwater contamination scenario to "model" improper disposal would be advisable. By selecting a groundwater contamination scenario, we did not mean to imply that other vectors are not important. However, we do feel that except in rare cases, control levels set using this model will be sufficient to protect against other routes of contamination.

The model is based on wastes creating a problem through migration of chemicals out of the disposal site and into a drinking water aquifer. I want to emphasize that the contamination model has been developed for definitional purposes only. It does not address particular disposal

methods that might be used by the regulated community.

The test scheme commonly referred to as the extraction procedure (EP) has been devised to meet the limited definition of toxic waste. The EP coupled with a model scenario of leachate transport related the concentrations of certain toxic components found in the extract of the waste to the EPA NIPDWS. Any waste whose EP extract contains heavy metals or pesticides controlled by the NIPDWS in a concentration greater than 10 times the drinking water standard is considered a hazardous waste.

A waste that has any of the above characteristics is a hazardous waste by RCRA definition *whether or not* that waste is listed. Consequently, use of characteristics in the hazardous waste definition implies responsibility on the part of waste generators to evaluate their wastes for these characteristics (or to declare their wastes hazardous) if there is any doubt about the status of their waste.

Hazardous Waste Listings

The second way a waste can be brought into the hazardous waste regulatory program is by including that waste on a list. Actually, EPA has developed four separate hazardous waste lists including:

- A list of generic hazardous wastes common to many different sources (i.e., electroplating wastes, paint wastes, etc.);
- A list of known sources of infectious wastes, such as hospital wastes from the laboratories;
- A list of industrial processes known to produce hazardous waste, such as heavy ends or distillation residues from carbon tetrachloride fractionation; and

- A list of some 275 substances, which, if disposed of in pure form or as a result of off-specification production, would be hazardous.

There are approximately 175 specific wastes, waste sources, and wastes from certain processes that EPA has identified as hazardous based on previous studies of industrial wastes, damage cases, testing of wastes, and State hazardous waste program data.

There may be cases, however, where a particular facility within a listed source or process category believes that its waste is nonhazardous because the facility uses different raw materials than normal, or has made process modifications or provides onsite treatment prior to disposition. In such cases, the individual facility can petition for exemption from the Subtitle C control program by submitting appropriate waste-testing data and requesting a determination of noncoverage of Subtitle C for the facilities' waste.

Summary

In summary, EPA is required to define hazardous wastes using dual approaches of identifying general characteristics and listing specific hazardous wastes. As regulation development evolved, the Agency found it necessary to defer proposing certain characteristics considered earlier pending further study. At the same time, EPA has added to and sharpened the focus of the hazardous waste list. We believe the net result of these changes will make it much easier for waste handlers to determine whether they are in or out of the Subtitle C regulatory program, and at the same time, focus the program on those wastes of most concern.

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FACTORS CONSIDERED IN EFFLUENT LIMITATIONS GUIDELINES DEVELOPMENT

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Abstract

In the area of coal conversion, studies conducted by the U.S. Environmental Protection Agency (EPA) have been directed primarily through its Office of Research and Development in Research Triangle Park. Information generated has proven useful in regulation writing. Most of the past studies were conducted in the laboratory. Onsite studies to evaluate wastewater characteristics and wastewater treatment technology applicability are necessary and encouraged. In addition to waste characterization and technology assessment, cost, industry profile, water quality criteria, nonwater quality-related impacts, and other factors must be considered in regulation development.

The Federal Water Pollution Control Act (as amended in 1977) required the establishment of technology-based and industry-specific effluent limitations guidelines for point source dischargers. The Effluent Guidelines Division (EGD) of the U.S. Environmental Protection Agency (EPA) has been delegated that responsibility. The Act does not specify the date when guidelines must be promulgated for coal conversion facilities.

In the area of coal conversion, activities by the Effluent Guidelines Division have been minimal. EGD has been relying on its Office of Research and Development to gather fundamental information. When EGD actively pursues guideline development, it is unlikely that all conversion processes will be addressed at the same time. The low-Btu gasification processes will probably be the first group to be considered.

Because EGD does not have any active program in this area, the only subject I can address at this time is the type of information that EGD will consider in its regulation development. The task of developing information to support tech-

nology-based effluent limitations guidelines can be divided into five discrete elements:

- Industry profile,
- Wastewater characterization,
- Selection of candidate treatment technologies,
- Cost analysis of candidate treatment options, and
- Subcategory review.

Information on the industry's current and projected distribution is important because the Agency must consider environmental impact and national cost implication in writing the guidelines. The type of data needed to define the industry includes:

- Description of the process,
- Number and size of existing and projected facilities using each of the processes,
- Geographical location and the type of coal used,
- Economics of this industry and its competitive industries,
- Current or anticipated regulations the industry is or will be subjected to, and
- Stage of process development.

Reports prepared by EPA's Office of Research and Development have provided much of the needed information.

Data on wastewater characteristics are necessary to assess the degree of environmental impact and applicability of treatment technology. The Agency must define the quality and quantity of pollutants from aqueous effluents. The effluents of concern include those which are process- and nonprocess-related. Normally, EGD conducts sampling and analytical studies at full-scale facilities whenever possible. Smaller units can be sampled if full-scale facilities are not available or accessible. In the past, EGD has successfully cooperated with the regulated industries and anticipates that this industry will be just as cooperative. The FWPCA (Section 308) authorizes the Agency to obtain informa-

tion necessary for regulation writing.

Analytical data of wastewater characteristics from bench-scale operation can be used in providing "order of magnitude" estimates of the potential problem and determining the applicability of wastewater treatment technologies. The Agency is required to assess the discharge of the 129 toxics substances as well as conventional and nonconventional pollutants. The analytical method used must be able to quantify the pollutants at parts-per-billion level. A lower detection level is required because the water quality criteria (proposed) for some of the pollutants are quite low. Studies have been conducted by EPA's Office of Research and Development on wastewater characteristics. These studies quantify the concentration of pollutants that are present at the 1-mg/L level and above. Some of the latter studies attempted to quantify the 129 priority pollutants to lower levels. The streams analyzed are primarily from bench-scale process operations. Despite some of the excellent studies conducted by ORD, an additional data base will be required prior to regulation writing.

Once the pollutants discharged are defined, the Agency must evaluate technology available to reduce the level of discharge. The Agency can require both end-of-pipe treatment and in-plant water use modification. The first technology option to be considered will be complete water recirculation and reuse. Other technology options such as end-of-pipe treatment without recirculation and best management practice requirements will also be considered. Alternative technologies must be evaluated during guidelines development in terms of cost, energy con-

sumption, water requirement, water quality criteria, effluent quality, pollutant reduction, and impact on air and solid media.

Currently, ORD is conducting wastewater treatment assessment programs on a bench-scale basis. Once the information from these and other programs becomes available, applicable technology options may be determined. These options should be tested in the pilot-plant scale whenever possible.

Cost strongly affects the selection of treatment options. An economic impact assessment will be performed to determine whether the cost would make the process economically unfeasible and the extent to which production cost would be increased.

Effluent limitation guidelines are national regulations. This does not mean that the effluent limitations will be the same for all the coal conversion facilities. The Agency can promulgate different guidelines for plants with certain unique features (subcategorization). The justification for subcategorization can be waste characteristic, land availability, cost, and treatment technology applicability.

In summary, EGD must consider various factors in writing regulations. The work that has been done to date is useful, but more studies are needed to generate the information necessary for regulation development. We may be at the stage (at least for some of the coal conversion processes) for EPA to interact directly with DOE and perform studies at the site where the processes are being developed. Use of information that represents real situations would be beneficial to both the regulator and the regulated.

WATER REQUIREMENTS FOR SYNTHETIC FUELS PLANTS

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Abstract

The water requirements for several synthetic fuel technologies have been estimated at given locations in the major coal- and oil shale-bearing regions of the United States. The synthetic fuel technologies examined include: coal gasification to convert coal to pipeline gas (Lurgi, Synthane, Hygas, and Bigas processes); coal liquefaction to convert coal to low-sulfur fuel oil (Synthoil process); coal refining to produce deashed low-sulfur solvent-refined (clean coal) (solvent refined coal process); and oil shale retorting to produce synthetic crude (Paraho Direct, Paraho Indirect, and TOSCO II processes). A total of 90 plant-site combinations were studied in the Appalachian, Illinois, Powder River, Fort Union, and Four Corners coal regions and in the Green River oil shale region. Results are presented for the total net water consumed by conversion process for each coal and oil shale region.

Particular emphasis has been placed on determining the water consumed for cooling because cooling is often the largest consumer of water in a conversion plant. Three cooling options were considered representing different degrees of wet evaporative cooling for turbine condensers and gas compressor interstage coolers. The cost and availability of water determines the degree to which wet or evaporative cooling should be used. Estimates have been made of the cost of transporting water from different sources to the conversion plant in the Western States to determine the most suitable cooling option. The criterion of water availability was used to determine the most suitable cooling options in the Eastern and Central States.

INTRODUCTION

Since the 1973 oil embargo, there has been considerable debate in the United States concerning the role coal or oil shale will play in solving the energy problem. There is one important

issue on which all sides agree, and that is the importance of water in the production of synthetic fuels. Converting coal or shale to a synthetic fuel is basically a hydrogenation process in which water is the source of the hydrogen. The weight ratio of carbon to hydrogen is higher for the raw material than for the gaseous or liquid synthetic fuel. In the conversion, sulfur and nitrogen are reduced to produce a cleaner fuel, and ash, oxygen, and nitrogen are reduced to produce a product with a higher heating value than the original coal or shale. Water is required to dissipate to the atmosphere the thermal energy not recovered in the process of converting the coal or shale to the synthetic fuel, to mine and prepare the raw material, and to dispose of the spent ash and shale and any other unwanted constituents removed in conversion. Water is also required for fugitive dust control within the plant, for sanitary and potable water usage in the mine and the plant, and for reclamation of the disturbed land.

This paper deals specifically with water requirements for integrated mine-plant designs for manufacturing gaseous, liquid, and solid synthetic fuels from coal and shale and how these requirements are affected by the local cost and availability of water. The work is based on a report recently completed for the U.S. Department of Energy (DOE Contract No. EX-76-C-01-2445) and the U.S. Environmental Protection Agency (EPA Contract No. 68-03-2207).¹ The range of water requirements for each conversion process—with no distinction made between coal- and oil shale-bearing region—is summarized in Reference 2. In the present paper, particular emphasis is placed on determining the water consumed for cooling because cooling is often the largest consumer of water in a conversion plant. The results will be summarized by conversion process and by coal- and oil shale-bearing region.

PROCESS AND SITE SELECTION

The synthetic fuel technologies examined in-

*Speaker.

clude: coal gasification to convert coal to pipeline gas; coal liquefaction to convert coal to low-sulfur fuel oil; coal refining to produce a de-ashed, low-sulfur solvent-refined (clean) coal; and oil shale retorting to produce synthetic crude. A number of processes were chosen for each conversion. Detailed conceptual designs for integrated mine-plant complexes were made for each of the representative conversion processes.¹ The processes and products chosen for comparison are shown in Table 1. Except for the commercially available Lurgi process, the processes chosen are representative of those that have undergone extensive development and that are sufficiently described in the available literature so detailed process calculations can be made. The products chosen are synthetic fuels; the production of chemicals from coal or shale (e.g., ammonia or methanol) was not considered. The specific designs given in Reference 1 are based on standard-sized plants with the given product output. A number of processes were chosen for each conversion. Detailed conceptual designs for integrated mine-plant complexes were made for each of the representative con-

version processes.¹ The processes and products chosen for comparison are shown in Table 1. Except for the commercially available Lurgi process, the processes chosen are representative of those that have undergone extensive development and that are sufficiently described in the available literature so detailed process calculations can be made. The products chosen are synthetic fuels; the production of chemicals from coal or shale (e.g., ammonia or methanol) was not considered. The specific designs given in Reference 1 are based on standard-sized plants with the given product output.

A large number of site and process criteria combinations were studied to obtain meaningful assessments on a regional and national level from detailed local results. For coal conversion, the process criteria have been defined based on the quality of the foul condensate recovered after gasification or liquefaction. Low-temperature gasifiers (e.g., Lurgi and Synthane) give a very dirty process condensate (typical values for bituminous coals: BOD ~ 10,000 mg/L, phenol ~ 3,000 mg/L, and ammonia ~ 4,500 mg/L), while high-temperature gasifiers (e.g.,

TABLE 1. PRODUCT FUEL OUTPUT OF STANDARD-SIZED SYNTHETIC FUEL PLANTS

Technology and Conversion Process	Product	Output	Product Heating Value (10 ¹¹ Btu/day)
Coal Gasification	Pipeline Gas	250x10 ⁶ scf/day	2.4
Lurgi			
Synthane			
Hygas			
Bigas			
Coal Liquefaction	Fuel Oil	50,000 barrels/day	3.1
Synthoil			
Coal Refining	Solvent Refined Coal	10,000 tons/day	3.2
SRC			
Oil Shale	Synthetic Crude	50,000 barrels/day	2.9
Paraho Direct			
Paraho Indirect			
TOSCO II			

Koppers-Totzek and Bigas), give a relatively clean condensate (typical values: ammonia ~ 4,500 mg/L, BOD and phenol ~ small). The Hygas gasifier, which is an intermediate temperature gasifier, gives a process condensate of intermediate quality. Both the solvent refined coal (SRC) and Synthoil processes have the foulest condensates. For oil shale conversion, the degree of water management depends on the type of retort used. For direct-heated retorting processes (e.g., Paraho Direct) most of the water is recovered. However, for indirect-heated processes, (e.g., Paraho Indirect and TOSCO II) the water in the combustion products is generally lost up the furnace stack and not recovered.

As for site criteria, brackish groundwater would have to be considered an important conjunctive supply to surface waters in the West, while surface waters are considered primarily in the East. Eastern and Central States have humid climates, while climates in the West are arid and semiarid. Eastern and central coals are both underground- and surface-mined, while western coals are primarily surface-mined. In the West, underground mining followed by surface retorting of oil shale has been investigated extensively. In-situ retorting was not considered in the present study because it is still under development and cannot yet be considered commercial, although it could drastically reduce the water consumption.

Site selection was based primarily on the availability of coal and oil shale, the rank of coal or oil shale, the type of mining (underground or surface) and the availability of surface water and groundwater. The coal mining regions chosen were those where the largest and most easily mined deposits are located. In the West, these include the Powder River and Fort Union regions in Montana, Wyoming, and North Dakota, and the Four Corners region in New Mexico. In the Central and Eastern regions, the Illinois and Appalachian coal basins were selected. Western coals are principally low-sulfur subbituminous and lignite, while eastern and central coals are mainly high-sulfur bituminous. Only high-grade shale from the Green River Formation was considered. Specific design examples were restricted to shales with yields of about 30 to 35 gal per ton (0.13 to 0.15 m³/metric ton), as might be found in Colorado or Utah. A total of 90 plant-site combinations are

listed in Table 2 for the Eastern and Central States and in Table 3 for the Western States. The locations of these sites with respect to the major energy reserves and the primary water resources characteristics are shown in Figures 1 and 2. The maps show more sites than the ones given in the tables. Primary sites correspond to sites listed in Tables 2 and 3, and secondary sites were selected to provide a larger study area for water availability.

WATER REQUIREMENTS

Estimates of water consumption are net; all effluent streams are assumed to be recycled or reused within the mine or plant after necessary treatment. These streams include the organically contaminated waters generated in the conversion process, which are unfit for disposal without treatment, and the highly saline water blown down from evaporative cooling systems. Water is only released to evaporation ponds as a method of salt disposal. These wastes may also be disposed of with the coal ash if the problems of runoff and groundwater contamination are adequately handled in an economic manner. The rest of the water consumed leaves the plant as vapor, as bonded hydrogen after hydrogenation, or as occluded water in the solid residues. Dirty water is cleaned, but only for reuse and not for return to a receiving water.

Conversion can never be fully efficient in any real process. All of the available energy of the coal or shale cannot be fully recovered in the synthetic fuel, and the unrecovered thermal energy must be dissipated to the atmosphere. Some of the unrecovered heat is lost directly to the atmosphere; e.g., in hot flue gases and in coal drying. The remainder of the unrecovered heat is dissipated either through wet cooling or dry cooling, depending on economic considerations. In general, the quantity of water evaporated in cooling is the prime determinant to the total quantity of water consumed in a plant.

There are four principal types of cooling loads in any synthetic fuel plant: process streams, gas purification, turbine condensers, and gas compressors. As shown,³ the most economical procedure for process streams is to cool them to about 130° F to 140° F with an air cooler and to cool below these temperatures by using a wet system. The acid-gas removal regeneration condenser can be economically dry cooled at all

TABLE 2. PLANT-SITE COMBINATIONS FOR EASTERN AND CENTRAL STATES

State	County	Water Source		Mining ^a	Coal ^b	Coal Gasification				Coal Liquefaction and Coal Refining		Plant-Site Combinations	
		Surface	Ground			High Temp. Gasifier	Low Temp. Gasifier			Synthoil	SRC	No.	Total State
Alabama	Jefferson	Alabama R.		U	B	X			X			3	
		Tombigbee R.	X	S	L	X			X		X	6	9
Illinois	Bureau		X	U	B		X		X		X	3	
	Shelby	Ohio R.		U	B		X					1	
	St. Clair	Ohio R.		U	B			X				1	
	White	Ohio R.		U	B						X	1	
	Bureau	Illinois R.		S	B		X					1	
	Fulton		X	S	B			X			X	2	
	St. Clair	Ohio R.		S	B			X				1	
	Saline	Ohio R.		S	B						X	1	11
Indiana	Gibson	White R.		U	B	X			X		X	3	
	Vigo	White R.		U	B		X					1	
	Sullivan	Ohio R.		S	B				X			1	
	Warrick	Ohio R.		S	B	X				X		2	7
Kentucky	Floyd	Ohio R.		U	B				X			1	
	Harlan	Ohio R.		U	B					X		1	
	Muhlenberg	Green R.		S	B			X				1	
	Pike	Ohio R.		S	B					X		1	4
Ohio	Gallia	Ohio R.		U	B				X			1	
	Tuscarawas	Muskingum R.	X	U	B	X				X		4	
	Jefferson	Ohio R.		S	B	X			X	X		3	8
Pennsylvania	Armstrong	Allegheny R.		U	B	X			X			2	
	Somerset	Allegheny R.		U	B					X		1	3
West Virginia	Fayette	Kanawha R.		U	B	X						1	
	Kanawha	Kanawha R.		U	B				X			1	
	Monongalia	Allegheny R.		U	B	X						1	
	Preston	Kanawha R.		U	B				X			1	
	Mingo	Kanawha R.		S	B	X				X		2	6

^a U = Underground; S = Surface.^b B = Bituminous; L = Lignite

TOTAL 48

**TABLE 3. COAL AND OIL SHALE CONVERSION PLANT-SITE COMBINATIONS
FOR WESTERN STATES**

State	Mine	Water Source		a	b	Coal Gasification				Coal Liquefaction and Coal Refining		Plant-Site Combinations	
		Surface	Ground	Mining	Coal	High Temp. Gasifier Hygas	Low Temp. Gasifier Bigas	Low Temp. Gasifier Lurgi	Synthane	Synthoil	SAC	No.	Total State
Montana	Decker-Dietz		X	S	S	X		X				2	
	Foster Creek	Tongue R.		S	S			X				1	
	U.S. Steel Chupp Mine	Yellowstone R.		S	L		X					1	
	East Moorhead	Powder R.		S	L	X						1	
	Pumpkin Creek	Tongue R.		S	L						X	1	
	Otter Creek		X	S	L						X	1	
	Colstrip	Yellowstone R.		S	S	X			X		X	3	
	Coalridge	Missouri River		S	L						X	1	11
New Mexico	Gallup		X	S	S	X		X		X		3	
	El Paso	San Juan R.		S	S	X		X				2	
	Wesco	San Juan R.		S	S			X				1	6
North Dakota	Scranton	Grand R.		S	L		X					1	
	Bentley	Knife R.		S	L					X		1	
	Underwood	L. Sakakawea		S	L					X		1	
	Knife River	Knife R.		S	L			X				1	
	Center	Knife R.		S	L		X					1	
	Slope	Yellowstone R.		S	L		X					1	
	Dickinson	L. Sakakawea		S	L					X		1	
	Williston	Missouri R.		S	L			X				1	8
Wyoming	Belle Ayr	Crazy Woman Cr.		S	S	X						1	
	Gillette-Wyodak	Crazy Woman Cr.		S	S	X					X	2	
	Spotted Horse Strip	Powder R.		S	S				X			1	
	Hanna	Medicine Bow		S	S	X						1	
	Antelope Creek Mine	Beaver Cr.	X	S	S	X			X		X	3	
	Lake-de-Smet	Tongue R.		S	S					X		1	
	Kemmerer	Hams Fork		S	B		X	X				2	
	Jim Bridger	Green R.		S	S					X		2	
	Rainbow #8	Green R.		U	B						X	1	14
TOTAL												39	

State	Mine	Water Source		a	c	Direct Retort		Indirect Retort		Plant-Site Combinations	
		Surface	Ground	Mining	Shale	Paraho Direct	Paraho Indirect	TOSCO II		No.	Total State
Colorado	Parachute Creek	Colorado R.		U	HG	X	X	X		3	3

a U = Underground; S = Surface
b B = Bituminous; L = Lignite; S = Subbituminous
c HG = High grade shale

TOTAL 3

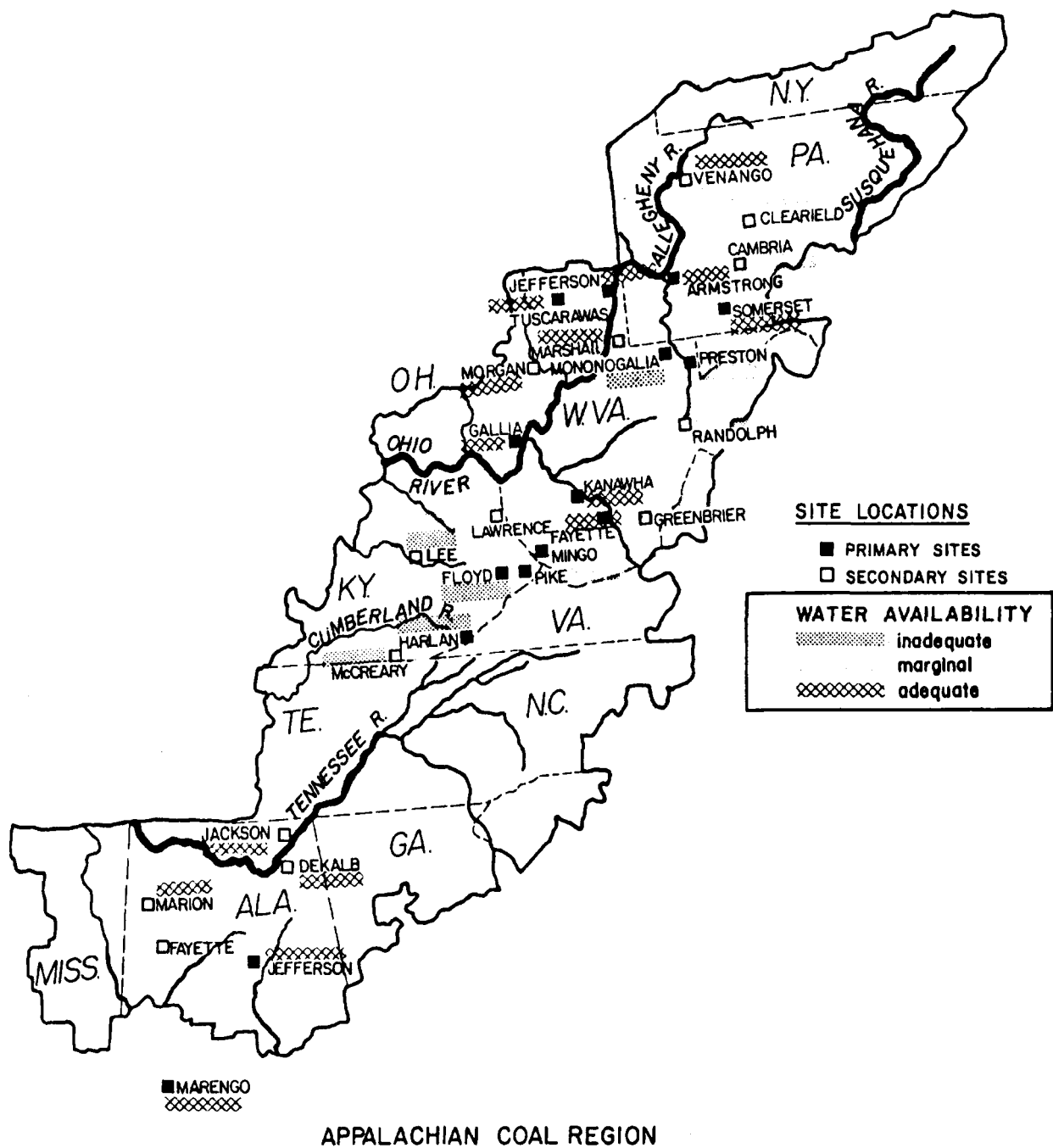
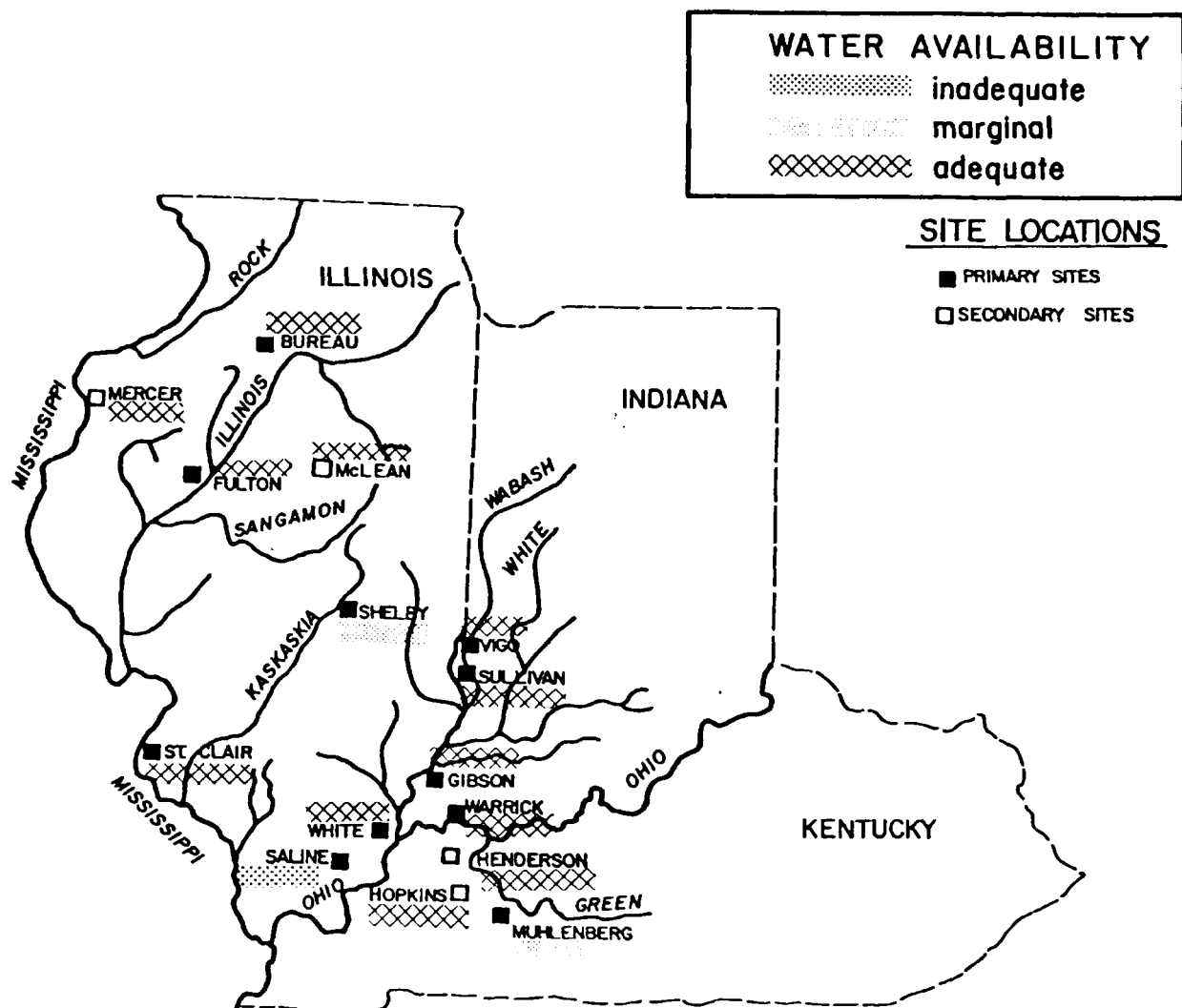


Figure 1. Site locations and water availability in Eastern and Central States.



ILLINOIS COAL REGION

Figure 1 (continued)

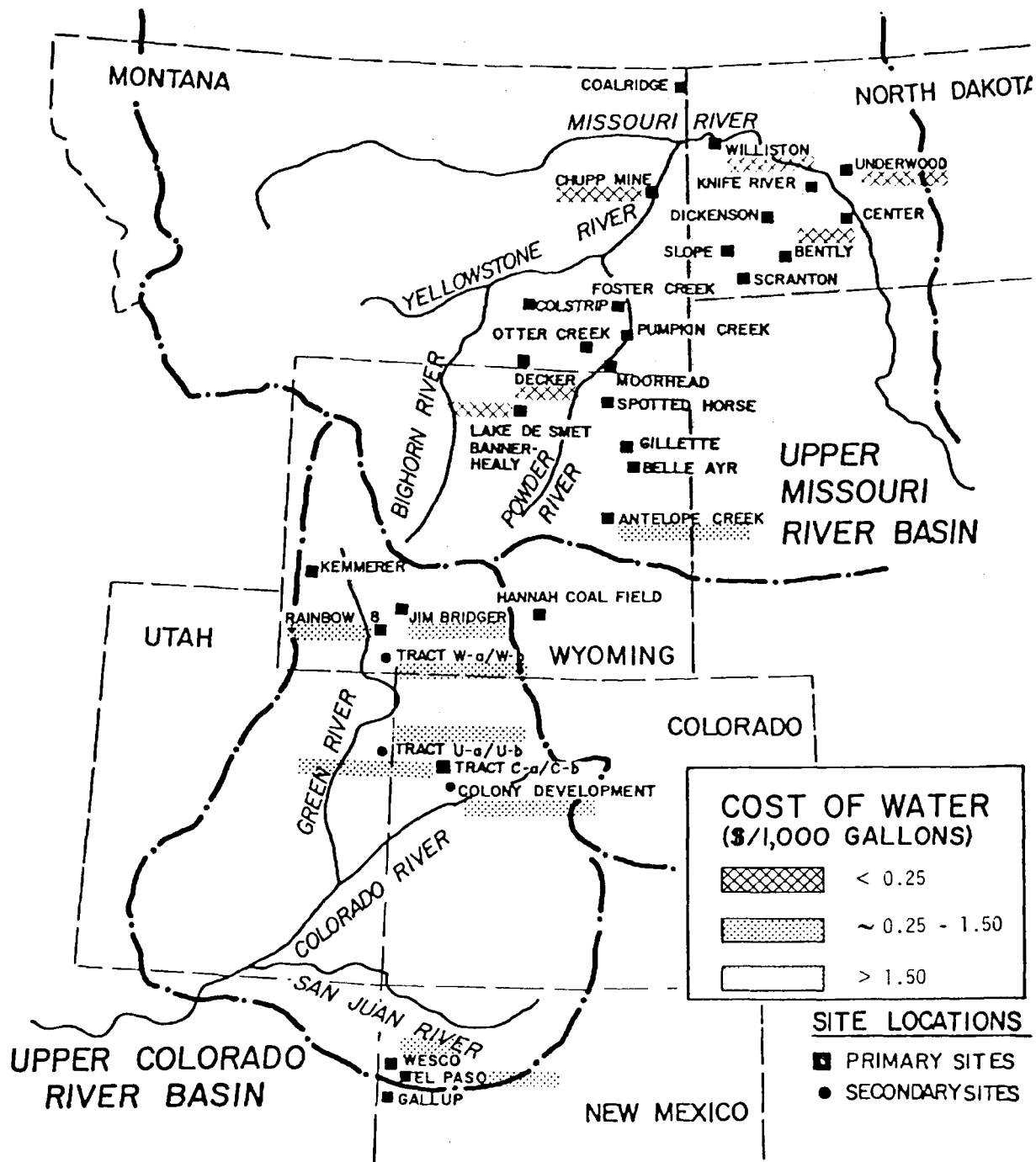


Figure 2. Site locations and the cost of transporting water in Western States.

plants when the hot potassium carbonate process is used and 90 percent dry-10 percent wet cooled when a physical solvent process is used.³ The gas purification system chosen by the original designers and assigned to each process is somewhat arbitrary and has little effect on cumulative water consumption.

The cooling of steam turbine condensers and of gas compressor interstage coolers depends on the cost and availability of water and, therefore, on the site. Three cooling options were considered representing different kinds of wet evaporative cooling for turbine condensers and gas-compressor interstage coolers (Table 4). The cooling option determines whether turbine condensers are all wet cooled, whether parallel wet and dry condensers are used, and whether gas compressor interstage coolers are all wet cooled or whether series dry and wet coolers are used. The decision depends in part on the economics of cooling.

Figure 3 shows the cost of steam turbine condenser cooling in Farmington, New Mexico. It is clear that there is a cost of water above which it is economical to use parallel wet/dry condensers. This cost is approximately \$0.20/1,000 gal. The load on the wet cooler is about 10 percent of the case for all wet cooling. Figure 4 shows the effect of cost on water consumption for cooling turbine condensers at two sites in the East and two sites in the West.

Figure 5 shows the effect of cost on water consumption for interstage cooling when 1,000 lb of air is compressed. When the price of water exceeds about \$1.50/1,000 gal, the use of series dry/wet interstage cooling is the least expen-

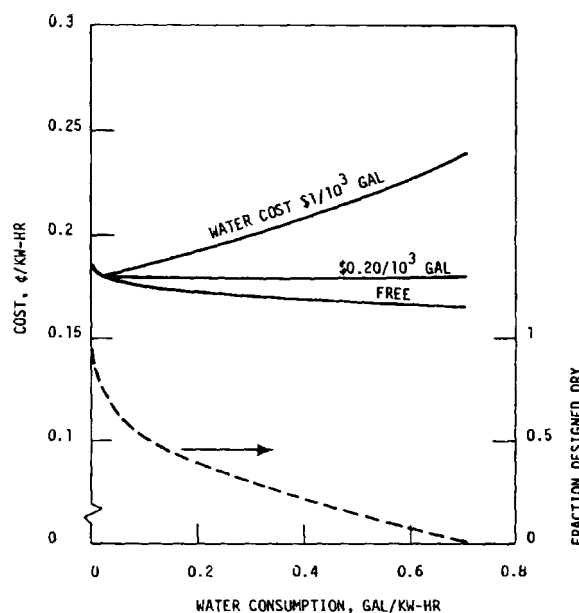


Figure 3. Cost of steam turbine condenser cooling in Farmington, New Mexico.

sive option. The fraction of the cooling load to be carried by the dry cooler varies significantly with the cost of water. The effect of the cost of water is more gradual than was found from the calculations on turbine condensers. Above a cost of \$1.50/1,000 gal, approximately 50 percent wet to 50 percent dry cooling should be used.

Where water is plentiful and inexpensive to transport, high wet cooling should be used. The cooling loads on both the turbine condensers

TABLE 4. THREE COOLING OPTIONS FOR CONVERSION PLANTS

Cooling Option	Water Cost (\$/1000 gals)	and/or Water Availability	% Turbine Condenser Cooling Load Wet Cooled	% Gas Compressor Interstage Cooling Load Wet Cooled
High	<0.20	Plentiful	100	100
Intermediate	0.20-1.50	Marginally Available	10	100
Minimum Practical	>1.50	Scarce	10	50

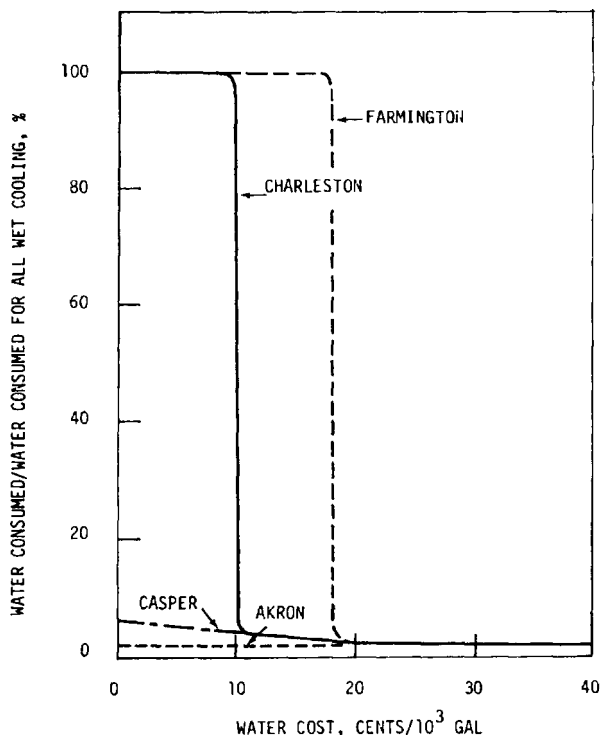


Figure 4. The effect of water cost on water consumed for cooling turbine condensers.

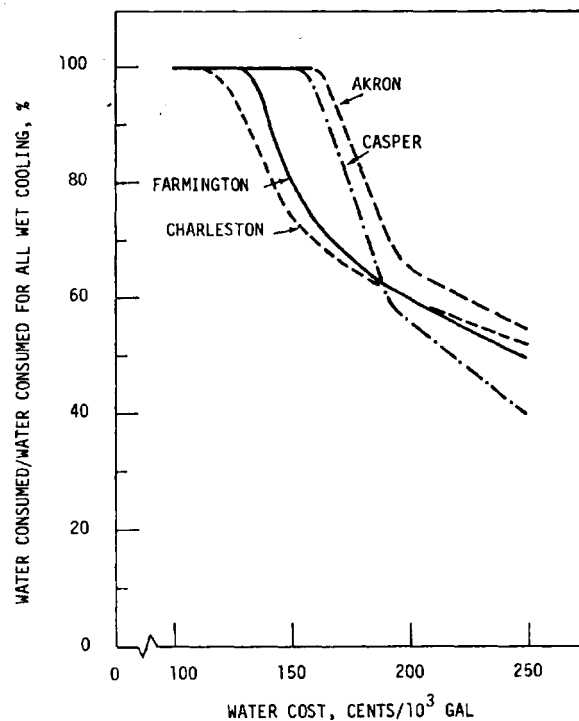


Figure 5. The effect of water cost on water consumed for interstage cooling when compressing 1,000 lb air.

and interstage coolers are taken to be all wet cooled. When water is marginally available or moderately expensive to transport, intermediate cooling should be used. Intermediate cooling assumes that wet cooling handles 10 percent of the cooling load on the turbine condensers and all of the load on the interstage coolers. Where water is scarce and expensive, minimum practical cooling should be used. Minimum practical cooling assumes that wet cooling handles 10 percent of the cooling load on the turbine condensers and 50 percent of the load on the interstage coolers. The amount of unrecovered heat dissipated by wet cooling varies from 33 percent for the Synthane process for high wet cooling, to 18 percent for intermediate cooling, to 15 percent for minimum practical cooling. The high value of 33 percent falls within the range of Lurgi design data. The El Paso design⁴ indicates that 36 percent of the unrecovered heat is dissipated by evaporative cooling, while the Wesco design⁵ indicates 26 percent dissipation.

Besides cooling, water consumption estimates include process water requirements, water required for mining and preparation of the coal and shale, and for the disposal of ash or spent shale, which is a function of location through the amount of material that must be mined or disposed. Sulfur removal also consumes water: the amount depends not only on the coal but also on the conversion process. Water is also essential for other purposes (e.g., land reclamation) dependent on climate. Generally, because any one requirement is not large, its needs can be met with lower quality water. Nevertheless, when the requirements are combined, they are significant and cannot be neglected in any plant water balance, although general rules for the amount consumed are not easily stated. Differences in consumption in this category for a given coal conversion process, however, do not vary by more than 15 percent between regions, except for the Four Corners region. The difference is greater when this

region is compared with others because larger amounts of water are needed for handling the high-ash Navajo coal and for dust control and revegetation.

REGIONAL RESULTS

Table 5 summarizes the total net water consumed for the three different cooling systems and for all of the conversion technologies and processes studied. The ranges in the total water consumed reflect the variation with site. For oil shale only intermediate cooling was considered.

The water requirements for standard-sized plants range from 4 to 7×10^6 gal/d for coal gasification and clean coal and from 3 to 6×10^6 gal/d for coal liquefaction; the range of net water consumed for oil shale conversion is 5 to 8×10^6 gal/d.

To explain the similarities and differences in net water consumed between the conversion technologies, it is necessary to examine the totals on a regional basis (Tables 6 and 7). For a limited number of process-region-coal rank combinations not covered in this study, the results given in Reference 6 have been used. It should be noted that a larger percentage of the unrecovered heat in the Lurgi process is dissipated by wet cooling in Reference 6 as compared to the present study, while for the SRC process the overall conversion efficiency is lower in the present study than that assumed in Reference 6, resulting in larger wet cooling loads. However, the data of Reference 6 present a useful data base for the present study. Figures 6, 7, and 8 show a breakdown of the average net water consumption by region and by process and for the three cooling options. Four water use categories are presented for each coal conversion process in each region: net process water based on reuse of all condensate; cooling water; flue gas desulfurization water, if necessary; and water for mining, dust control, solids disposal, water treatment, revegetation, and other uses. For oil shale it is convenient to break down the water use categories in a different way to reflect the large quantities of water required for spent shale disposal: net process water for retorting and upgrading; cooling water; water for spent shale disposal and revegetation; and water for dust control, mining, and other uses. For the cases where the net process water is negative

(i.e., net water is produced in the process), the cooling water requirements can be obtained from Figures 6, 7, and 8 by adding the absolute value of the process water to the cooling water component.

Except for the Hygas process, the net water consumed for the Four Corners region is higher than for the other regions because of the larger amount of water needed for dust control and the handling of ash for the high-ash Navajo, New Mexico coal. Water is required for revegetation in New Mexico because the rainfall is less than 10 in/yr but is not required at any other location. For the Hygas process, there are many competing demands that make the above generalization invalid.

In the Illinois coal region, the average water requirements for coal gasification are relatively independent of the particular conversion process, with the variation being no more than 15 percent for the high and intermediate wet-cooling options and no more than 25 percent for the minimum practical wet-cooling option. More water is required for coal gasification than for coal liquefaction which, in turn, requires more water than coal refining. The water requirements range from a low of 9 gal/ 10^6 Btu to a high of 28 gal/ 10^6 Btu, greater by more than a factor of 3. In the Appalachian coal region, water requirements (normalized with respect to the heating value of the product fuel) for coal gasification are greater than the requirements for coal liquefaction for plants using bituminous coal. For plants using lignite coal, water requirements for coal gasification are slightly lower than for coal refining. In the latter case, this can be attributed to the high moisture content of the lignite coals and the very large quantities of process water produced in the Lurgi process. The Lurgi process accepts wet coal, and the large quantities of dirty condensate produced are treated for reuse (at a cost) and are subtracted from the process requirement. It should also be pointed out that the net water consumed in the Synthane, Hygas, and Synthoil processes is virtually identical in both the Illinois and Appalachian coal regions for bituminous coals. However, the net water consumed in the SRC process is higher for lignite coals than for bituminous coals because of the lower conversion efficiency attributed to the larger quantity of energy required for drying the higher

**TABLE 5. SUMMARY OF NET WATER CONSUMED FOR STANDARD-SIZED
SYNTHETIC FUEL PLANTS**

	<u>Total Water Consumed (10^6 gpd)</u>			<u>Total Water Consumed (gal/10^6 Btu)</u>		
	High Wet Cooling	Intermediate Cooling	Minimum Practical Cooling	High Wet Cooling	Intermediate Cooling	Minimum Practical Cooling
Coal Gasification						
Lurgi	4-7	2-5	2-5	18-30	9-22	7-21
Synthane	5-6	4	4	22-27	16-19	15-17
Hygas	5-6	4-5	4-5	21-26	16-19	15-19
Bigas	6	4	3-4	25-27	16-18	14-17
Coal Liquefaction						
Synthoil	5-6	3-5	3-4	17-21	11-14	10-14
Coal Refining						
SRC	4-7	3-4	2-4	13-21	8-13	7-11
Oil Shale						
Paraho Direct		5			18	
Paraho Indirect		8			28	
TOSCO II		8			29	

TABLE 6. REGIONAL SUMMARY OF NET WATER CONSUMED IN 10^6 gal/d FOR
STANDARD-SIZED SYNTHETIC FUEL PLANTS

	Appalachian Region						Illinois Region						Powder River/Ft. Union Regions						Four Corners						Green River
	Bituminous			Lignite			Bituminous			Subbituminous-Bituminous			Lignite			Subbituminous			subbituminous			Oil Shale			Oil Shale
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3				2
Coal Gasification																									
Lurgi	6.4*	5.7*	4.3*	4.3	2.1	1.7	6.2-6.8	4.5-5.0	4.1-4.7	5.6-6.9	3.7-5.1	3.3-4.8	5.3-5.7	3.3-3.6	2.9-3.2	7.0-7.2	5.1-5.3	4.7-4.9							-
Synthane	5.2-5.7	3.8-4.2	3.6-3.9	-	-	-	5.3-5.5	3.9-4.1	3.6-4.1	6.0-6.4	4.1-4.4	3.7-4.1	5.7*	3.5*	3.1*	6.5*	4.1*	3.8*							-
Hygas	5.6-6.1	4.3-4.6	4.2-4.5	5.0	3.7	3.5	5.8-5.9	4.5-4.6	4.3-4.5	4.9-5.4	3.7-4.2	3.5-4.0	5.0	3.8	3.6	5.4-5.5	4.2-4.3	4.0-4.1							-
Bigas	-	-	-	-	-	-	6.0-6.4	3.9-4.2	3.5-3.9	5.9	3.7	3.4	6.3-6.5	4.2-4.3	3.9-4.0	-	-	-							-
Coal Liquefaction																									
Synthoil	5.5-6.4	3.9-4.7	3.6-4.4	-	-	-	5.7-5.8	4.0-4.1	3.7-3.8	5.2-5.3	3.3-3.4	3.0-3.1	6.1*	4.3*	4.0*	6.0-6.7*	4.3-5.1*	4.0-4.8*							-
Coal refining																									
SRG	3.2*	1.8*	1.7*	6.6	3.9	3.4	4.7-5.5	3.2-4.0	2.9-3.7	4.3-4.9	2.6-3.0	2.3-2.6	4.9-6.5	2.9-3.7	2.5-3.1	4.8*	3.4*	3.3*							-
Oil Shale																									
Paraho Direct																									5.1
Paraho Indirect																									8.2
TOSCO II																									8.3

1 = High Wet Cooling, 2 = Intermediate Wet Cooling, 3 = Minimum Practical Wet Cooling

*Data from Ref. 6; only applies to particular number and not range.

**TABLE 7. REGIONAL SUMMARY OF NET WATER CONSUMED NORMALIZED WITH
RESPECT TO THE HEATING VALUE IN THE PRODUCT FUEL IN gal/10⁶ Btu**

	Appalachian Region						Illinois Region			Powder River/Ft. Union Regions						Four Corners	Green River
	Bituminous			Lignite			Bituminous			Subbituminous-Bituminous			Lignite			Subbituminous	Oil Shale
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2
Coal Gasification																	
Lurgi	27*	24*	18*	18	9	7	25-28	19-21	17-19	23-29	15-21	14-20	22-24	14-15	12-13	29-30	21-22
Synthane	22-24	16-17	15-16	-	-	-	22-23	16-17	15-16	25-27	17-19	16-17	24*	15*	13*	28*	18*
Hygas	23-26	18-19	17-1 ^a	21	16	15	24-25	19-20	18-19	21-23	16-18	15-17	21	16	15	23	18
Bigas	-	-	-	-	-	-	25-27	16-18	15-16	24	16	14	26-27	18	16-17	-	-
Coal Liquefaction																	
Synthoil	18-21	13-15	12-14	-	-	-	19	13	12	17	11	10	19*	14*	13*	20-22*	14-16*
Coal Refining																	
SRG	11*	7*	6*	21	12	11	15-17	10-13	9-12	13-15	8-9	7-8	15-21	8-9	7-8	15*	11*
Oil Shale																	
Paraho Direct																	18
Paraho Indirect																	28
TOSCO II																	29

1 = High Wet Cooling, 2 = Intermediate Wet Cooling, 3 = Minimum Practical Wet Cooling
*Data from Ref. 6; only applies to particular number and not range.

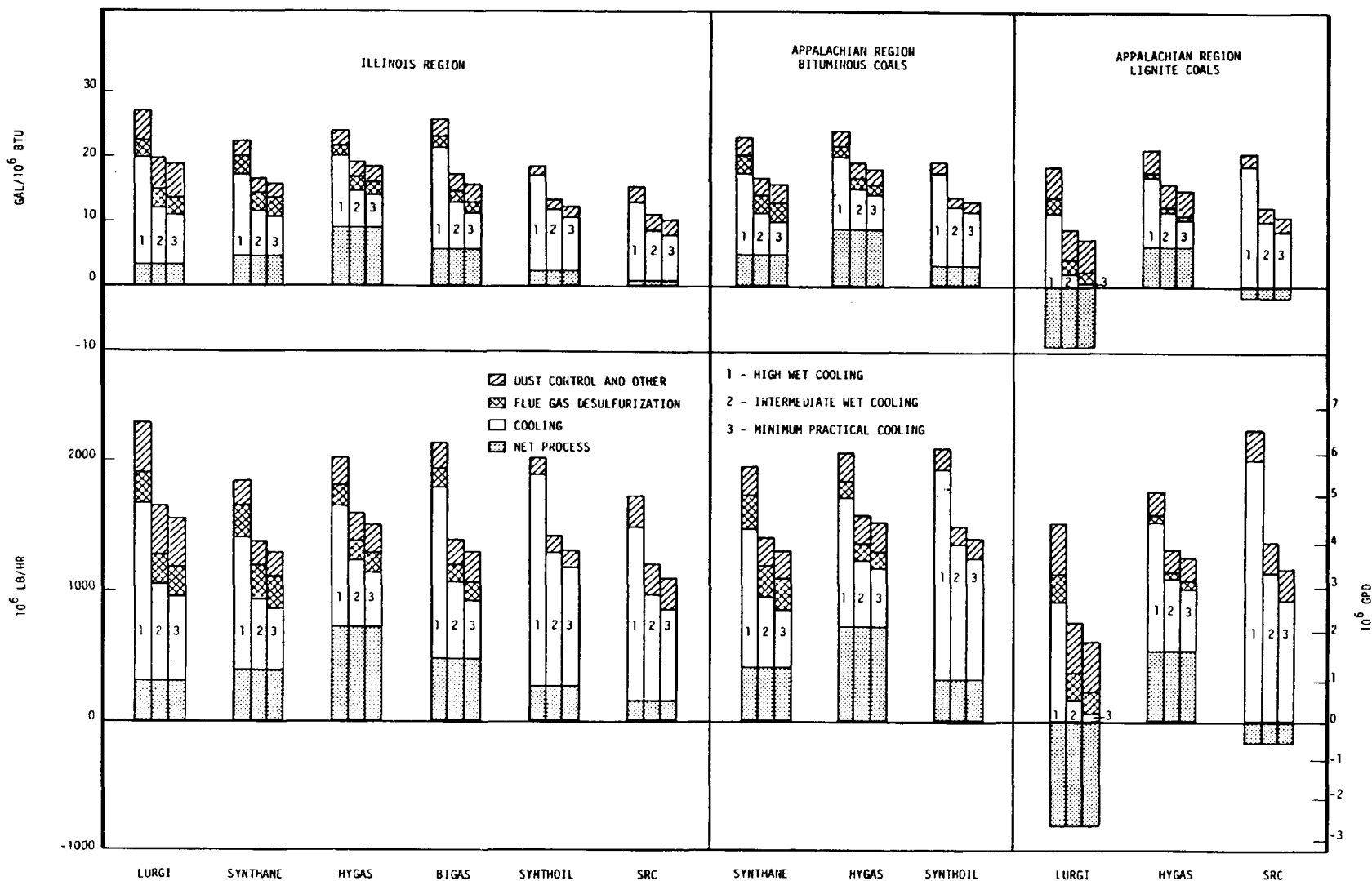


Figure 6. Summary of average net water consumed for standard-sized coal conversion plants located in the Central and Eastern States.

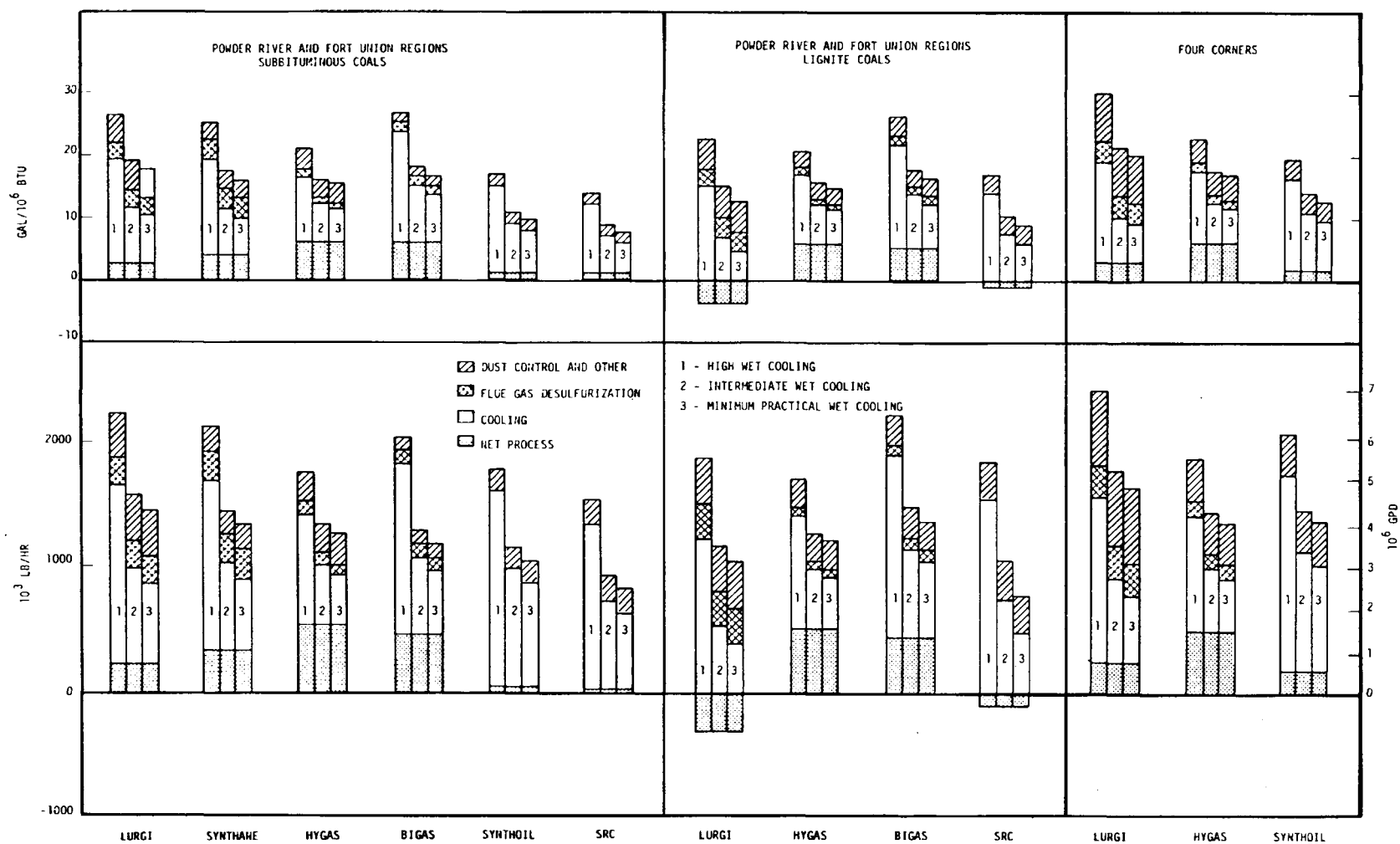


Figure 7. Summary of average net water consumed for coal conversion plants located in the Western States.

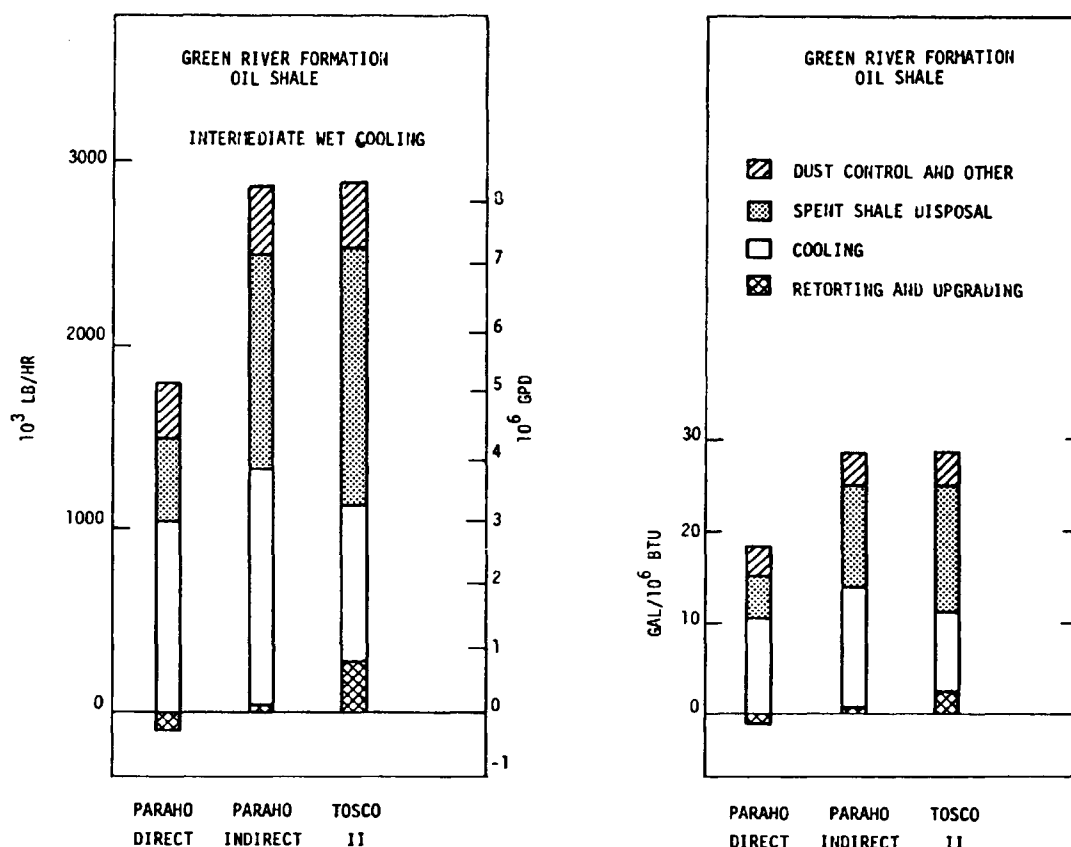


Figure 8. Summary of net water consumed for oil shale conversion plants located in the Western States.

moisture lignite coals prior to dissolution. The slight difference in the results for the Hygas process is caused by different process water requirements for lignite and bituminous coals.

For each of the three basin-coal combinations in the West, the net water requirements are largest for coal gasification, followed in turn by coal liquefaction, and coal refining (see Figure 7). The larger requirement for the Four Corners region is attributed to the high-ash Navajo, New Mexico coal. In the Powder River and Fort Union coal regions the average wet water requirements for the Lurgi, Hygas, and Bigas processes are virtually identical for lignite and subbituminous coals. The differences in the SRC water requirements between the lignite and subbituminous coals are attributed to the large difference between the moisture content of the two coals.

The net water requirements for the Synthoil

and oil shale plants can be compared because the products are roughly the same. The water consumed in the Synthoil and ParaHo Direct processes is about equal. However, the water consumed in the two indirect-heated oil shale processes is 60 percent higher mainly because of larger requirements for spent shale disposal and revegetation.

Differences in water consumption between the Illinois coal region and the Powder River and Fort Union regions for subbituminous coals for a given coal conversion process are relatively small—no more than 15 percent with the absolute difference being no more than 2.5 gal/10⁶ Btu. However, for lignite coals, differences between the Appalachian coal region and the Powder River and Fort Union regions are much larger, the maximum being about 6 gal/10⁶ Btu for the Lurgi process and 4 gal/10⁶ for the SRC process, with the Lurgi water requirements

being smaller in the Appalachian region and the SRC requirements being smaller in the Powder River and Fort Union regions.

In a particular coal-bearing region, differences in the water requirements for the four coal gasification processes that we have considered are principally caused by differences in the process water requirement and the differences in the estimated overall efficiency resulting in different cooling water requirements.

WATER AVAILABILITY AND COSTS

Two limiting cases were examined with respect to water availability in the West: low water demand and high water demand.¹ Low water demand corresponds to the production of approximately 1.0×10^6 bbl/d of synthetic crude, or its equivalent in other fuels. For high water demand, 1×10^6 bbl/d of synthetic crude, or its equivalent in other fuels of 5.8×10^{12} Btu/d, were produced in each of the three principal coal-bearing regions (Fort Union, Powder River, and Four Corners) and in the principal oil shale region (Green River Formation), for a total production of 4×10^6 bbl/d.

Low water demand can be accommodated by available supplies in most of the hydrologic regions. However, chronic water shortages do exist, especially in the northern Wyoming area of the Powder River coal region and the Tongue-Rosebud drainage area in the Fort Union coal region. In the Four Corners-San Juan region in northwestern New Mexico and the Belle-Fourche-Cheyenne basin in northeast Wyoming, water demands are excessive. For high water demand, projected loads cannot be accommodated by available supplies in most subregions. Only in the Yellowstone, Upper Missouri, Lower Green, and Upper Colorado mainstem basins does it appear that sufficient supplies are available for the expected loads of energy production. However, water availability in the Upper Colorado River Basin may be limited because the water rights to most of the free-flowing water in the Basin are already allocated. These rights would have to be transferred to support additional energy development or water transferred by transbasin diversion.

Estimates have been made of the cost of transporting water to the point of use from major interstate rivers and riverways. Figure 2

shows the cost of transporting water to all sites for low water demand. The cost of water determines the degree to which wet cooling should be used. If water costs less than \$0.25/1,000 gal, a high degree of wet cooling should be used; if it costs more than \$1.50/1,000 gal, a minimum degree of wet cooling should be used. In between these extremes, intermediate wet cooling should be used. Figure 2 shows that except for plants located near the mainstem of major rivers or near large reservoirs, intermediate or minimum practical wet cooling is desirable for most of the sites in the Western study area.

For large-scale synthetic fuel production, it is more economical to have a large single pipeline built to transport water to a large number of plants than to have a large number of individual pipelines supplying individual plants. Figure 9 shows the cost of transporting large quantities of water (for high water demand) to some of the major coal-producing areas and indicates that except for large-scale development near the mainstem of major rivers, intermediate cooling is desirable for most of the study region.

The criterion of water availability is used to determine the most suitable cooling option in the Eastern and Central States. In this region the adequacy of the water supply was assessed by comparing a typical plant use with expected low flows in the stream.¹ In the Appalachian coal region where coal is available, there are many large rivers contiguous or adjacent to sites with sufficient and reliable supplies of water to support one or more large mine-plant coal conversion complexes. This applies to all plant sites in the vicinity of the Ohio, Allegheny, Tennessee, Tombigbee, and Kanawha-New Rivers. In most of these instances present water use data and future demand projections indicate a significant surplus beyond expected use, even under low flow conditions.

The surface water supplies are less reliable in the smaller streams, away from the major rivers. Regions generally found to have limited water supplies for energy development include: the upper reaches of the Cumberland and Kentucky Rivers in eastern Kentucky; the eastern Kentucky and adjacent West Virginia coal regions in the Big Sandy River Basin; and northern West Virginia and western Pennsylvania in the Monongahela River Basin, except those areas that can be supplied from the Allegheny, Ohio, or Susquehanna Rivers. Under future con-

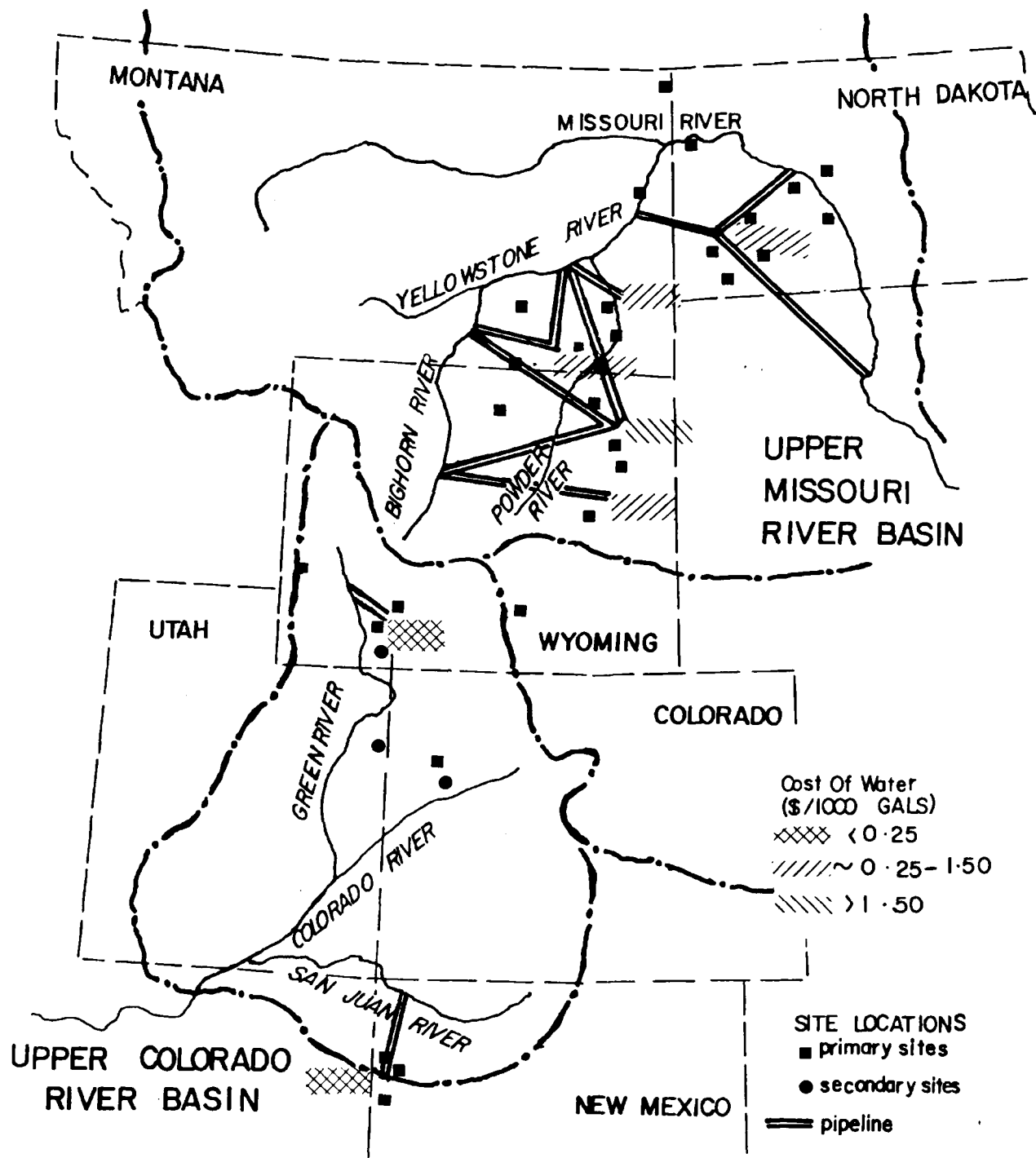


Figure 9. Cost of transporting water to coal regions in the Western States.

ditions a minor surplus will exist for the Tuscarawas River in Ohio. In these water-limited areas, extreme low flows are practically zero, and a coal conversion complex could easily represent a significant portion of the seasonal low flow. In order for a plant to be sited here an alternative or supplemental supply must be assured. Figure 1 shows the availability of water in the Appalachian coal region.

Within the Illinois coal region, the Ohio and Mississippi Rivers have sufficient and reliable water supplies to support one or more large mine-plant coal conversion complexes. The lower section of the Kaskaskia, Illinois, and Wabash Rivers in Illinois; the Wabash and White Rivers in Indiana; and the Green River in Kentucky also have reliable supplies. Under future conditions, deficit supplies are indicated for the Wabash River in Illinois.¹ Figure 1 shows the availability of water in the Illinois coal region.

For each process, the average water consumed is relatively insensitive to the coal-bearing region, and variations for a given cooling option from site to site within the region are expected to be small for all of the processes except for possibly the SRC process, as discussed above. However, within a given region, water availability and cost may vary, and different cooling options at different sites will produce large differences in the cooling water consumed and the plant water requirements.

REFERENCES

1. Gold, H., and Goldstein, D. J. *Water-Related Environmental Effects in Fuel Conversion*. Volume I. Summary and Volume II. Appendices. Office of Research and Development. U.S. Environmental Protection Agency, Washington, D.C. EPA 600/7-78-197a, b. October, 1978 (also to be published as a DOE report, 1979).
2. Gold, H., Nardella, J. A., and Vogel, C. A. *Water-Related Environmental Effects in Fuel Conversion*. (Paper presented at AIChE 71st Annual Meeting. Miami Beach. November, 1978. [also to be published in Chemical Engineering Progress, 1979].)
3. Goldstein, D. J., and Yung, D. *Water Conservation and Pollution Control in Coal Conversion Processes*. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Report No. EPA-600/7-77. June 1977.
4. Gibson, C. R., Hammons, G. A., and Cameron, D. S. Environmental Aspects of El Paso's Burnham I Coal Gasification Complex. In: *Proceedings, Environmental Aspects of Fuel Conversion Technology*. Research Triangle Park, U.S. Environmental Protection Agency, October 1974. p. 91-100.
5. Berty, T. E., and Moe, J. M. Environmental Aspects of the Wesco Coal Gasification Plant. In: *Proceedings, Environmental Aspects of Fuel Conversion Technology*. Research Triangle Park, U.S. Environmental Protection Agency, October 1974. p. 101-106.
6. Probstein, R. F., and Gold, H. *Water in Synthetic Fuel Production—The Technology and Alternatives*. Cambridge MIT Press, 1978.

APPLICABILITY OF PETROLEUM REFINERY AND COKE OVEN CONTROL TECHNOLOGIES TO COAL CONVERSION

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Abstract

There are similarities between many of the process and waste streams of the petroleum refining and coke oven industries, particularly the latter, and streams in the coal conversion industry. The well established environmental and process control technologies of petroleum refining and coke oven industries have been reviewed. The process/waste streams from several coal conversion processes were characterized and streams with refinery and coke oven counterparts were identified. The control technologies currently used in refining and coke oven industries for the management of the identified streams were evaluated for their applicability to the counterpart coal conversion streams.

For many of the major controls needed (e.g., desulfurization, fugitive emissions, and wastewater treatment), the current industrial practice seems adequate for the coal conversion industry. Significant composition differences prevail among the comparable streams, however, and additional testing and development of pollution control strategies for the coal conversion industries are indicated.

Based on current technology, primarily derived from petroleum refining and coke oven industrial practice, the evolution of the technology needed to operate a coal conversion facility in an environmentally safe manner appears possible. Cost analyses have not been made here, but they are expected to be significant.

INTRODUCTION

A major effort has been mounted by government and private industry to develop the technology necessary to increase the Country's capability to become less dependent on foreign sources of energy. A significant part of this effort is directed at conversion of coal to gaseous and liquid energy sources (fuels), and to sources

of industrially useful chemicals. The U.S. Environmental Protection Agency has initiated a comprehensive assessment program to anticipate potential environmental problems in the coal conversion industry, to help evaluate and develop suitable control measures, and to build the data bases needed for establishing appropriate regulations.

This paper reviews the technologies currently used by two large fossil fuel industries to identify those environmental control processes that may be applicable to the coal conversion industry. The petroleum refining and coke oven industries both have extensive experience in developing pollution control strategies and are continuing to improve their control techniques to meet even more demanding regulations. Those refinery streams having compositions (or components) which have similarities in coal conversion processes have been examined, and the applicability of the control technology has been evaluated. Only the recovery type of coke oven plant was studied here. This so-called "by-product" plant has several process streams with components and compositions similar to those expected in the coal conversion industry. The by-product coke oven industries have developed several control strategies that appear to be useful in the coal conversion industry. Both the petroleum refining and coke oven industries face similar problems, and both have shared in the development of control technologies.

Several selected conversion processes have been scrutinized for the applicability of petroleum refinery or by-product coke oven process/effluent control technologies. These processes are the Koppers-Totzek low/medium-Btu gasification, the Lurgi (dry ash) high Btu gasification, and the COED (Char-Oil-Energy Development) liquefaction processes. Some comparison was made to the Synthane gasification process and the solid-product Solvent-Refined Coal (SRC-I) process. SRC-I is a specialized

process whose primary purpose is deashing of coal, rather than forming coal-derived liquids or gases. Selected processes represent a range of operating conditions, typify processes with more data available on waste stream characteristics, and have commercial status impending or already realized. Figure 1 is a generalized flow diagram for both liquefaction and gasification of coal. Normally only one of the paths from coal to product would be followed depending on whether the major product was a gas or a liquid.

Two primary references^{1,2} were used in developing the material presented here. Both are excellent reviews. The first pertains to the applicability of petroleum refinery control technologies to coal conversion. The second reviews coke oven processes and control technologies and assesses their applicability to the coal conversion industry.

No attempt has been made to consider all the refinery or the coke oven industry control techniques. The coal conversion industry suffers from the disadvantage that urgency, technology, and design have outdistanced full-scale plant experience. As a result, the control technology must be based on some uncertainty coupled with the expectation that further development and even new techniques will be necessary as more data and experience become available.

REFINERY CONTROL TECHNOLOGY

A major obstacle to a detailed assessment of the applicability of refinery control technologies to coal conversion waste streams stems from the nonexistence of commercial substitute natural gas (SNG) and liquefaction facilities in the United States. Commercial gasification and liquefaction facilities operating in foreign countries do not generally incorporate those design and operating features to minimize waste generation and to control discharges that would be employed in a similar facility in this Country. The coals used at the foreign facilities differ from those available to commercial plants in the United States; thus, the waste stream characteristics would also differ. The availability of detailed data from foreign commercial facilities is not extensive, although some progress is being made in this area.

Data from U.S. pilot coal conversion facilities are normally not completely applicable to com-

mmercial-sized plants; nevertheless, they give certain clues upon which some generalizations may be made. Relatively much data are available for many refinery waste streams. Figure 2 is a highly schematic flow diagram for a petroleum refinery.

Based on the review of the available data and from a control technology applicability viewpoint, a limited number of refinery and coal conversion process/waste streams appear to have certain similar characteristics. These streams and the basis for their similarities are listed in Table 1. Despite the noted similarities, there appears to be significant composition differences between the analogous streams which would affect applicability and design of a control technology. For example, while both the refinery process sour gases and the quenched product gas from coal gasification contain H_2S and CO_2 , the H_2S concentration is considerably higher and the CO_2 level is significantly lower in most refinery sour gases. Even when selective H_2S removal processes are used, the treatment of the coal conversion raw product gas results in production of a concentrated acid gas stream with CO_2 levels much higher than those in refinery sour gases. High CO_2 levels significantly affect the efficiency and cost of operating subsequent equipment used to remove sulfur. Unlike sour waters from refineries which contain high levels of both sulfides and ammonia, most coal conversion condensates contain low levels of sulfide and moderate levels of ammonia. Because of the differences in the nature of the raw material and the processing steps employed, the dissolved and particulate organics found in coal conversion wastes are different than those in refinery wastewaters. The organics in coal conversion wastes are generally more aromatic; organics in refineries are largely aliphatic. The differences in wastewater characteristics also are reflected in the characteristics of oily sludges and biosludges resulting from wastewater treatment. In comparing coal conversion waste streams with their analogues in refineries, it should be noted that there can be wide differences between stream compositions from different coal conversion plants depending on the coal processed, conversion process used, and on-site product upgrading methods employed.

The refinery control technologies which may find application to coal conversion are listed in Table 2. Some of the control processes, such as

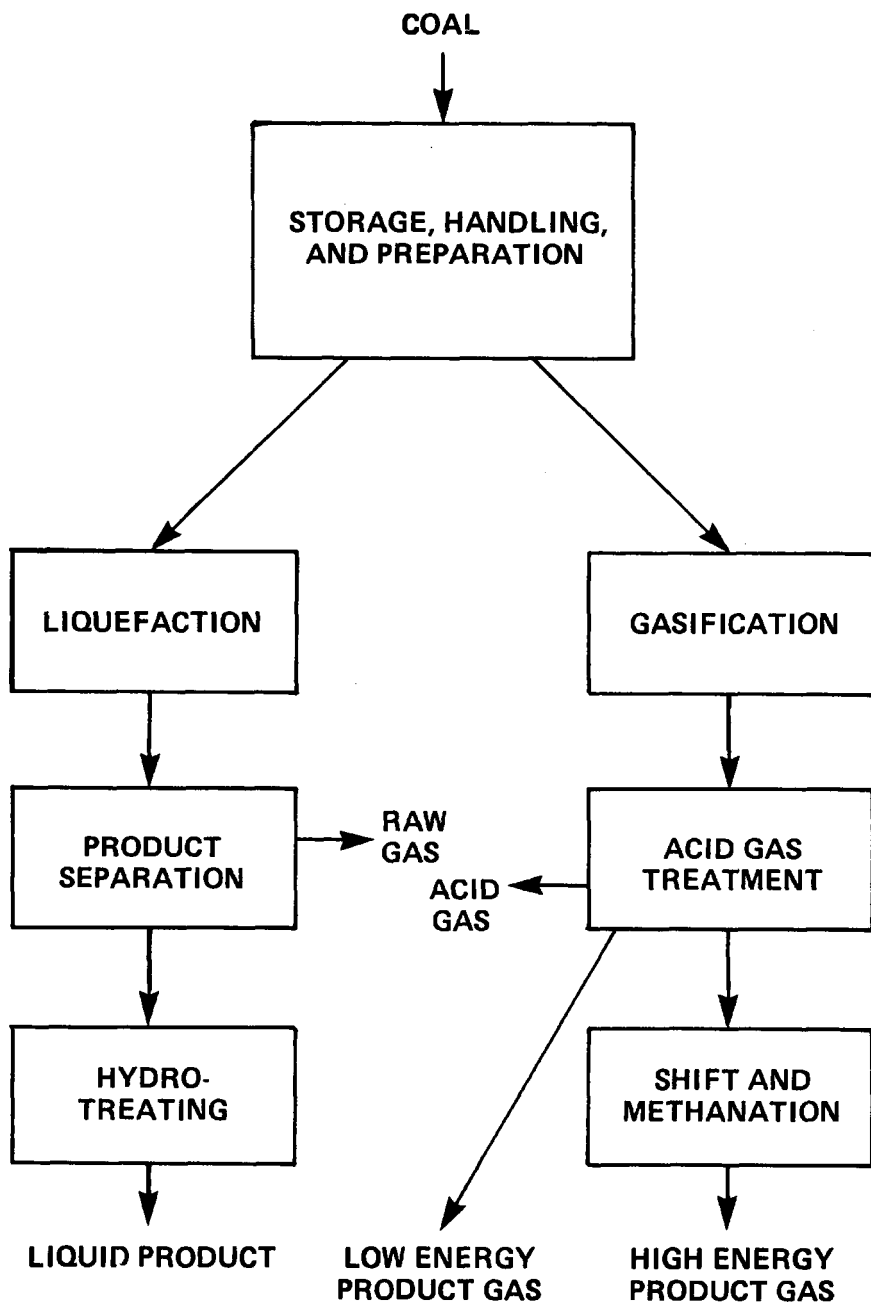


Figure 1. Coal conversion processes.

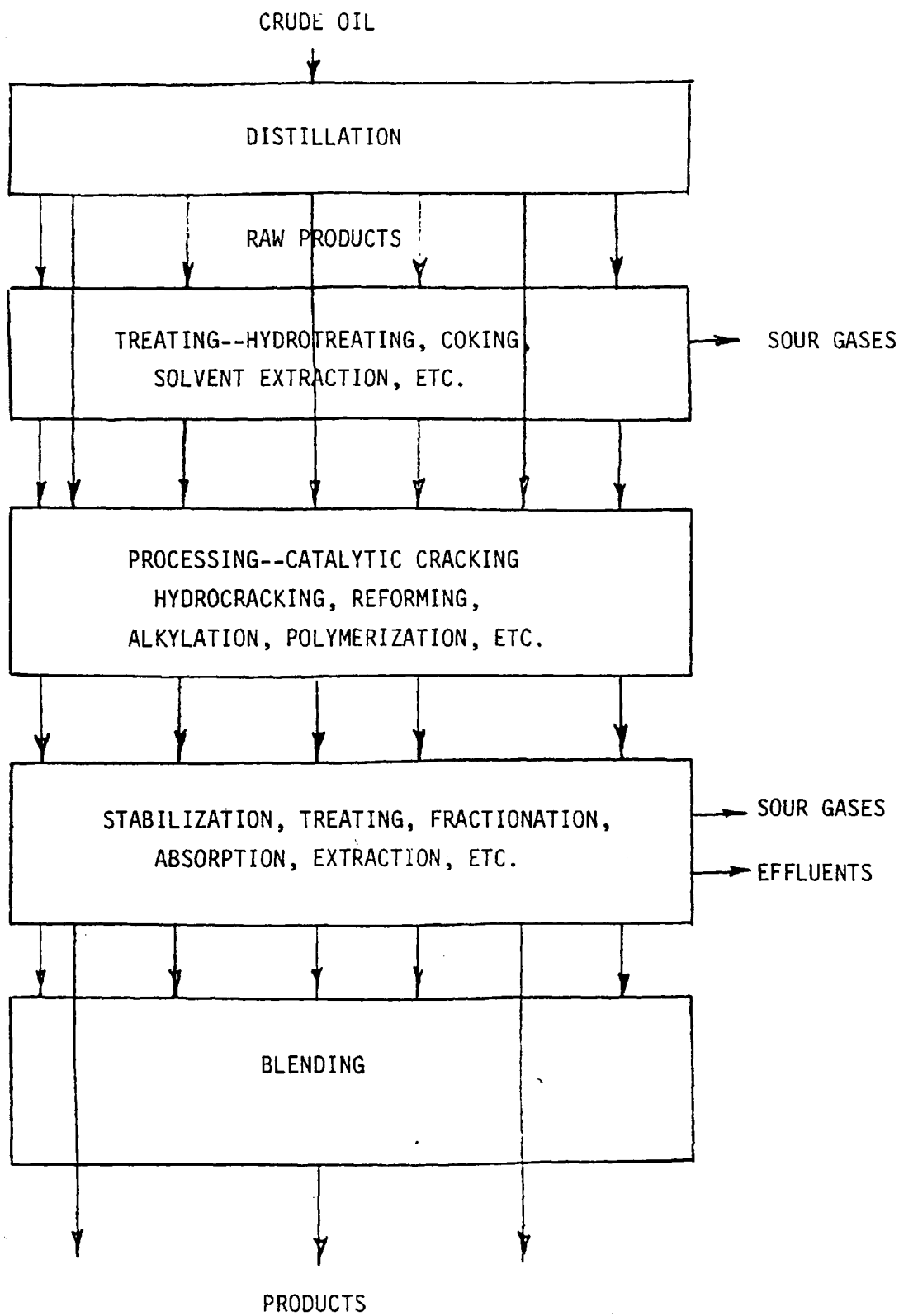


Figure 2. Petroleum refinery.

TABLE 1. SIMILAR REFINERY AND COAL CONVERSION WASTE STREAMS

Refinery Streams	Coal Conversion Counterparts	Major Similarities
<u>Gaseous</u>		
Process sour gas	Quenched product gas, acid gas, and fuel gas (from liquefaction)	High H_2S and ammonia content; presence of CO_2
Catalyst regenerator off-gas	Raw product gas and char combustion flue gas	High CO and particulates, NO_x , and N_2
Fugitive emissions	Fugitive emissions	Hydrocarbons, sulfur compounds, and ammonia
<u>Liquid</u>		
Sour waters	Raw product gas quench condensate, waste liquor purge (from liquefaction), and shift condensate	Ammonia, sulfide, phenols, oils, and grease/tars
Oily waters	Raw product gas quench condensate and waste liquor purge (from liquefaction)	Oil and grease/tar; phenols
<u>Solid</u>		
Spent catalysts	Spent shift, methanation, hydro-treating, and Claus plant catalysts	Metals (Ni, Co, Mo, etc.), bauxite
Sludges	Oil and biosludges	Oil and grease/tar, inerts, biomass, refractory organics

**TABLE 2. REFINERY CONTROL TECHNOLOGIES AND THEIR APPLICABILITY
TO COAL CONVERSION**

Refinery Control Technology	Applicability to Coal Conversion Waste Streams
Acid Gas Treatment Diethanolamine (DEA), Fluor Econamine, Diisopropanolamine (ADIP), etc. Physical Solvents Slexol, Rectisol, etc.	Potentially suitable for non-selective removal of H_2S and CO_2 from product gases from atmospheric/low pressure gasification/liquefaction. Also suitable for hydrocarbon removal from concentrated acid gases and for concentrating dilute H_2S streams for feeding to Claus plant. Extensive solvent degradation may be encountered in coal conversion applications. Potentially suitable for selective removal of H_2S and CO_2 from product gases. Best suited to high pressure application. The resulting concentrated acid gas stream may contain high levels of hydrocarbons, thus requiring further treatment prior to sulfur recovery.
Sulfur Recovery Claus Stretford	Split-flow mode applicable to coal conversion acid gases containing more than 15% H_2S. Sulfur burning mode applicable to feeds containing as low as 5% H_2S. Removal of ammonia and hydrocarbons from feed gases would be required to prevent ammonium bicarbonate scaling and carbon deposition on catalyst, respectively. Most existing applications are to acid gases containing low levels (around 1%) of H_2S. High CO_2 levels necessitate pH adjustment and result in high blowdown rates. Relatively large unit sizes would be required with high CO_2 gases. Process does not remove non-H_2S sulfur compounds.
Tail Gas Treatment IFP-1, Sulfreen SCOT, Beavon, and Cleanair	Suitable for Claus plant tail gas treatment; cannot achieve very low levels of total sulfur in the off-gas which may be required by emission regulations. Efficiency decreases with increasing CO_2 level in the feed. Sulfur removal efficiencies decrease and CO_2 levels in tail gas increase when acid gases contain high CO_2 levels.

TABLE 2 (continued)

Refinery Control Technology	Applicability to Coal Conversion Waste Streams
Tail Gas Treatment (cont.) Chiyoda Thoroughbred 101, Wellman-Lord, IFP-2, and Shell CuO	Potentially suitable. Requires feed incin- eration to convert reduced sulfur to SO ₂ .
Fugitive Emissions and Odor Control Vapor recovery, incineration, source elimination	Applicable to analogous sources.
Sour Water Stripping Conventional Stripping and Chevron Wastewater Treatment Process	Applicable to coal conversion sour waters. The design must be modified to allow for the lower sulfide and often higher ammonia levels in coal conversion sour waters.
Oily Water Treatment API Separator and Flota- tion	Applicable; units must be designed based on specific wastewater characteristics.
Biological Wastewater Treatment	Generally applicable; biodegradability of coal conversion waste components not established.
Carbon Adsorption and Chemical Oxidation	Should be applicable; design basis must be established for the specific wastewater.
Slop Oils and Sludge Treatment (thickening, centrifugation, emulsion breaking, drying beds)	Generally applicable; design basis must be established for the specific waste.
In-Plant Waste Volume and Strength Reduction	Applicable.
Resource Recovery	Applicable to spent catalysts for material recovery; sale of tars/oils
Incineration	Applicable to organic wastes; incinerator and emission control designs would be feed specific.
Land Disposal	Applicable.

sulfur recovery plant tail gas treatment, would be applicable to waste streams in a coal conversion plant, and their design may be essentially the same as in refinery applications. However, as noted in Table 2 under *Tail Gas Treatment*, with high CO₂ levels in the tail gas, as would be expected in coal conversion applications, the efficiency is low for some of the processes (IPF-1, Sulfreen, SCOT, Beavon, and Cleanair). Other processes such as Stretford, Claus, and steam stripping would require extensive modifications to account for differences in waste compositions. Because of limited data on certain waste characteristics (e.g., the biodegradability of some aromatic organic compounds and the settleability of coal conversion solids in wastewaters) the applicability and efficiencies of processes such as bio-oxidation, flotation, sludge dewatering, and emulsion breaking in coal conversion application cannot be accurately assessed at this time. With the exception of the few processes that have been tested in coal conversion applications, such as the Rectisol and the Fluor Econamine (diglycolamine [DGA]) acid gas treatment processes and the Stretford tail gas treatment process, the processes listed in Table 2 have not been employed in such an application. For the processes that have been used in coal conversion, only limited data are available on process design and performance. Even though the processes listed in Table 2 appear applicable to coal conversion wastes, additional testing will be required to confirm applicability and to define criteria for large-scale design and cost estimation. It should be noted that the suitability of a control process for use in coal conversion plants cannot be determined separately from other processes and waste treatment operations within an integrated coal conversion facility. The selection of a specific control process is merely an element in the overall facility waste management plan, which includes considerations of overall emission/effluent limitations, energy and raw material availability, and costs.

Some of the components in refinery and coal conversion wastes are important from the standpoint of presenting potential occupational health hazards to plant workers and adverse health impacts on the general population. Several hazardous waste compounds (e.g., H₂S, CO, and mercaptans) are not unique to refinery or coal conversion wastes and are emitted from a

variety of other industrial and nonindustrial sources. The hazardous characteristics of many of these commonplace substances are generally well documented. The hazardous chemicals which are unique to coal conversion and refineries fall into three categories: polynuclear aromatics, heavy metals and organometallic compounds, and low molecular weight aromatic substances. Many of the control technologies used in both refineries and coal conversion plants should result in partial or total removal of the hazardous waste components. The fate of many of the hazardous components in pollution control processes is not well known, and the requirements for additional controls cannot be defined at this time.

COKE OVEN CONTROL TECHNOLOGY

Coke is produced by destructive distillation—also referred to as pyrolysis or carbonization—of low-sulfur bituminous coal in an oven or retort in the absence of air. The coking temperature of about 1,100° C is generally higher than most coal conversion pyrolysis and is conducted in a reducing atmosphere in the coke oven as contrasted to a more oxidizing atmosphere in coal conversion units. The latter are generally operated at a higher pressure than the coke oven, which is essentially at atmospheric pressure. Coal used in coke making is usually a blend of high-volatile coal with a 10 to 50 percent low-volatile coal. The blend usually does not contain over 1.5 percent sulfur or 9 percent ash. Approximately 16 percent of the bituminous coal mined in the United States is converted to coke, which is used principally in blast furnaces and foundries. More than 98 percent of the total U.S. coke is produced from by-product coke oven systems. The by-product process is oriented toward the recovery of the gases and chemicals produced during the coking cycle.

Figure 3 shows a typical by-product coke oven process. The major steps or process units involved in the by-product coke plant, in sequence, are: coal handling and preparation equipment, coke ovens, quench stations, primary cooler, tar separator, tar extractor, ammonia removal unit, final cooler, light oil scrubber, and sulfur removal unit(s). In addition, some modern coke plants have chemical refining facilities for recovery of benzene, toluene, and xylene from the light coal oils.

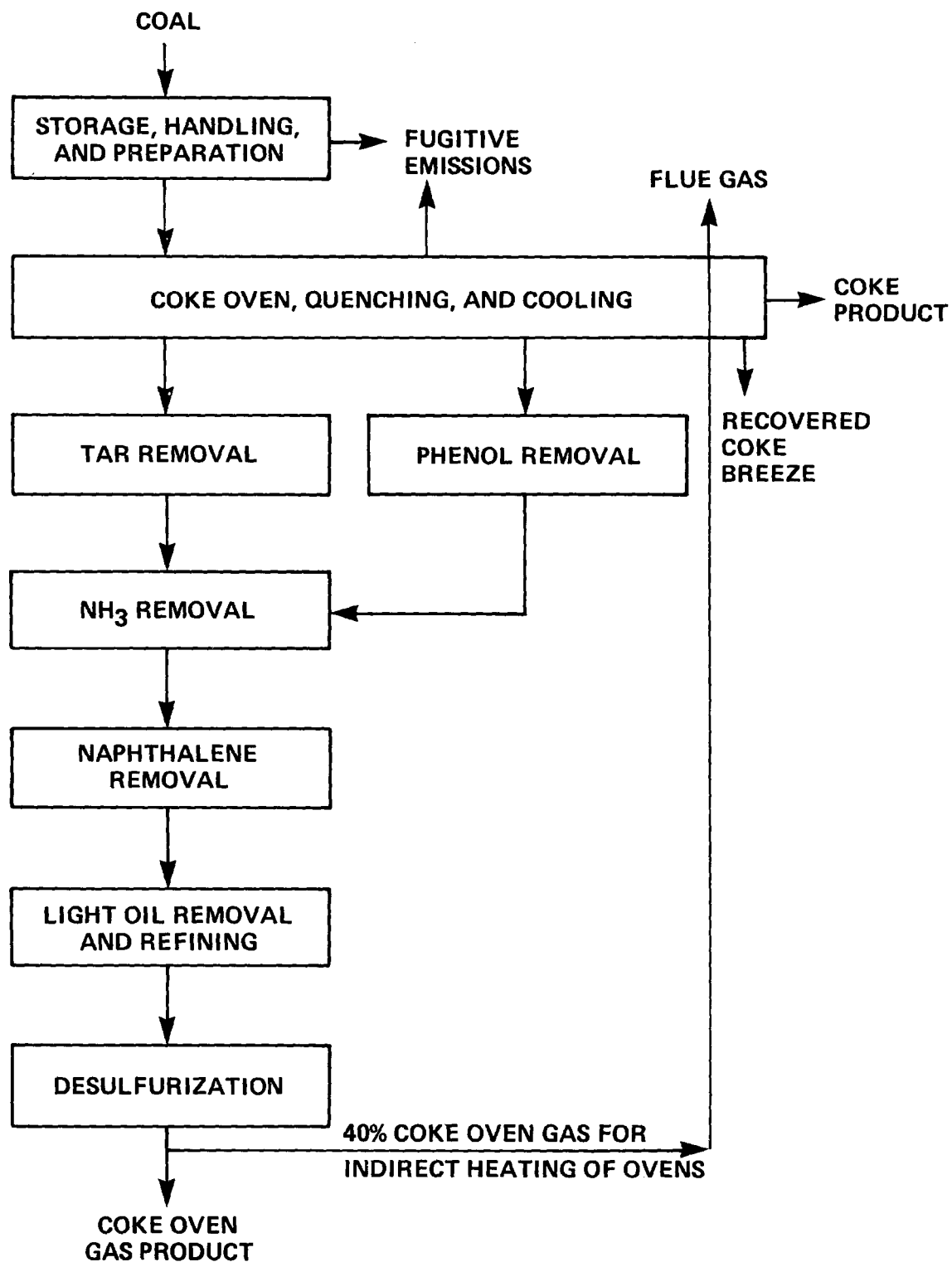


Figure 3. Byproduct coke oven process.

The core of the process is the coke ovens, which are narrow chambers usually about 12 m long, 5 m high, and tapering in width from about 50 cm at one end to 40 cm at the other. The ovens hold about 18 Mg of coal each and are built in batteries of about 100 ovens. Although coke production from each oven is basically a batch process, a coke oven plant operates such that the battery of ovens continuously produces coke oven gas and byproduct chemicals. In the by-product coke oven process, coking is accomplished at temperatures of 1,090° to 1,150° C and atmospheric pressure for a period of 16 to 27 hr.

One Mg of the low-sulfur bituminous coal fed into a by-product coke oven would yield the following:

	kg
Coke	715
Coke breeze	46.5
Tar	39.0
Anhydrous ammonia	2.5
Light oil	10.0
Gas, 293 m ³ (10,350 std ft ³)	154.5
Water	32.5
	1,000

Coal gasification processes may be subdivided into low-, intermediate-, and high-temperature operations. These may be further subdivided by operating pressures. The low-temperature gasification processes tend to show a complete product and by-product slate, including oils, tars, and phenols. As the gasification temperature increases, the quantity of oils, tars, and phenol decreases in preference to lighter products. The operating pressure also affects the yields. As the pressure increases, the product slate becomes heavier.

Table 3 is a comparative listing of coke oven and coal conversion process and waste streams. The gaseous streams listed in Table 3 include the raw gas from the coke oven and from coal conversion counterparts. Fugitive emissions are listed under gaseous streams, but a significant component in coke oven fugitive emissions results from airborne coal particles and coke. Fugitive emissions in the coal conversion process are varied in composition and source. Gas-borne solid particulates include coal from the coal pile and coal particles airborne in such handling processes as crushing, sizing, transporting, and

oven loading. Coke particulates in the unrecovered coke breeze caused by the coke handling and quenching operations account for a major share of the gaseous fugitive emissions. Solid tar particulates are among the fugitive emissions from the tar separator, exhauster, and electrostatic precipitator. Liquid H₂SO₄ mist and solid ammonium sulfate particulates may be generated in the ammonia removal steps. Solid particulates may also be generated in the underfiring of the coke ovens by the clean coke oven gas. Odors are among the fugitive emissions from the coke ovens, coke handling and quenching operations, tar separators, ammonia removal, naphthalene removal, light oil recovery, and desulfurization steps. Other specific major sources of fugitive emissions include coal-charging hole lids, coke-pushing operations, and door-seal leaks. Additional sources include pumps, compressors, valves, and flanges. Most of the latter group are universal problems in facilities where chemicals are processed. Diligence in simple maintenance procedures can often significantly reduce emissions from many of these sources.

The coke breeze listed under the coke oven solid waste streams is the solid coke fines that are recovered during the quenching operation.

Table 4 presents data comparing gas streams from a coke oven plant, a refinery, and two gasification plants. Many similarities are apparent in the components present and in their compositions. Differences, some of which are important from a process standpoint, can also be seen. The hydrocarbon content of the refinery process sour gas stream is much higher than that of either the coke oven gas or the coal conversion gases. There is more hydrogen sulfide in the refinery stream than in the other streams. Note the bottom entry in the table, the ratio of CO₂ to H₂S in the streams. For the refinery gas, the ratio is much lower than either the coke oven gas or particularly the coal conversion streams. High CO₂/H₂S ratios in the latter make sulfur removal and recovery more difficult in the coal conversion processes.

A number of processes are being utilized to remove hydrogen sulfide and recover sulfur from coke oven gas. These processes are divided into three major categories: liquid absorption processes (Vacuum Carbonate, Sulfiban [amine], Firma Carl Still); wet oxidative processes (Stretford, Takahax, Giammarco Vetro-

TABLE 3. COKE OVEN AND COAL CONVERSION STREAM SIMILARITIES

Coke Oven Streams	Coal Conversion Counterparts	Major Common Pollutants or Similarities
<u>Gaseous</u>		
Raw gas and acid gas	Raw gas and acid gas from gasification, and off-gas from liquefaction	H ₂ S, NH ₃ , CO, CO ₂ , COS, CS ₂ , and hydrocarbons. See Table 4 for further details.
Fugitive emissions	Fugitive emissions	Same as above, plus particulates. See Table 6 for some detail.
<u>Liquid</u>		
Ammonia liquor quench water	Process wastewater	NH ₃ , phenols, oils, sulfides, and cyanides. See Table 5 for some details.
Coal pile run-off	Coal pile run-off	Suspended solids and organic extracts.
<u>Solid</u>		
Coke breeze	Coal fines, chars	Similar by-products.
Oily solids and biosludges	Oily solids and biosludges	Oil, grease and tar, biomass, and refractory organics.
Tar, naphthalene, light oil, phenol, and ammonia	Tar, naphthalene, light oil, phenol, and ammonia	Similar by-products.

coke); and dry oxidative processes (Iron Oxide or dry box). Historically, the Iron Oxide process has been used most extensively. However, the Vacuum Carbonate process, the Stretford process, and more recently, the Sulfiban process have moved into commercial prominence. The liquid adsorption processes are called sulfur removal processes, in that they remove sulfur compounds, notably H₂S, COS, and CS₂, from gaseous streams. When the solvent is regenerated, generally a gaseous stream more concentrated in H₂S results. The oxidative processes described are sulfur recovery processes in which elemental sulfur is the product. The Stretford process does not remove COS or other

organic sulfur compounds from the gas stream. The Claus sulfur recovery process is also used but initially had some problems associated with hydrogen cyanide, iron sulfide, and iron cyanide. These problems were resolved by adjusting the Claus unit. A Sulfiban unit removes both CO₂ and H₂S from the coke oven gas stream utilizing a nonselective solvent. A Claus unit is required to convert H₂S to sulfur to recover the sulfur.

The H₂S removal or sulfur recovery efficiencies achievable for the processes in the coke oven industry are: Iron-Oxide process, 99 percent (for low gas volumes); Vacuum Carbonate process, 93 to 98 percent; Sulfiban process, 90 to

TABLE 4. COMPARISON OF GASES

Component/Parameters	Raw Coke Oven Gas	Refinery Process Sour Gases	Gasification	
			Lurgi	Koppers- Totzek
	Vol %	Vol %	Vol %	Vol %
H ₂	38.22	--	22.63	26.37
CH ₄	25.51	8.4	6.75	--
C ₂ H ₄	2.99	5.2	0.23	--
C ₃ to C ₆	--	19	--	--
CO	6.18	--	11.65	51.79
CO ₂	1.33	4.9	16.16	8.82
O ₂	1.26	--	--	--
N ₂	0.452	--	0.18	0.69
NH ₃	0.70	--	0.55	0.08
HCN	0.16	--	0.16	0.02
H ₂ S	0.51	62.5	0.203	0.41
COS	0.018	--	0.017	0.04
CS ₂	0.01	--	--	--
Light Oil	0.79	--	0.14	--
Tar Oil	--	--	0.11	--
Tar	0.78	--	0.10	--
Phenol	0.04	--	0.05	--
H ₂ O	21.05	--	41.07	11.78
Total	100.00	100.00	100.00	100.00
Temp., °C	538	48	188	1,500
Pressure, MPa	0.099	0.10	3.10	0.105
CO ₂ /H ₂ S	2.6	0.078	79.6	21.5

98 percent; Stretford process, 99.5 + percent (for H_2S only); and Claus (sulfur recovery) process, 95 to 96 percent.

Among the acid gas removal processes in the coke oven industry, the amine and carbonate solvent processes should have application in low-pressure gasification processes or in treating low-pressure off-gases from liquefaction processes. The two most common sulfur recovery processes in the coke oven industry are the Claus and Stretford processes. Both of these processes will have wide application in the coal conversion industry. Care must be taken to consider the effect of the CO_2 composition on both the Claus and Stretford processes when used for coal conversion applications having high CO_2 compositions. High CO_2 affects the stability of the flame in the Claus reactor and also results in higher COS concentrations in the tail gas from the Claus unit. In the presence of NH_3 , an ammonium bicarbonate can form that reduces the performance of the Claus catalyst. CO_2 neutralizes the Stretford solution and reduces the absorption rate of the H_2S , thus necessitating a higher solvent circulation rate and larger units. For coal conversion applications, such as a gasification process having a high hydrocarbon and CO_2 composition in the acid gas stream, an enrichment step using an amine process such as ADIP would probably be effective. The enriched gas would be fed to a Claus unit for sulfur recovery. Additional treatment of the tail gas from the Claus unit would be required before discharge to the atmosphere. Generally, the Stretford process is more economical when the acid gas stream contains less than 15 percent H_2S , whereas the Claus process is the choice for levels about 15 percent.

The wastewater characteristics of the different processes are compared in Table 5. All of the major coke oven wastewater treatment processes should have applications in coal conversion waste treatment. The process wastewaters from the by-product coke plants contain large amounts of phenol, ammonia, sulfide, cyanide, and oil and grease. Various control technologies are being used to remove these pollutants.

Ammonia is being removed and recovered by steam stripping at alkaline pH, or by Phosam-W, a proprietary (U.S. Steel) process that uses an ammonium phosphate scrubbing solu-

tion and distillation in combination to produce an anhydrous ammonia product. Sulfide removal from wastewater by steam stripping is not commonly practiced in the coke oven industry.

Phenols are being removed by solvent extraction, steam stripping and/or biological oxidation, and carbon adsorption. Biological treatment has been successful with coke oven wastewaters in meeting existing phenol regulatory limitations. Phenol removal efficiency of about 99.8 to 99.9 percent has been achieved by the activated sludge system: BOD removal has ranged from 85 to 95 percent. Activated carbon adsorption as a final polishing treatment has been practiced in the coke oven industry. Carbon adsorption may have applicability in coal conversion processes, especially if char could be used as an activated carbon.

Many coke oven plants recycle cyanide-containing wastewaters and use them for coke quenching. There would be no counterpart operation in coal conversion operations with the possible exception of the ash quenching. In the coal conversion industry, levels of HCN are generally lower than in the coke oven industry.

Some coke oven plants use a by-product light oil upgrading process which has a potential application in the coal conversion industry. This process, called the Litol process, has been developed and licensed by the Houdry Division of Air Products and Chemicals, Inc. It is a catalytic process by which coke oven light oils are refined and dealkylated to produce high-quality, even reagent-grade benzene at essentially stoichiometric yields.

The coke ovens are a major source of air pollution emissions in the steel industry. Top-side coke oven workers have a substantially higher risk of lung cancer than the average worker, probably from carcinogenic materials associated with the particulate fraction of the coke oven emissions. Various schemes to control these emissions and alleviate potentially adverse health effects are being developed including collecting and removing the smoke, particulate matter, and gaseous emissions that occur during the charging, coking cycle, and pushing and coke-quenching operations. An enclosed coke-pushing and quenching system is being developed jointly by the EPA and the National Steel Corporation. In this system, the coke will

TABLE 5. COMPARISON OF PROCESS WASTEWATERS

Constituent	Coke-Oven Plant Liquor	Synthane	Lurgi	Koppers- Totzek	SRC-I
	mg/l	mg/l	mg/l	mg/l	mg/l
Ammonia	5,000	8,100	11,200	25	5,600
Carbonate	--	6,000	10,000	1,200	--
Chloride	6,000	500	--	600	--
Cyanide	50	--	--	0.7	--
Phenol	1,000	2,600	3,500	--	4,500
Sulfide	1,250	1,400	--	--	4,000
Thiocyanate	1,000	152	--	--	--
pH	8.4	8.6	8.9	8.9	8.0
COD, mg/l	10,000	15,000	12,500	70	15,000
Suspended Solids, mg/l	4,000	600	5,000	50	300

remain totally enclosed, from the moment it leaves the oven until after it is quenched. Emissions evolved during the push and transfer to the quench station are drawn off and removed by a high-energy scrubber. Another system, developed by Koppers Company, is being tested at the Ford Motor Company to abate coke oven fugitive emissions. Principal features of this system are a fume-collecting hood, a fume main, a venturi scrubber, and a modified quench car with a synchronization system for coordinating the quench car's movement with that of the pusher. The Air Pollution Control Association's April 1979 conference on "Control of Air Emissions from Coke Plants" reflects the industry's continuing efforts to improve the technology in this area. These types of fugitive emission controls may have potential applications in the Synfuels industry in analogous situations; e.g., in

ash quenching or SRC solidification unit operations. A summary of the coke oven control technology for fugitive emissions is shown in Table 6. In general, the problem of fugitive emissions is expected to be much less in a coal conversion plant than in the coke oven industry. Analogous operations, after the coal storage, handling, and preparation steps, would be in feeding the lockhoppers in the coal conversion industry and charging the coke ovens. The aspiration systems, the closed charging systems, and the "smokeless" charging systems used in the coke oven industry would have applications to the lockhopper charging operation in coal conversion industry. Other possible applications are indicated in Table 6.

Table 7 summarizes the various coke oven control technologies that may have potential applications in the coal conversion industries.

TABLE 6. COKE OVEN CONTROL OF FUGITIVE EMISSIONS

Operation/Emission Source	Pollutants	Control Technology	Coal Conversion Applicability
Charging	Coal Particulates, SO _x , Hydrocarbons, CO, NO _x , & Ammonia	Aspiration Systems Larry-Mounted Scrubbers Smokeless Charging System with Steam Jets Closed Charging Systems	Applicable N.A. P.A. Applicable
Discharging	Coke Particulates, Hydrocarbons, Ammonia, & CO	Bench-Mounted Self-Contained Hoods Coke Car - Mounted Hoods Fixed Duct Hoods Spray Systems Coke-Side Enclosures	N.A. N.A. P.A. P.A. N.A.
Quenching	Coke Particulates, & Coke Breeze	Internal Baffles Dry Quenching Closed Quenching	N.A. P.A. Applicable
Improved Operating Procedures and Maintenance	Particulates, Hydro- carbons, CO, Ammonia, & NO _x	Mechanical Lid Lifters Electric Eye Synchronization Oven and Door Maintenance	N.A. N.A. P.A.

N.A. - Not Applicable

P.A. - Possibly Applicable

**TABLE 7. COKE OVEN PLANT CONTROL TECHNOLOGIES AND THEIR
APPLICABILITY TO COAL CONVERSION**

Coke Oven Plant Control Technology	Applicability to Coal Conversion Systems
Acid Gas Treatment	
Amine solvents	Suitable for removal of H ₂ S and CO ₂ from low pressure raw product and off gases. Solvent degradation may be encountered. Can produce high H ₂ S concentration streams.
Carbonate solvents (e.g., Vacuum Carbonate and Benfield)	Same as above. Processes partially remove carbonyl sulfide and cyanides. Benfield process suitable for high pressure application.
Sulfur Recovery	
Stretford	Suitable for low H ₂ S (less than 15%) containing gases. Organic sulfur not removed. High CO ₂ levels require large units.
Claus	Applicable for high H ₂ S (greater than 15%) containing gases. Removal of high levels of cyanide, ammonia, and hydrocarbons will be required.
Fugitive Emissions Control	
Coal handling and loading	Potentially suitable.
Enclosed coke pushing and quenching system	Potentially suitable for ash quenching, SRC solidification applications.
Fume recovery and scrubbing	Applicable to analogous sources.
By-product Recovery/Refining	
Ammonia from wastewater (Stripping, Phosam - W)	Suitable for sour waters.
Ammonia from raw gases (Scrubbing, Phosam - W)	Applicable for low pressure gas purification.
Phenol from wastewater (Solvent extraction)	Suitable for process wastewater containing 1,000 mg/l or more phenol.

TABLE 7 (continued)

Coke Oven Plant Control Technology	Applicability to Coal Conversion Systems
Tar, naphthalene, and light oil from raw gases	Suitable, but design must be modified for different pressures, temperatures, and compositions.
Light oil refining (e.g., Litol process and solvent extraction)	Suitable for recovery of benzene, toluene, and xylene (BTX) from coal derived naphthas.
Wastewater Treatment Technology	
Biological oxidation; carbon adsorption; ammonia, phenol, and oil removal processes	Generally applicable; design basis must be established for the specific waste.

Most of the control technologies listed in Table 7 have been tested in coal conversion applications; however, most of these applications have been in process development units or pilot-scale coal gasification and liquefaction systems. A few successful uses have been with commercial first-generation coal gasification processes; e.g., the Lurgi process. Applicability of the control technologies does not mean that the control technology can be duplicated from the coke oven design to the coal conversion application. In general, the composition, flow rate, temperature, and pressure of the specific coal conversion system wastes will not be identical to the coke oven case. These differences, however, must be taken into consideration during the design of the specific controls. Design information or scale-up factors in comparison to coke oven application should be developed through laboratory or pilot-scale testing with actual coal conversion wastes to determine the system design and to develop its costs.

The health effects of coke oven emissions were recently assessed.³ The summary findings are:

- Exposure to coke oven emissions provides an elevated risk for cancer and nonmalignant respiratory diseases to coke oven workers and an increased risk among lightly

exposed workers (nonoven workers in the coke plant).

- The general population, which includes the young, the old, and the infirm in the vicinity of a coke oven plant, should be considered more susceptible than the workers, especially for development of chronic bronchitis.
- Lightly exposed workers are exposed to emissions about 100 times more concentrated than the people living in the immediate vicinity of a coke plant. Since the people living in the immediate vicinity of a coke plant experienced an elevated risk for cancer and nonmalignant respiratory disease, it is reasonable to assume that levels as high as 1 percent of those to which lightly exposed workers are subjected could cause an increased risk to the general population.
- Coke oven emissions contain an array of identified carcinogens, irritants, particulate matter, trace elements, and other chemicals. The toxic effects observed in both humans and animals are greater than the effects that can be attributed to any individual component. Thus, "coke oven emissions" as a whole should be considered the toxic agent.

Since coke oven and coal conversion systems have many of the same hazardous waste components, such as H₂S, CO, CO₂, hydrocarbons, and

polynuclear aromatics, there is a potential occupational health hazard to coal conversion plant workers and the general population in the vicinity of the plant. Indications are that the population living within a radius of 15 km from a coke oven plant would suffer the maximum potential exposure risk. Many of the new control technologies under development, especially those for fugitive emissions control, should result in significant removal of these hazardous pollutants for the coke oven industry. The applicability of these control technologies to coal conversion processes is not altogether clear, except, perhaps, in the coal preparation and handling areas.

For the most part, the types of emissions expected from the coal conversion plant would not only be less concentrated, but also far less toxic. The fumes and particulate matter from the coke ovens themselves, and the subsequent pushing and quenching operations, account for the major pollutants which result in the majority of health hazards encountered in the coke oven industry. The particulate and fugitive emission problems in the coal conversion industry are expected to be several orders of magnitude lower than are presently found in the coke oven industry. The coal conversion industry will need to continue to be vigilant to avoid health problems similar to those found in the coke oven industry.

CONCLUSIONS

Acid gas and tail gas treatment processes used in both the petroleum refinery and in the coke oven plant are adaptable to coal conversion processes. The efficiency for most of these processes would decrease by the CO₂ levels which are expected to be higher for coal conversion processes. The current technology for removing ammonia, phenol, cyanides, hydrocarbons, oil, and grease from vapor and liquid streams all seem applicable to coal conversion plants.

Much of the fugitive emission control technology, particularly that found in the coke oven industry, would have applications in the coal conversion industry. Many new developments are emerging in this field pertaining to the coal pyrolysis and quenching operations which

would positively impact on the coal conversion industry.

Wastewater treatment involving biological action appears to be useful in coal conversion, but the biodegradability of coal conversion waste components has not been established. Carbon adsorption of organic components from wastewaters may be necessary for many wastewater streams, especially those containing polynuclear aromatic compounds.

Sludge, oily solid waste, and other solid waste disposal techniques now in use seem currently applicable and satisfactory for the control technology needed in the coal conversion.

The fate and the composition of trace organic compounds (e.g., benzo(a)pyrene and polynuclear aromatic compounds) and inorganic components (e.g., arsenic, lead, and selenium) are presently not well known for coal conversion processes. Whether control strategies will need to be developed for these components remains to be seen.

Even though many of the control technologies appear applicable to coal conversion wastes, additional testing will be required to confirm the applicability for large-scale design and cost estimation. It is expected that additional development of control technologies will be needed for the coal conversion industry.

REFERENCES

1. Ghassemi, M., et al. *Applicability of Petroleum Refinery Control Technologies to Coal Conversion*. TRW, Inc. Redondo Beach, Calif. EPA-600/7-78-190 (NTIS PB 288630). October 1978.
2. Hossain, S. M., et al. *Applicability of Coke Plant Control Technologies to Coal Conversion* (draft). Catalytic, Inc. Philadelphia, Pa. U.S. Environmental Protection Agency. Contract Number 68-02-2167. December 1978.
3. Stellman, J. M. *An Assessment of the Health Effects of Coke Oven Emissions* (external review draft). U.S. Environmental Protection Agency, Office of Research and Development, Office of Health and Ecological Effects. Washington, DC. April 1978.

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, IV (April 1979, Hollywood, FL)		5. REPORT DATE
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Franklin A. Ayer and N. Stuart Jones (Compilers)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709		10. PROGRAM ELEMENT NO. EHE623A
		11. CONTRACT/GRANT NO. 68-02-3132, Task 1
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final: 9/78 - 9/79
		14. SPONSORING AGENCY CODE EPA/600/13
15. SUPPLEMENTARY NOTES IERL-RTP project officer is T. Kelly Janes, Mail Drop 61, 919/541-2851.		
16. ABSTRACT The proceedings document presentations made at the symposium on Environmental Aspects of Fuel Conversion Technology. The symposium acted as a colloquium for discussion of environmentally related information on coal gasification and liquefaction. The program included sessions on program approach, environmental assessment, and control technology development. Process developers, process users, research scientists, and state and federal government officials participated in this symposium, the fourth to be conducted by IERL-RTP on the subject since 1974.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Fuels	Stationary Sources	21D
Coal Gasification	Fuel Conversion	13H
Liquefaction	Environmental Assessment	07D
Assessments		14B
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 582
	20. SECURITY CLASS (This page) Unclassified	22. PRICE