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ENVIRONMENTAL RESEARCH PROGRAM FOR SLAGGING FIXED-BED COAL GASIFICATION

Status Report

November 1981

by

K. E. Wilzbach, J. R. Stetter,
C. A. Reilly, Jr., and W. G. Willson

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FOREWORD

This technical memorandum provides initial observations from an environmental research program designed to define the health and environmental effects associated with coal gasification. The work reported is a collaborative effort involving investigators within Argonne National Laboratory's Synfuels Environmental Research Program and technical personnel at the Grand Forks Energy Technology Center. Principal contributors at Argonne in addition to the authors include: R. E. Flotard, D. A. Haugen, R. E. Jones, F. R. Kirchner, T. Matsushita, M. J. Peak, and V. C. Stamoudis. L. E. Paulson is an additional contributor from Grand Forks.

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EXECUTIVE SUMMARY

A collaborative environmental research program to provide the Department of Energy with information needed to assess the health and environmental effects associated with large-scale coal gasification technology is being conducted by Argonne National Laboratory (ANL) and the Grand Forks Energy Technology Center (GFETC).

The objectives of the program are to:

- Investigate the toxicology and chemical composition of coal gasification by-products as a function of process variables and coal feed
- Compare the characteristics of isokinetic side-stream samples with those of process stream samples
- Identify the types of compounds responsible for toxicity
- Evaluate the chemical and toxicological effectiveness of various wastewater treatment operations
- Refine methodology for the collection and measurement of organic vapors and particulates in workplace air
- Obtain preliminary data on workplace air quality.

The program was initiated in FY 1981. Since then, the toxicities of a set of process stream samples (tar, oil, and gas liquor) and side-stream condensates from the GFETC gasifier have been measured in a battery of cellular screening tests for mutagenicity and cytotoxicity. Preliminary data on the effects of acute and chronic exposures of laboratory animals to process tar have been obtained. The process tar has been chemically fractionated and the distribution of mutagenicity and compound types among the fractions has been determined. Organic vapors and particulates collected at various times and locations in the gasifier building have been characterized.

Some of the more significant conclusions are:

Toxicology -

- Process tar and the heavier side-stream condensates are mutagenic in the Ames Salmonella assay, having a specific mutagenicity 1-4% that of benzo[a]pyrene.
- Process oil and the lighter side-stream condensates are not significantly mutagenic.
- Organic material extracted from the aqueous phase of materials collected from the side-stream sampler is not mutagenic.
- Process tar and oil are significantly less cytotoxic to mouse myeloma cells than a coal-derived oil reference material.

- Ocular toxicity of process tar in rabbits is transitory, being significant only within 24 hours of application.
- Six applications of process tar (at 50% concentration) to the skin of hairless mice produced only a mild reaction (slight hyperemia and trauma from scratching).

Chemical Characterization -

- The neutral fraction of a process tar sample contains two thirds of the total sample mutagenicity and mass.
- The neutral fraction of process tar contains a wide variety (> 180 individual compounds) of one- to five-ring aromatic hydrocarbons, sulfur and oxygen heterocycles, and C_{12}-C_{30} aliphatic compounds.
- The basic fraction of process tar has the highest specific mutagenicity, having one third of the total mutagenicity in less than 3% of the total mass.
- The basic fraction of process tar contains one- to five-ring nitrogen heterocycles (azaarenes) along with smaller quantities of the corresponding primary aromatic amines.
- The acid fraction of process tar is not mutagenic.

Work Place Air -

- Organic vapors collected in the gasifier building resemble process oil in composition.
- Levels of individual compounds are low; e.g. benzenes are well below Threshhold Limit Values.
- The concentrations of individual compounds decrease with increasing molecular weight and ring size.
- Particulate-associated organic compounds are concentrated on particles in the respirable size range.
- Both the nature and the amount of adsorbed organic compounds are a function of particle size.
- Trace element distributions are bimodal with respect to particle size, resembling data for ambient air.
- The physical characteristics of particles collected in the gasifier building are similar to those resulting from coal combustion.

1. INTRODUCTION

The Department of Energy's (DOE's) Grand Forks Energy Technology Center (GFETC) is operating the only pilot-plant-scale slagging gasifier in the United States. A primary objective of this project has been to develop the data base required for demonstration of the slagging fixed-bed gasifier (SFBG) process, with emphasis on environmentally related data on effluents. At Argonne National Laboratory (ANL), the toxicological and chemical characteristics of process streams and effluents from this gasifier are evaluated, as are the chemical and physical characteristics of workplace air. This report documents ANL activities to date.

Growing concerns as to the type and character of effluents from fixed-bed gasification of bituminous coals dictated that the unit be modified in an effort to process these caking coals in addition to lignite. A major part of the assessment of liquid effluents and their subsequent treatment is believed to be substantially applicable to the fixed-bed, dry-ash gasifiers proposed for the first-generation plants. Thus, the SFBG can provide environmentally related data desired by the public on specific feed coals proposed for dry-ash substitute natural gas (SNG) projects, such as the commercial-scale plant being constructed in Beulah, North Dakota by the Great Plains Gasification Association (GPGA).

1.1 The Slagging Fixed-Bed Gasifier

The GFETC gasifier is a pilot-scale slagging version of a pressurized, fixed-bed gasifier. In the commercial dry-ash process, gasification temperatures are maintained sufficiently low by excess steam to prevent fusion so that ash can be removed in the dry state. The slagging gasifier differs in that only steam required for the gasification reaction is supplied, and operating temperatures are high enough to melt the ash for discharge as a molten slag. This gives the slagging process several advantages, including higher throughput, less steam consumption, and less wastewater production.

Process variables include coal type, operating pressure, oxygen rate, and oxygen/steam ratio. For a given fuel and operating pressure, there is a limited range over which process conditions can be varied.

Figure 1.1 is a cross-section view of the present GFETC gasifier. Up to 1 ton/hr of lignite can be gasified in the unit at operating pressures up to 400 psig. Coal is batch-charged to lockhoppers and is gravity-fed into the gasifier. As coal descends, it is heated by countercurrent flow of hot gases in successive reaction zones. Conceptually, four zones exist whose relative location and vertical depth may vary and overlap depending on the operating conditions and feedstock. Vertical temperature gradients may vary accordingly, from over 3000°F at the bottom to under 350°F at the gas offtake.

1) Drying zone. In the drying zone at the top of the gasifier, coal is heated and dried by ascending gases. The offtake temperature

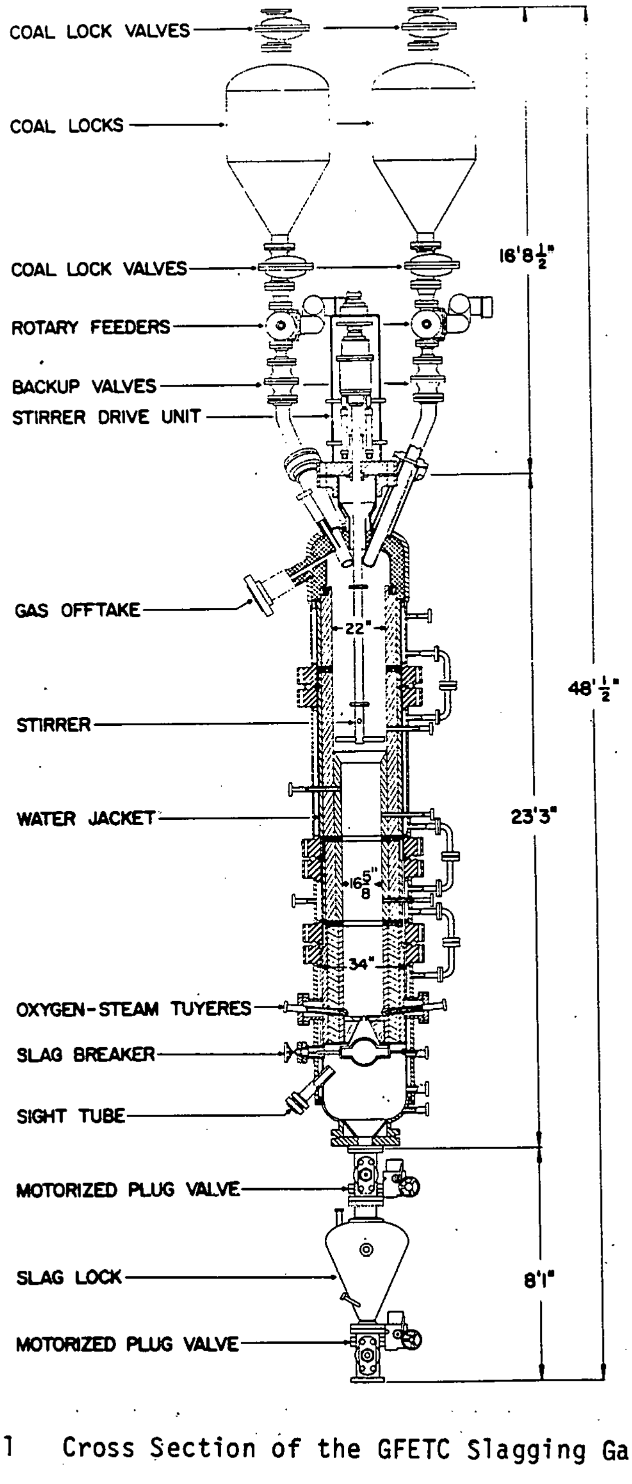

Figure 1.1 Cross Section of the GFETC Slagging Gasifier

of the overhead gas is largely determined in this zone, since sensible heat in ascending gas is required to vaporize the water.

2) Devolatilization zone. After moisture is removed, the coal enters the devolatilization zone where the tars and oils are vaporized and some water and product gas are formed. Products of drying and devolatilization, which leave the gas, are mainly water, hydrogen, carbon monoxide, carbon dioxide, and hydrocarbons, oils, and tars.

3) Quiescent zone. The devolatilized coal or char then descends into a quiescent zone where it is further heated. Some gas reactions take place, but little carbon is consumed.

4) Gasification/combustion zone. In the fourth zone, the gasification/combustion zone, hot char reacts with the oxygen-steam mixture introduced through four tuyeres positioned at 90° intervals just above the hearth. The exothermic combustion reactions produce the heat to support the endothermic gasification reactions: carbon, steam, and carbon dioxide react to form carbon monoxide and hydrogen. The oxygen/steam ratio must be such that a sufficiently high temperature is maintained to completely consume the carbon of the char and transform the ash to a molten liquid. The rate of the gasification reactions is influenced by the characteristics of the coal, as well as by operating conditions.

The molten ash (slag) drains through a central taphole into a water quench bath. A critical temperature must be maintained at the hearth and taphole areas to maintain slag flow. If the temperature is too high, the slag can cause melting and erosion of the refractory lining. In addition, some components of the ash will vaporize and condense in the cooler upper regions to form a bridge in the fuel bed. If the temperature is too low the slag will not flow through the taphole. The temperature balance is determined by such factors as oxygen-steam penetration into the bed, coal composition, and heat input from a taphole burner. Slag viscosity, which varies with coal type, influences heat and temperature requirements. Quenched slag in the water bath produces a frit resembling coarse sand which settles to the bottom of a water-filled lockhopper and is periodically removed.

A schematic diagram of the pilot plant is shown in Figure 1.2. The product gas stream is a mixture of the desired gas (methane) plus a variety of gaseous and condensible components produced from the coal in the gasification, devolatilization, and drying zones. This stream enters the spray precooler where, in the case of low-moisture coals, the gas temperature is lowered to below 700°F and the high-boiling, heavy tars are partially condensed through contact with a spray of cold water. The precooled gas then enters a washer where a spray of cooled, recycled gas liquor condenses water, light oil, and tar vapors and removes entrained dust particles. These accumulate in the spray washer and are periodically discharged to the tar/oil/water (T/O/W) separator. Tar, oil, and wastewater are fractionated by gravity and removed from the T/O/W separator for subsequent treatment studies or disposal via incineration. The clean gas is cooled in a heat exchanger, depres-

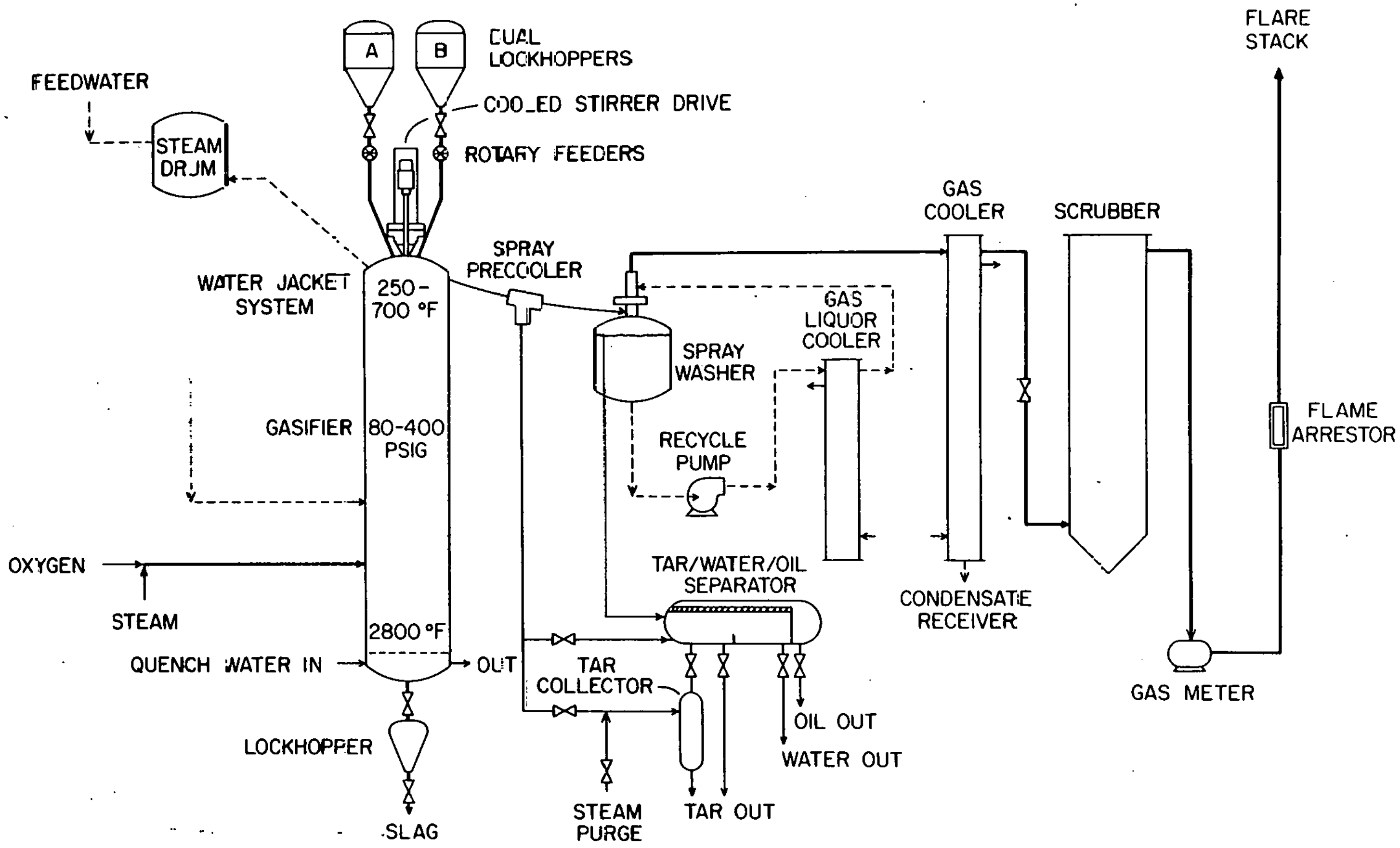

Figure 1.2 Process Flow Sheet of the GFETC Slagging Gasifier

surized, and passed through a coke-filled scrubber before being metered and analyzed.

Modifications to the GFETC gasifier that are provided for operation on caking bituminous coals are the stirrer, as shown in Figure 1.1, and a spray precooler, as shown in Figure 1.2. The latest version of the stirrer is water cooled and has a vertical travel of 4 feet, which will allow the deep penetration into the bed that is judged to be necessary to break up agglomerates formed from caking coals. The precooler is required on bituminous coal to reduce the high offgas temperature associated with low moisture content before the gas enters the spray cooler; the precooler is not required for operating on lignite where the off-gas temperature is approximately 300°F.

1.2 Background and Current Environmental Studies at GFETC

A major obstacle to proposed commercial coal conversion projects in the U.S. has been the delay and uncertainty in satisfying environmental permit requirements. Additional environmental data on effluent characteristics and advanced control technologies are needed for specific candidate coals if rapid growth of a substantial coal gasification industry is to occur.

Waste effluent streams from a fixed-bed gasification process consist of (1) gaseous contaminants (chiefly H_2S, NH_3, CO_2, and light hydrocarbons), which are cleaned from the product gas by commercially available processes to meet end use requirements; and (2) solid and liquid effluent streams consisting of slag, slag quench water, and the gas liquor, composed of condensed tar, oil, and wastewater (see Figure 1.2). Additional solid wastes are also generated by raw water and wastewater treatment processes.

Liquid and solid wastes from the pilot slagging gasifier are being evaluated at GFETC using in-house analytical procedures, and through contracts with major universities on methods of effluent treatment and disposal that will be environmentally acceptable. Current investigations have the following objectives:

- Characterization of slags and their leachates
- Fate of trace organics in water treatment processes
- Prediction of organic partition coefficients
- Evaluation of solvent extraction and biodegradation for wastewater treatment
- Characterization of biosludges and their leachates
- Evaluation of anaerobic digestion for wastewater treatment.

The effluent streams under study are recognized to be a specific set relating to the design of the GFETC gas quenching separation systems. In general, the waste streams from commercial operations will differ somewhat from those obtained at GFETC, depending on the gasifier offgas temperature and the design of the separation equipment. Two factors have been considered in making the GFETC data as general and representative as possible: (1) isokinetic samples are routinely obtained at the outlets from the GFETC gasifier to permit characterization of total effluents before quenching and separation; and (2) the design of the wastewater separation equipment at GFETC yields a wastewater stream that is similar to the combination of contributing streams which would be treated in a commercial dry-ash Lurgi plant, including the GPGA plant.

The most noxious waste stream from the gasifier is the gas liquor obtained from the condensation of tars, oils, phenols, and water in the spray cooler. The spray cooler is operated on recirculating waste liquor which is indirectly cooled in a heat exchanger; the blowdown (bleed stream) from this loop is determined by the moisture content of the coal for high-moisture lignite and by the water makeup rate in the case of bituminous coal. The source of the gas liquor is the moisture, volatile matter, and coal dust carried from the gasifier by countercurrent flow of the product gas. Since evolution of the volatile matter occurs in the upper elevations in the gasifier, at temperatures much lower than those at which combustion and gasification occur, the nature of the pollutants is thought to be largely insensitive to the type of gasification that occurs below, be it slagging or dry-ash. The condensation of the excess steam introduced in a dry-ash unit will, of course, affect the level of dilution. However, the chemical nature of the pollutants should be mostly a function of the parent coal for any fixed-bed gasifier operated at the same pressure.

In commercial gasifier designs, tar and oil are gravity separated from the wastewater and recycled to the gasifier or burned to generate steam. Therefore, the chief concern is one of industrial hygiene in the event of spills or leaks. Accordingly, samples of these materials from each coal and at each different operating condition will be screened for toxicity.

The contaminated wastewater after separation of the tar and oil represents by far the largest waste stream volumetrically. This stream must be processed in an environmentally acceptable manner for reuse within the plant to achieve zero discharge. To achieve this goal, as well as to investigate alternate or novel processes in an effort to reduce the high cost for rendering wastewater and its attendant sludges "environmentally acceptable," the existing environmental program at GFETC has the following objectives:

- Assess the adequacy and efficiency of commercial wastewater treatment processes to render gasification wastewater amenable for reuse as feed to a cooling tower or boiler.

- Evaluate conventional biological treatment techniques for SFBG wastewater.

- Test alternate/novel physical, chemical, or biological wastewater treatment processes.

- Evaluate disposal methods for biological, physical, and chemical wastewater treatment sludges, and characterize their leachates employing RCRA guidelines.

In addition to the GFETC-sponsored efforts, SFBG wastewater is being employed in feasibility studies by other laboratories. In one such study funded by the Pittsburgh Energy Technology Center (PETC), effectiveness of a pilot-scale anaerobic wastewater treatment unit operated by the Celanese Corp. will be evaluated. PETC is currently operating a small in-house continuous wastewater treatment train which includes air flotation, flocculation, pH adjustment, ammonia stripping, biochemical oxidation, carbon adsorption, etc. While data are non-scalable, the unit will provide information on the use of an integrated, continuous wastewater treatment train, which because of its size readily permits testing of different configurations or adding other unit operations. Toxicological characterization of influent and effluent samples from the various wastewater treatment systems and unit operations will be conducted at ANL.

Since all of the wastewater research discussed above is performed on such a small scale, none of the data generated will be directly extrapolatable to demonstration or commercial operations. Instead, the more fundamental questions of gasifier wastewater treatability are addressed. Application of commercially available wastewater treatment processes is discussed in the next section.

1.3 Commercial Wastewater Treatment Applications

Processes for wastewater treatment that are commercially available appear to be applicable to the water effluent streams from coal gasification plants. However, each treatment plant must be configured with a combination of appropriately designed process units to meet the specific requirements of the gasification technology and coal feedstocks used, and the environmental and economic constraints imposed, at that particular installation. Existing coal-specific data on nature and amounts of contaminants and effectiveness of treatment processes for wastewater streams from SFBG operations are not adequate to support reliable process designs.

The wastewater phase separated from the SFBG gas liquor contains concentrations of organics and inorganics high enough to render direct biological oxidation very difficult, and probably impractical. Extraction with solvent in one of the proprietary extraction processes such as Lurgi's Phenosolvan process will remove phenols, cresols, etc., to levels amenable to biological oxidation. The extracted phenol may either be recovered or recycled to the gasifier. Steam stripping will remove volatile species such as hydrogen sulfide and ammonia, which may then be treated as a separate gaseous stream.

There are several schools of thought regarding the level of treatment required prior to reuse of wastewater. One is that the wastewater from the ammonia stripper is sufficiently clean for reuse as feed to a cooling tower. This is the approach used in the design of the GPGA plant. Potential problems associated with this approach include contamination of the cooling tower drift by the evaporation of organics from the partially treated wastewater and potential for severe fouling of the heat transfer surfaces in heat exchangers.

Another, more cautious approach, is to perform a further biological treatment step in an activated sludge system, trickling filter, or aerated lagoon. Inclusion of a biological oxidation treatment in addition to tar/oil separation, solvent extraction, and ammonia stripping prior to feeding a cooling tower is the treatment scheme that had been proposed for the slagging fixed-bed gasification demonstration plant. Coal-specific data on the performance of these types of unit operations could be obtained effectively in the GFETC pilot plant by installing the appropriate systems downstream of the tar/oil/water separator and operating them during the normal course of pilot plant operation. Preliminary design of a commercially available treatment train, shown in Figure 1.3, consisting of a solvent extraction, ammonia-stripping, and cooling tower simulation unit equipped with portable heat transfer fouling units, has been completed. If the decision is made to proceed with procurement and operation of these units, influent and effluent samples from each unit operation could be tested in an extension of the ANL/GFETC environmental research program. The data would be specifically applicable to the design of water treatment plants for SFBG of the various low-rank and bituminous coals that will be tested in the pilot plant, and more generally applicable to a wider range of similar gasification processes and coals.

1.4 SFBG Operating Plan

The operating plan for January-May 1982 is shown in Table 1.1. The inside diameter of the gasifier will be enlarged from 16 to 22 inches to determine if the "hang-slip" behavior which is sometimes observed in the coal bed can be reduced. Remaining SFBG tests will be performed in the enlarged gasifier for the primary purpose of generating quantities of steady state lignite-derived wastewater. The lignite to be used is from the North American Coal Company's Indian Head mine, which is the same seam that will be used in the commercial GPGA plant.

The operations will be terminated in May 1982 as a result of a Fossil Energy decision to eliminate FY 1983 funds, and rescind some FY 1982 funds, for fixed-bed gasifier operations at GFETC and METC.

Liquid Effluent Sampling Plan

When tests are performed on lignite to accumulate wastewater for subsequent treatability studies, effluent collected in the spray washer and T/O/W separator during the first eight hours of operation is

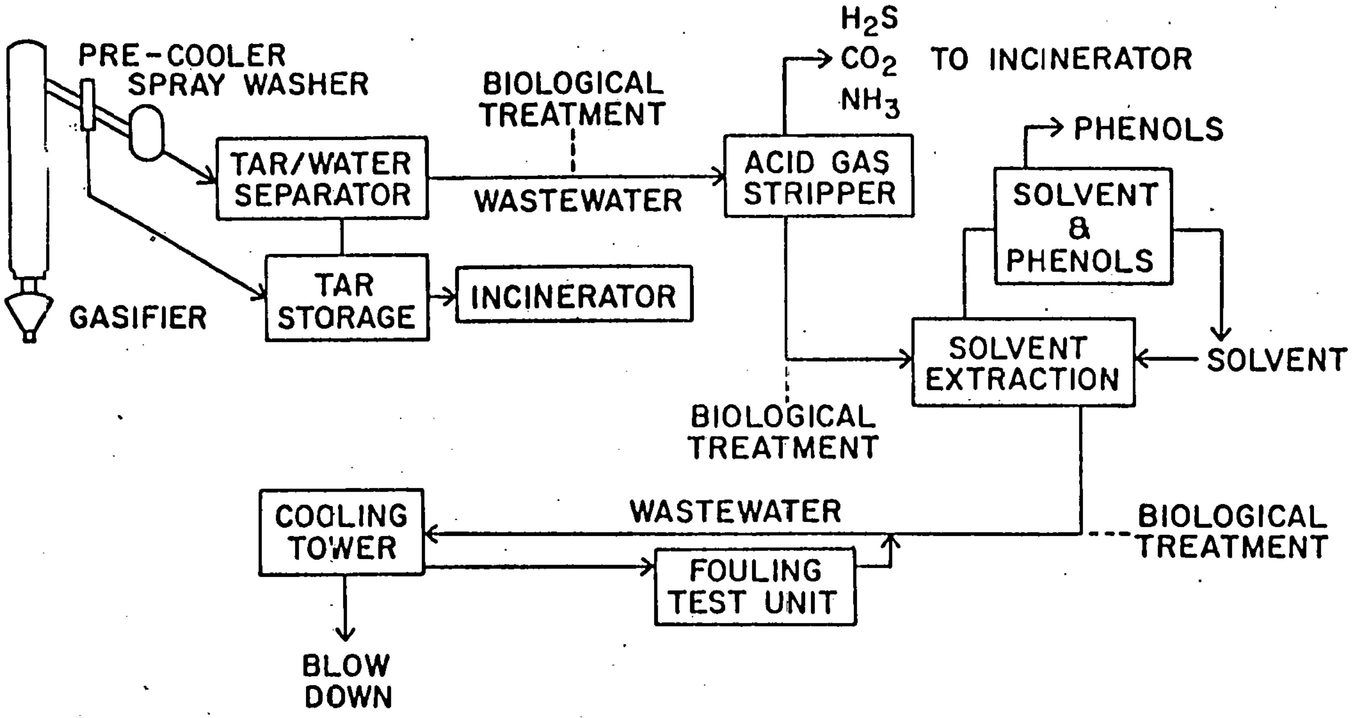

Figure 1.3 Proposed GFETC Slagging Gasifier Wastewater Treatment Train

TABLE 1.1 Proposed GFETC Slagging Gasifier Operating Schedule
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						Samples				
Date	Modification	Feed	Coal Moisture Wt. %	Pressure psig	O_2/Steam mole ratio	Side-stream	Tar	Oil	Waste-Water	Slag-Water
1-12-82	Enlarged Gasifier[a]	Indian Head	30	300	1.00	X				
1-26-82	"	"	"	"	"	X				
2-09-82	"	"	"	"	"	X	X	X	X	
2-23-82	"	"	"	"	0.9	X	X	X	X	
3-09-82	"	"	"	"	0.8	X				
3-23-82	"	"	"	"	0.9	X				
4-13-82	"	"	"	"	1.0	X				
4-28-82	"	"	"	Optimum	Optimum	X	X	X	X	
5-14-82	Shutdown									

[a] Internal diameter, 22 inches.

discarded. This period of time, which is necessary to obtain stable temperatures in the gasifier, allows for at least four complete turnovers in the inventory of the spray washer, approaching 99% process-derived wastewater. This is only practicable for high-moisture coals such as lignite, which can yield over 600 lb. of wastewater per ton of coal.

Fortunately, since the samples required for toxicological assessment are small, a representative sample from operation on bituminous coal can be condensed from the product gas stream. An effort has been made to compare mass rate results obtained from the total liquids condensed during an entire run of the SFBG on lignite with those collected by a side-stream sampler (SS) located immediately downstream of the gasifier, for a short time during steady-state operation. Wastewater mass rates obtained from the entire run compared very favorably with those calculated from the SS. This will also be true in future tests as long as the initial amount of tap water used to start up the spray washer is known and no further dilution is required. Also, values for tar and oil calculated from the SS were equivalent to those recovered at the end of the run.

One of the initial efforts in the assessment program during operation on lignite will be to compare both chemically and biologically the nature of the samples collected in the SS and bulk samples of tar, oil, and wastewater collected from the T/O/W separator. Development of the correlation of effluents collected from the SS with bulk samples will enable meaningful data to be generated from the SS alone during operations that do not reach steady-state in the spray washer.

The liquid effluent sampling plan for the environmental assessment program is indicated on Table 1.1 along with the SFBG operating schedule. The side-stream samples will be obtained by operating the side-stream sampler (Fig. 1.4) for about one hour during steady-state gasifier operation. During the runs indicated, one quart each of tar and oil along with two gallons of wastewater will be taken from the T/O/W separator after steady-state operation has been reached. An additional 1-gallon sample of the slag quench water will be obtained during each run. Samples will be frozen to effect preservation to the largest degree possible, and then shipped to ANL by air.

Additional samples of influent and effluent will be obtained by ANL from each of the research laboratories performing treatability studies on wastewater. Table 1.2 presents the source, availability, and relevance of SFBG effluent samples that will be analyzed by ANL.

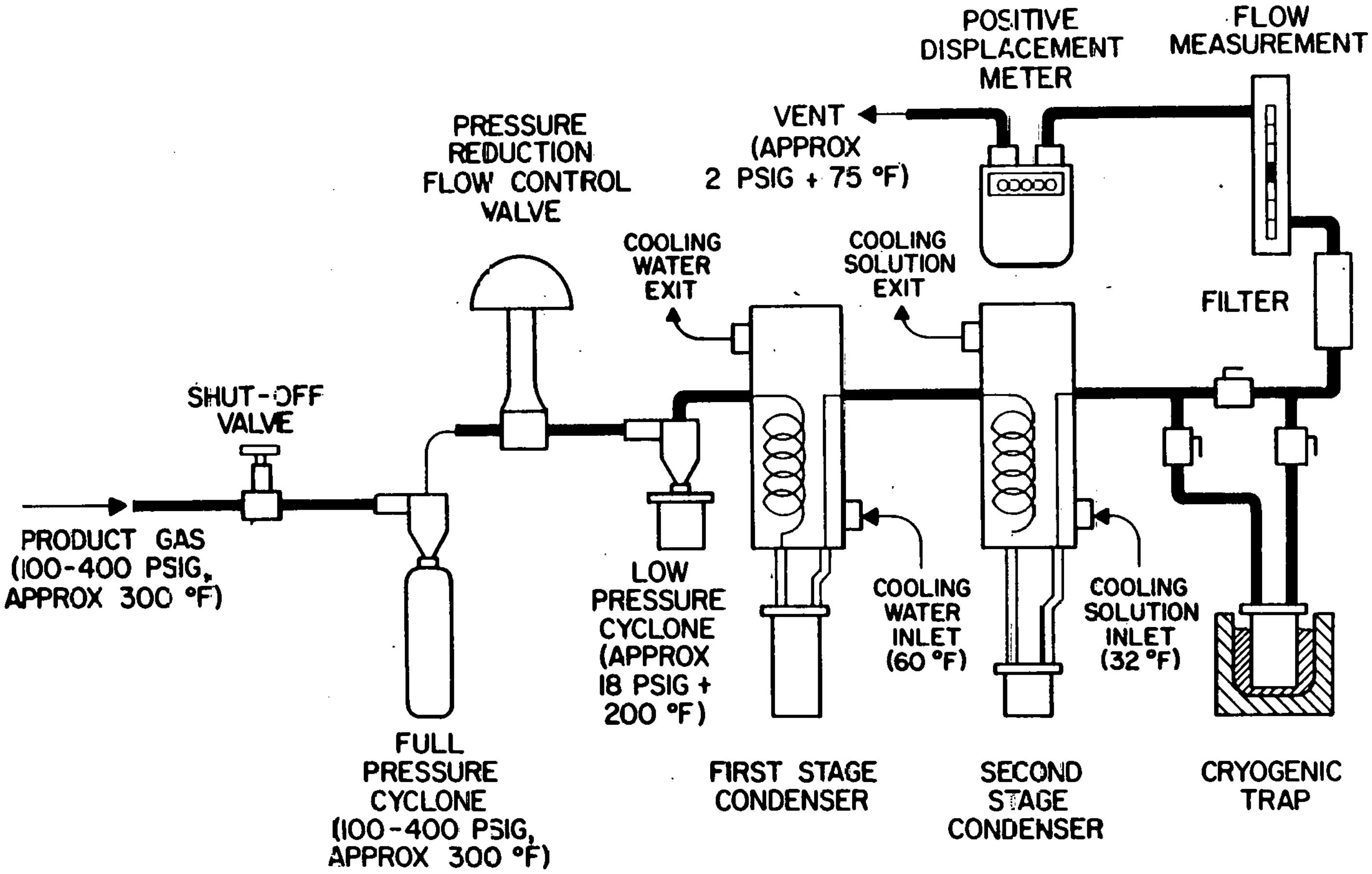

Figure 1.4 Schematic of Side-stream Sampling System

TABLE 1.2 Source, Availability, and Relevance of SGBG Effluents

Source	Materials	Availability	Relevance Towards Commercialization
SFBG-T/O/W Separator	Wastewater, tar and oil	1-81	Dependent on method of gas cooling and condensation; operation on lignite where dilution can be negated should yield scalable data for ANG plant.
SFBG-Slag Quenchwater	Quenchwater	1-81	Dependent on water recycle and makeup rates; probably scalable for closed system.
SFBG-SS	Wastewater, tar and oil	1-81	Source of samples independent of recycle/dilution requirements for gas cooling due to rapid quenching, tars and oils may differ slightly from those quenched in the spray washer; differences to be elucidated on lignite operation.
University of North Dakota	Solvent-extracted wastewater	6-81	Non-scalable data, representing potential effects of solvent-extraction as well as activated sludge treatment on wastewater quality.
Georgia Institute of Technology	Wastewater treated by anaerobic digestion	4-82	Non-scalable; data will indicate possible benefits of novel anaerobic treatment process.
Celanese Corp.	Anaerobically treated wastewater	9-81	Scalable data on effluents obtained from anaerobic treatment of wastewater derived from steady-state operation on lignite; treatment to be performed on pilot-plant-sized equipment.
Pittsburgh Energy Technology Center	Wastewater from various stages of treatment	1-82	Data not scalable due to small scale of the continuous process units, but biological evaluations of influents and effluents will provide the first information from an integrated, continuous wastewater treatment train; size allows for testing different configurations and unit operations.

2. TOXICOLOGICAL EVALUATION OF SLAGGING FIXED-BED COAL GASIFICATION PROCESS STREAMS AND EFFLUENTS

2.1 Approach

Process stream samples from the Grand Forks Energy Technology Center's SFBG should be representative of materials produced by commercial Lurgi gasifiers. The planned experimental test runs prior to the recent funding decision were to cover three coal types (lignite, subbituminous and bituminous), as well as a host of operating variables, to provide the breadth of samples necessary for definitive results. Thus, a thorough toxicological characterization of these process materials would have provided a reasonable base of information for assessment of the potential health effects associated with high-BTU coal gasification. The current plans are limited to low-rank coal feedstocks.

To achieve the necessary toxicological characterization, process materials are studied at two operational levels, as shown in Table 2.1. In the first level, potentially hazardous samples are identified through a variety of short-term assays amenable to raw process samples. These assays include: bacterial mutagenicity determinations in the Ames Salmonella assay, mammalian cell genotoxicity (sister chromatid exchange) and cytotoxicity (growth inhibition and lethality) in a mouse myeloma cell, and cytotoxicity (lethality and impairment of phagocytosis) in rabbit alveolar macrophages.

TABLE 2.1 Tiered Approach for Characterization of Toxicity

Level One	Cellular Tests	
	- Genetic Toxicity	
	a) Mutation	Ames Salmonella assay
	b) Sister chromatid exchange	Mouse myeloma cells
	- Cytotoxicity	
	a) Growth inhibition, lethality	Mouse myeloma cells
	b) Lethality	Rabbit alveolar macrophages
	c) Functional impairment	Rabbit alveolar macrophages
Level Two	Whole Animal Studies	
	- Acute Toxicity	
	a) Oral and intraperitoneal (LD_{50})	Mouse, albino guinea pig
	b) Ocular (corneal, lens, and retinal irritation)	Rabbit
	c) Dermal	Rabbit
	- Chronic Dermal Exposure	
	a) Delayed-type hypersensitization	Albino guinea pig
	b) Carcinogenesis	Hairless mouse
	c) Systemic damage	Hairless mouse

Following initial identification of toxic materials, samples deemed toxicologically significant are further tested in the second level. This level involves a variety of acute and chronic animal toxicological studies including evaluation of carcinogenicity. Acute exposures determine the effects of the test substance on skin, eyes, and whole animals (oral and intraperitoneal LD_{50}). Although LD_{50} values are usually of limited value with respect to assessing hazards, they are useful for comparison with the values found for other compounds or processes. Chronic animal studies are inherently relatively long term, but presently available in vitro assays do not provide meaningful appraisals of human health effects without supportive evidence from animal studies.

2.2 Results

Side-stream sample materials from run #80 and process samples from run #87 are presently under toxicological evaluation. Operating conditions for these two runs are presented in Table 2.2.

TABLE 2.2 Operating Data for Runs Selected for Toxicological Characterization

	Run	
	#80	#87
Slagging time, hours	21.0	65.8
Moisture in coal, %, (Indian Head Lignite).	30.6	27.8
Run conditions:		
Oxygen rate, scfh	6,000	5,000
Oxygen/steam ratio	1.0	0.9
Fuel rate, lb/hr as fed	1,694	1,661
MAF fuel rate, lb/hr	1,074	1,084
Product gas rate, scfh	30,330	31,255
Slag rate, lb/hr	92.8	61.5
Oxygen consumed, ft /lb maf fuel	5.58	5.20
Steam consumed, lb/lb maf fuel	0.26	0.26
Product gas, scf/lb maf fuel	28.23	28.85
Product gas composition, % (N_2 free):		
H_2	24.7	29.0
CO	57.9	57.0
CH_4	6.7	5.4
CO_2	9.3	8.0
C_2-C_4 Hydrocarbons	1.4	0.6
Average gas offtake temperature, °F	357	333
Elemental mass balance, % accounted for:		
C	102	96
H	117	98
N	106	89
O	119	107
Heat balance, %, (p = potential, s = sensible);		
Heat in:		
Fuel (p)	97.2	96.3
Steam	2.6	3.3
Oxygen	0.3	0.4
Heat out:		
Product gas (p)	83.4	85.8
(s)	1.6	1.5
Drawdown gas (p&s)	0.0	0.0
Slag	0.7	0.5
Water vapor	7.6	5.4
Tar	5.5	5.0
Unaccounted for	1.1	1.9

In general, the side-stream samples were an oil-water mixture with the aqueous phase being the principal component (Table 2.3).

TABLE 2.3 Weight (grams) Composition of GFETC Side-Stream Samples

Sample	Gross	Aqueous Phase		Oil Phase	
		Gross	NVO Fraction[a]	Gross	NVO Fraction[a]
High Pressure Cyclone	1336	1202	4	134	63
Low Pressure Cyclone	79	55	0.2	24	12
First Heat Exchanger	1634	1564	18	70	39
Second Heat Exchanger	130	107	0.8	23	13
Total	3179[b]	2928	23	251	127

[a] Non-volatile organic components.

[b] Corresponds to gasification of 4370 g moisture ash free lignite.

In this report, we include results of Ames mutagenicity tests on the nonvolatile organic (NVO) fractions obtained from water and oil materials collected during run #80 from each of the four side-stream sampling points. In addition, Ames assay data are presented for a number of raw (unfractionated) tar and oil process samples from run #87. Included are results from a large sample of process tar obtained from run #87 that will be used for animal tests. Assay of samples in the mouse myeloma and rabbit alveolar macrophage systems have not been completed, but the available test results are presented in this report. The initial results of whole animal tests are reported as well.

2.2.1 Ames Salmonella Mutagenicity Assay

The Ames *Salmonella* assay for mutagenicity was applied to all process samples and was also used to monitor biological activity in the chemical fractionation of the tars and oils. Samples tested were dissolved in dimethyl sulfoxide and assayed for mutagenicity by the plate-incorporation method. After 48 hr incubation, histidine revertants were counted in *S. typhimurium* TA98. Only strain TA98 was used in this initial screen since past experience with coal-derived materials clearly demonstrates that it is consistently the most sensitive strain. In all cases, Aroclor 1254-induced rat liver S-9 activating enzyme (Bionetics Laboratory) was a requirement for mutagenicity, and was used at a concentration close to optimal.

Samples were tested at a range of concentrations within the linear region of the dose-response curve. Mutagenic activities were calculated from best-fit regressions obtained from 4 to 6 points, each assayed in triplicate, within this region.

Assessments of relative mutagenicity are based on comparison with the spontaneous frequency. There was no evidence of significant cytotoxicity at any of the concentrations used. Positive controls using benzo[a]pyrene were included with each assay to check cellular response and enzyme preparation.

The results of mutagenesis assays of the side-stream samples listed in Table 2.3 are shown in Table 2.4. The NVO fractions generated from extracts of the aqueous phases were not significantly mutagenic and thus are not included. The NVO fractions prepared from the oil phases varied considerably in mutagenicity, with the specific activity of the samples decreasing sequentially as the gas passed through the sampling train. The oil phase NVO fraction of the high pressure cyclone sample contained more than 90% of the total mutagenicity (in approximately 5% of the sample weight).

Table 2.4 Ames Salmonella Mutagenicity Assay of NVO Fractions from Run #80 Side-Stream Oil Samples and HYGAS Recycle Oil

Sample	Specific Activity rev/μg	Total Activity rev (%)
High pressure cyclone	19	1199 (92.9)
Low pressure cyclone	5	46 (3.6)
First heat exchanger	1	39 (3.0)
Second heat exchanger	< 1	5 (0.4)
HYGAS recycle oil (NVO)	7[a]	
Benzo[a]pyrene	260	

[a] Average value for 18 samples in four pilot plant runs.

Process materials, including samples of oil and tar collected concurrently at three different times during run #87, were tested for toxicity both in the Ames Salmonella assay and in the mouse myeloma assay. The results of these assays are presented in Table 2.5 along with toxicity data for a large sample of tar (collected for level two testing) and for selected reference materials.

Table 2.5 Toxicity of GFETC Gasifier Process Tars and Oils

Sample	Ames Salmonella Assay[a] rev/μg	Mouse Myeloma Assay Cytotoxicity L/g[b]	Mouse Myeloma Assay Genotoxicity L/g[c]
Oil - G87PL2	< 1	11	9
- G87PL4	< 1	14	3
- G87PL10	< 1	9	23
Tar - G87PT2	1	11	6
- G87PT4	8	11	20
- G87PT10	4	11	14
- G87PT17	2	9	26
Coal-derived oil[d]	13	53	N.T.[e]
HYGAS recycle oil (NVO)	7	17	15
Benzo[a]pyrene	260	112[a]	1230[a]

[a] Samples metabolically activated (rat liver S9).

[b] The reciprocal of the NVO concentrations producing 50% growth inhibition.

[c] The reciprocal of the NVO concentration that doubles the frequency of sister chromatid exchange.

[d] ORNL reference material CRM-1.

[e] Not tested.

2.2.2 In Vivo Animal Toxicity Tests

Finally, preliminary data on acute toxicity in animal studies are shown in Tables 2.6 and 2.7. Ocular toxicity resulting from a single exposure to GFETC tar was transient, being significant only within the first 24 hours after treatment. No overt acute dermal toxicity was noted in mice receiving skin treatment with a 50% concentration of GFETC tar three times per week for two weeks.

Table 2.6 Ocular Toxicity (Albino Rabbits)

Sample	Day[a] 1	3	7	14	21
GFETC tar	32.8	0	0	0	0
NVO fraction of HYGAS recycle oil	31.0	17.0	4.0	3.0	0

[a] Mean score for 6 rabbits. Score above 20 is considered to indicate significant irritation.

Table 2.7 Subacute Dermal Toxicity (SKH Hairless Mice)

Sample	Dose	Results[a]
GFETC tar/acetone	50:50	mild hyperemia and trauma from scratching
HYGAS recycle oil NVO/ acetone	70:30	severe scaling, hyperplasia, and trauma from scratching.

[a] Observations made after eight weeks of treatment.

3. CHEMICAL CHARACTERIZATION OF GFETC GASIFIER PROCESS LIQUIDS AND TARS

3.1 Process Liquids

A series of process liquids from run #87 of the GFETC gasifier was analyzed by our newly developed rapid analysis scheme using capillary column GC and GC/MS.

Three oil samples collected over a two-day period during run #87 were analyzed. The raw samples (G87PL2, G87PL4, and G87PL10) as well as the separated volatile and non-volatile organic fractions, were analyzed. The results are summarized in Tables 3.1 to 3.3 and representative gas chromatograms are shown in Figures 3.1 and 3.2. As seen from these tables, the major constituents are toluene, xylenes, phenol, cresols, indene, C_2-phenols, naphthalene, methylnaphthalene, and acenaphthylene.

3.2 Isolation of Bases from Tar

In processing the GFETC samples, we have explored modifications of the pH fractionation procedure used to separate acidic, basic, and neutral components. The modified procedures were designed to assure good recovery of the basic components having four rings. Previously, bases were extracted from methylene chloride solutions of the samples using 1 or 2 N hydrochloric acid. This procedure has been found to be satisfactory for two- and three-ring aromatic bases, but inadequate for recovery of the higher molecular weight aromatic bases. To improve the method, we have included methanol or isopropanol in the aqueous acid to increase the solubility of the heavier bases.

Initial results indicated that the presence of methanol enhanced the solubility of phenols in the aqueous acid, requiring that the phenols first be removed by extraction of the methylene chloride solution with aqueous sodium hydroxide. The solution was then extracted once with aqueous HCl (3 N) and twice with methanolic HCl (3 N). The bases found in the aqueous extract are listed in Table 3.4; those in the first methanolic extract are listed in Table 3.5. The major components were two- to five-ring azaarenes. In addition, two- to five-ring primary aromatic amines were present as minor components. The mutagenicities of the various fractions are shown in Table 3.6. Note that there is more mutagenicity in the methanolic HCl extracts than in the aqueous HCl extract.

Basic fractions prepared by this or a similar method will be separated by cation exchange HPLC to better understand the nature of the mutagens present. This method has been developed at ANL, and has been successfully applied to characterization of bases from other coal-derived materials.

TABLE 3.1 Compounds Identified[a] in Raw Process Liquids (G87PL2, G87PL4, G87PL10) from the GFETC Gasifier

Compound Name	Concentration (mg/g) PL2	PL4	PL10
Benzene	5.1	7.8	15.7
Toluene	12.5	16.2	26.7
Ethylbenzene	2.8	3.2	4.6
m- and p-Xylene	12.5	15.1	21.8
Styrene	2.8	5.7	6.9
o-Xylene	4.4	6.9	8.1
Benzofuran	4.9	7.0	7.0
Methylstyrene	9.4	13.8	14.4
Phenol	54.6	71.3	64.6
Acetophenone	8.2	7.3	9.2
Indene	29.5	46.3	44.6
o-Cresol	32.3	44.1	40.5
Methylbenzofuran	2.4	4.3	3.6
m- and p-Cresol	69.4	96.4	86.3
1,2-Dihydronaphthalene	9.2	12.7	12.0
Methylindene	3.5	5.1	4.7
1,4-Dihydronaphthalene	4.7	6.8	6.3
C_2-Phenol	22.4	29.8	27.3
Naphthalene	98.1	125.4	121.8
Benzothiophene	1.9	3.0	3.3
C_2-Phenol	16.9	34.7	34.5
C_2-Indane & C_2-Phenol	7.0	9.7	9.1
Hydroxystyrene	1.3	1.4	1.3
2-Methylnaphthalene	21.9	27.2	27.8
1-Methylnaphthalene	9.3	12.7	11.7
Biphenyl	3.3	3.2	7.1
C_2-Naphthalene	1.0	2.0	2.8
C_2-Naphthalene	2.8	3.6	3.7
C_2-Naphthalene	4.3	5.4	5.7
Acenaphthylene	10.4	15.1	16.2
Acenaphthene	3.6	3.8	4.7
Methylbiphenyl	1.4	1.5	1.7
Dibenzofuran	4.0	3.6	5.7
Fluorene	4.5	5.2	6.2
Phenanthrene	1.0	1.7	2.2
Anthracene	0.8	1.5	1.9
Total Identified	484.1	660.5	671.7
Total Chromatographable	661.9	860.1	859.9

[a] Gas chromatography using fused silica capillary columns with a flame ionization detector, and mass spectrometry.

TABLE 3.2 Compounds Identified in the Volatile Fractions of GFETC Gasifier Oils (G87PL2, G87PL4, and G87PL10)

RRI[a]	Compound Name	Concentration[b] (mg/g) PL2	PL4	PL10
215	Pyridine	6.3	8.1	6.7
224	Toluene	--	--	2.8
258	Ethylbenzene	--	--	2.0
262	1,3 & 1,4-Dimethylbenzene	--	1.0	12.5
270	Styrene	--	1.8	7.1
271	1,2-Dimethylbenzene	--	1.8	7.2
304	Benzonitrile	5.5	6.7	9.5
305	C_3-Benzene	--	--	7.3
307	C_3-Benzene	--	--	2.8
311	Indan	--	--	2.8
312	C_3-Benzene	--	--	1.6
315	Benzofuran	4.5	6.2	15.5
318	C_3-Benzene	1.2	8.4	31.2
326	Azaindan	--	--	3.4
327	Phenol	173.9	124.1	106.6
330	C_3-Benzene	15.5	8.8	20.6
334	Acetophenone	10.2	7.7	19.0
338	Indene	64.9	65.9	103.7
349	C_4-Benzene	--	--	2.3
351	C_4-Benzene	--	--	2.1
356	2-Methylphenol	65.2	52.4	31.0
360	Methyl-benzofuran	15.8	9.3	5.2
362	Methyl-benzofuran	2.9	1.6	2.3
364	Methyl-benzofuran	9.3	6.8	8.2
367	Methylindan	17.2	12.7	12.7
368	3- & 4-Methylphenol	59.7	66.2	39.3
374	C_4-Benzene & Methylindan	5.8	--	5.7
376	n-C_{12}-Alkane	3.1	--	2.6
379	Methylindan	7.7	6.5	7.6
384	Methylindan	6.2	3.1	3.7
386	1,2-Dihydronaphthalene	31.1	24.9	21.0
389	1,4-Dihydronaphthalene	15.4	8.9	10.8
338	C_2-Phenol	4.8	8.2	2.9
400	Naphthalene	180.0	182.2	114.6
414	C_2-Indan	3.8	5.2	2.1
416	C_2-Indan	4.8	6.8	2.5
417	C_2-Benzofuran	9.7	7.8	6.7
422	n-C_{12}-Alkane	9.4	5.2	6.0
444	2-Methylnaphthalene	7.9	12.0	4.9
449	1-Methylnaphthalene	3.0	5.2	2.3
456	C_{12}-Alkane	3.1	3.3	2.0
460	n-C_{13}-Alkane	4.0	4.1	2.2
	Total Identified	745.6	680.9	667.0

[a] Relative Retention Index with the following arbitrary assignments: benzene 200, naphthalene 400, phenanthrene 600, and chrysene 800.

[b] Concentrations based on FID-GC. For RRI below 300 the response factor of benzene was used; for RRI above 300 the response factor of naphthalene was used.

TABLE 3.3 Compounds Identified in the NVO fractions of the GFETC Gasifier Process Oil (G87PL2, G87PL4, and G87PL10)

RRI[a]	Compound Name	Concentration[b] (mg/g) PL2	PL4	PL10
327	Phenol	23.5	21.4	19.3
334	Acetophenone	1.5	1.4	1.4
356	2-Cresol	28.5	23.5	22.1
368	3- and 4-Cresol	73.8	78.3	63.6
386	1,2-Dihydronaphthalene	3.2	2.1	4.3
388	1,4-Dihydronaphthalene	4.6	2.0	2.4
392	C_2-Phenol	5.6	5.5	3.8
396	C_2-Phenol	29.0	30.4	22.7
400	Naphthalene	80.4	61.9	74.2
406	C_2-Phenol	42.8	46.2	35.4
415	C_2-Phenol and C_2-Indan	8.0	8.8	7.3
419	C_2-Phenol	1.1	2.1	1.7
431	Azanaphthalene	7.0	7.4	6.0
432	C_3-Phenol	4.6	5.3	4.3
444	2-Methylnaphthalene	26.6	28.1	28.0
449	1-Methylnaphthalene	13.9	13.9	10.8
453	C_3-Indan	3.8	2.7	2.4
456	C_3-Indan	3.4	2.2	2.5
460	C_3-Indan	4.5	3.4	3.5
474	Biphenyl	8.4	7.8	7.1
480	C_2-Naphthalene	7.2	2.8	3.5
485	C_2-Naphthalene	6.2	5.3	5.3
490	C_2-Naphthalene	4.5	4.2	3.8
491	C_2-Naphthalene	6.0	6.3	5.3
497	Acenaphthylene	16.0	18.8	15.3
501	C_2-Naphthalene	2.2	2.2	2.2
509	Acenaphthene	5.6	5.2	5.1
521	Dibenzofuran	0.5	7.0	6.2
531	Methylbiphenyl	1.8	2.0	1.9
542	Fluorene	8.9	7.1	6.2
545	C_3-Naphthalene	2.3	2.5	2.3
555	Methyldibenzofuran	.4	.7	.6
556	Methyldibenzofuran	.6	.9	.8
560	Methyldibenzofuran	2.0	2.8	2.4
564	Aliphatic hydrocarbon	1.3	1.6	1.4
600	Phenanthrene	2.5	2.2	2.1
605	Anthracene	2.0	2.2	1.8
	Total Identified	504.2	428.3	389.0

[a] Relative Retention Index with the following arbitrary assignments: benzene 200, naphthalene 400, phenanthrene 600, and chrysene 800.

[b] These are preliminary data based on FID-GC. For RRI below 500 the response factor of naphthalene was used; for RRI above 500 the response factor of phenanthrene was used.

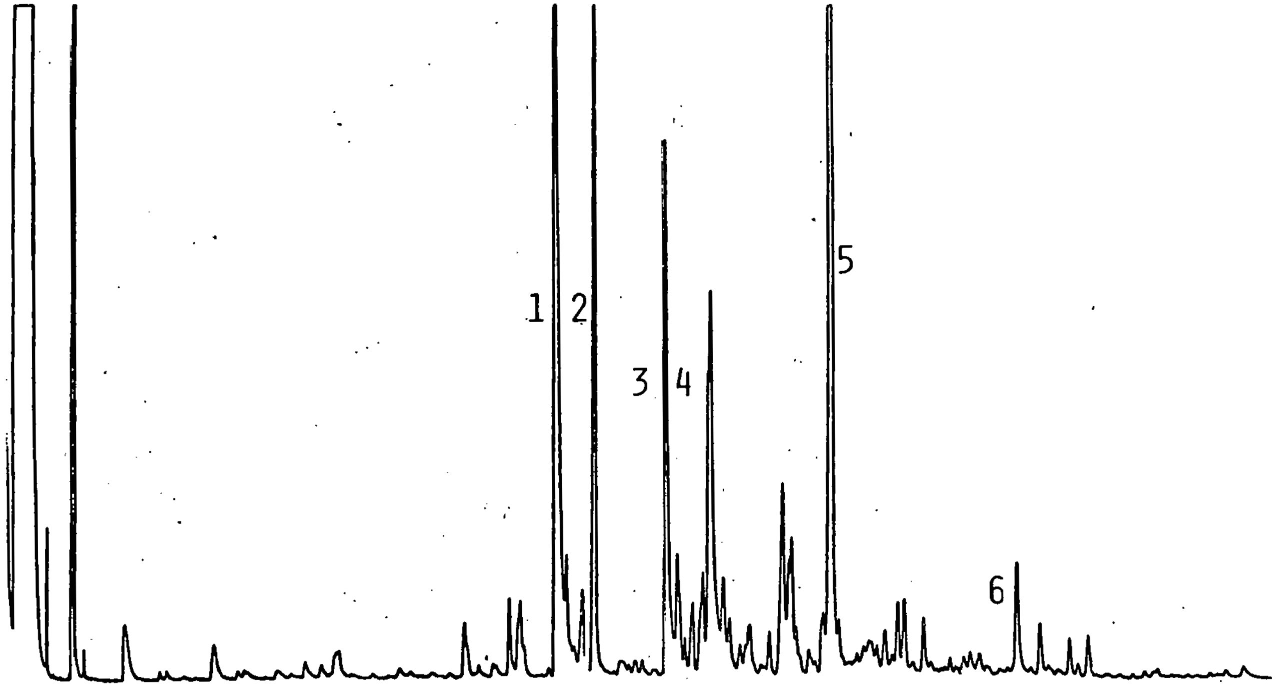

Figure 3.1 Gas chromatogram of the more volatile components of process oil from the GFETC Gasifier. 1, phenol; 2, indene; 3, o-cresol; 4, m- and p-cresol; 5, napthalene; 6, 2-methylnaphthalene.

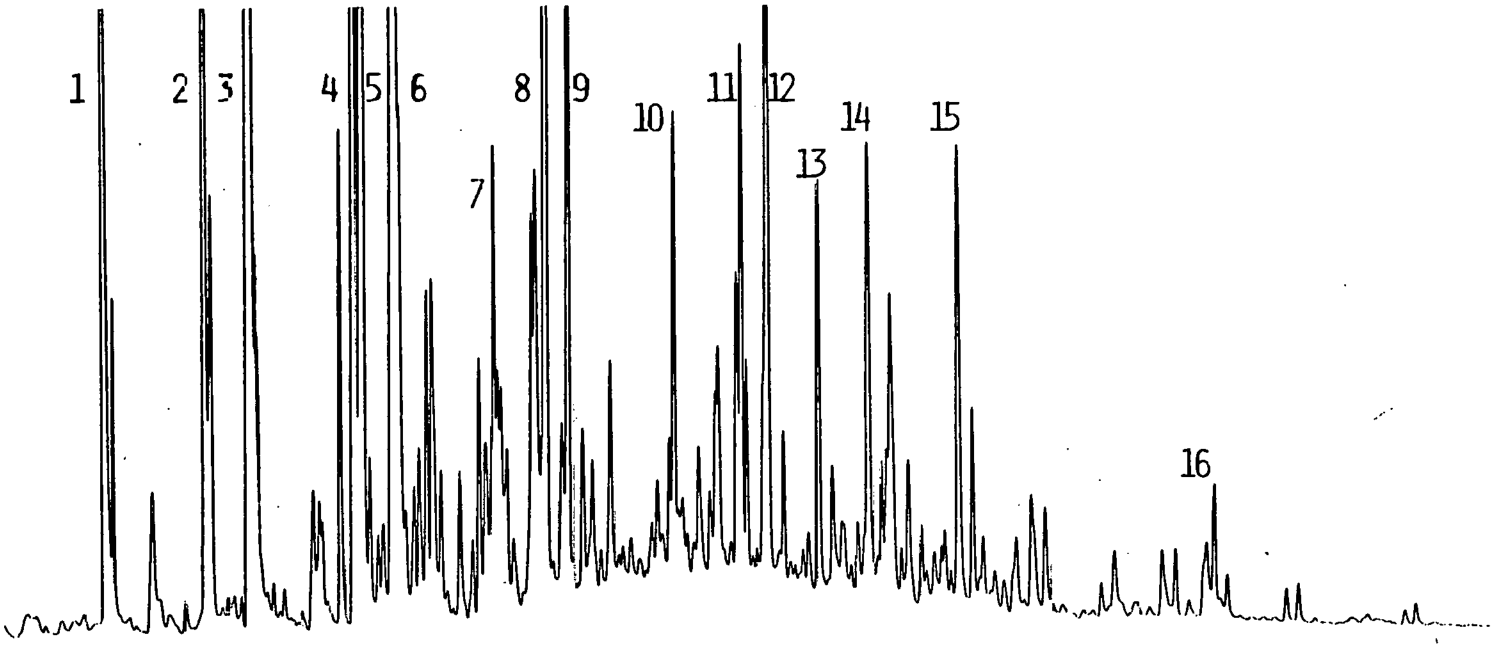

Figure 3.2 Gas chromatogram of less volatile components of process oil from the GFETC Gasifier: 1, phenol; 2, o-cresol; 3, m- and p-cresol; 4, C_2-phenol; 5, naphthalene; 6, C_2-phenol; 7, quinoline; 8, 8, 2-methylnaphthalene; 9, 1-methylnaphthalene; 10, biphenyl; 11, C_2-naphthalene; 12, acenaphthylene; 13, acenaphthene, 14, dibenzofuran; 15, fluorene; 16, phenanthrene.

TABLE 3.4 Major Classes of Compounds Identified in an Aqueous HCl Extract of a GFETC Coal-Gasification Tar (G87PT17)

Alkylation)	Compound Class[a]	Relative Amount
(C_2-C_4)-	Phenols	Low
(C_0-C_6)-	Azanapthalenes[a]	High (C_2-C_3); Med (C_0-C_4); Low (C_5-C_6)
(C_0-C_6)-	Azabiphenyls[a]	Med (C_1-C_3); Low (C_0, C_4, C_6)
(C_0-C_5)-	Azaacenaphthenes[a]	Med (C_1, C_2); Low (C_0, C_3-C_6)
(C_0-C_5)-	Azafluorenes (or Azabenzoindans, or Azaacenaphthylenes)[a]	High (C_0-C_2); Med (C_3); Low (C_4-C_5)
(C_0-C_5)-	Azaphenanthrenes [a] and Azaanthracenes	High (C_0-C_1); Med (C_2-C_3); Low (C_4-C_5)
(C_0-C_4)-	Azafluoranthenes and Azapyrenes[a]	High (C_0-C_1); Med (C_2); Low (C_3-C_4)
(C_0-C_3)-	Azaphenylnaphthalenes[a] and Azacyclopentaphenanthrenes[a]	Med (C_0); Low (C_1-C_3)
(C_0-C_3)-	Azachrysenes[a] and Azabenzo-(phenanthrenes and anthracenes)	Med (C_0); Low (C_1-C_3)
(C_0-C_1)-	Azabenzpyrenes, Azaperylenes, and isomers	Low
C_0	Azabinaphythyls	Low

[a] There is evidence of presence of very low levels of primary aromatic amines and also diazaarenes.

TABLE 3.5 Major Classes of Compounds Identified in a Methanolic HCl Extract of a GFETC Coal-Gasification Tar (G87PT17)

(Alkylation)	Compound Class[a]	Relative Amount
(C_0-C_5)-	Azanaphthalenes	High (C_1-C_3); Med (C_0,C_4); Low (C_5)
(C_2-C_3)-	Azaindenes	Low
(C_0-C_4)-	Azabiphenyls	High (C_0-C_1); Med (C_2); Low (C_3-C_4)
(C_0-C_3)-	Azaacenaphthenes	Med (C_0-C_1); Low (C_2-C_3)
(C_0-C_3)-	Azafluorenes (or Azabenzoindans or Azaacenaphthylenes)	High (C_0); Med (C_1); Low (C_2-C_3)
(C_0-C_3)-	Azaphenanthrenes and Azaanthracenes	High (C_0-C_1); Med (C_2); Low (C_3)
(C_0-C_2)-	Azafluoranthenes and Azapyrenes	Med (C_0); Low (C_1-C_2)
(C_0-C_1)-	Azaphenylnaphthalenes and Cyclopentaphenanthrenes	Low
C_0	Azachrysene and Azabenzo(phenanthrenes and anthracenes)	Low

[a] There is evidence of presence of very low levels of primary aromatic amines and also diazaarenes.

TABLE 3.6. Distribution of Mutagenicity in pH Fractions of GFETC Gasifier Process Tar

Fraction	Weight %	Mutagenicity[a] rev/μg	Mutagenicity[a] %
Base			
Aqueous HCl	0.87	60	13.2
Methanolic HCl	0.87	68	14.9
Methanolic HCl	0.64	38	6.1
Neutral	65.2	4	65.8
Acid	30.0	0	0

[a] Ames assay, S. typhimurium TA98 with Aroclor-induced rat liver S-9.

3.3 Characterization of Neutral Fraction

A detailed GC and GC/MS characterization of the neutral fraction (G87PT17A10) indicated the presence of a wide variety of one to five ring aromatic hydrocarbons, oxygen- and sulfur-heterocycles, and C_{12}- to C_{30}- aliphatic hydrocarbons. Percentage composition of this neutral fraction by major chemical class is shown in Table 3.7; more than 180 individual compounds were identified. The major components are the same as those found in the process liquids.

TABLE 3.7 Composition of the Neutral Fraction of the GFETC Gasifier Process Tar

Component	Wt. %
Aliphatics	
alkanes	8.0
alkenes	4.1
Aromatics	
benzenes	2.6
indanes/indenes	7.5
polycyclic HC	54.5
heterocycles	7.3
phenols	15.9

4. CHARACTERIZATION OF WORKPLACE AIR AT GFETC

This section of the report presents preliminary data on the chemical and physical characterization of workplace air at the GFETC slagging fixed-bed gasification pilot plant facility in Grand Forks, North Dakota. The results were obtained as part of a program (sponsored by DOE/FE) designed to develop appropriate methodologies for effective measurement and monitoring of workplace air hazards and to provide environmental support for the DOE coal technology development program.

Atmospheric emissions of toxic vapors and particulate matter in the raw product gas and by-products of coal gasification are important potential hazards to human health and the environment. Raw product gas contains such toxic gases as CO, H_2S, NH_3, HCN, and carbonyls. Trace elements are present and may be associated with the entrained particulates at toxic levels. A variety of toxic organic vapors may be present ranging from the highly volatile benzenes, toluenes, xylenes, and phenols to the condensible high molecular weight polycyclic aromatic hydrocarbons that include known carcinogens. All of these compounds can be released to the environment as fugitive emissions or as a result of accidents or process upsets. Organic compounds appear either as vapors, respirable aerosols, or adsorbed on dusts and char particulate matter.

Studies at GFETC are intended to establish effective methods for determining the chemical nature of organic vapors, organics associated with particles, and trace elements associated with particles in the workplace. Both the physical and chemical nature of the particles are important. The larger particles are deposited on surrounding vegetation, leading to potential environmental effects, and the smaller particles can be deposited in the lower lung, creating possible health hazards.

4.1 Air Sampling Measurements

Air sampling was performed on three separate occasions with differing objectives. The gasifier was operating on Indian Head lignite during all of the sampling periods. The list of specific samples with their descriptions is given in Table 4.1.

TABLE 4.1 GFETC Workplace Air Characterization Sample Description

Collection Period	Description	Samples Collected
4/6/80	Tenax resin samples of workplace air	3
5/19 to 6/12/80	XAD resin samples and total particulates from workplace air, background air, and analytical blanks.	45
10/20 to 10/23/81	Size fractionated particulate samples from workplace air	2

The initial sampling, in April 1980, was a limited effort designed to determine the types and approximate concentrations of organic compounds present in the air of the gasifier building. On this occasion a bed of Tenax resin was used to trap the organic vapors. The second sampling, during May and June of 1980, was more extensive. Numerous samples of vapors and particulates were collected at various times and locations to investigate the overall reproducibility of measurement as well as temporal and spatial variations of air quality within the gasifier building. The sampler used on this occasion contained a porous Teflon filter to trap the particulates and their adsorbed organic compounds, followed by a bed of Amberlite XAD-2 resin to trap organic vapors. The third sampling effort, in October 1981, was devoted specifically to the collection of particulate matter for characterization of the adsorbed organic compounds and for microscopic examination. Aerosols were collected with a five-stage Sierra high volume impactor for organic analysis and morphological examination (by scanning electron microscopy) and with an Andersen low-volume impactor for atomic adsorption analysis.

4.2 Procedures

The organic compounds contained on the resin and particles were analyzed with a Hewlett-Packard Model 5880 gas chromatograph equipped with a flame ionization detector (FID) interfaced with an HP model 5982A mass spectrometer. The Tenax-absorbed organic compounds were thermally desorbed at 200°C directly onto the GC column, with the inlet maintained at a temperature of -20°C. The Teflon filters and XAD-2 resin samples were extracted with methylene chloride for two hours in a Soxhlet extractor. After removal of the particulates by filtration, the extracts were concentrated in a Kuderna-Danish apparatus prior to GC/MS analysis. Because the initial sampling effort was intended to provide largely qualitative information on the organic vapors present, the organic compounds desorbed from the Tenax resin were identified and determined only by GC/MS. Flame-ionization detection, which is capable of providing more quantitative information, was used in addition to GC/MS in the analysis of subsequent samples. Details of the analytical procedures have been reported previously (ANL/ PAG-3, R.D. Flotard, July, 1980). The Teflon substrates used for collection of size-fractionated particulates in the impactor stages were processed similarly. Size-fractionated particulate samples remaining on the filter were characterized by scanning electron-microscopy coupled with energy dispersive X-ray analysis.

4.3 Results

Roughly fifty compounds were identified in the gas chromatograms of the Tenax-sorbed air samples. The bulk of the compounds contained from 7 to 11 carbon atoms and fell into three broad categories - aliphatic hydrocarbons, aromatic hydrocarbons, and phenols. A rough estimate of sample composition was made by assuming that the fraction of total ion count appearing in a particular category was equivalent to the fraction of the total sample in that category. The results, shown in Table 4.2, indicate that the vapors are highly aromatic in nature. Aromatic hydrocarbons account for nearly one half of the sample and phenols account for an additional one third.

TABLE 4.2 Percentage Composition of Organic Vapors Collected on Tenax Resin by Compound Type and Number of Carbon Atoms[a]

Number of C atoms	Hydrocarbons Aliphatic	 Aromatic	Phenols
7	1.0	24.2	--
8	2.0	--	18.1
9	10.7	0.2	16.0
10	4.5	17.4	--
11	--	4.3	--
12	--	1.6	--
Total, %	18.2	47.7	34.1

[a] Based on the proportionality of ion counts to mass.

Gas chromatographic analysis of the vapors collected on XAD-2 resin indicated the presence of more than 150 compounds, ranging in size from benzene and cyclohexane to compounds containing twenty or more carbon atoms. The concentrations of individual compounds, based on the proportionality of fractional FID area to fractional mass ranged from about 2 $\mu g/m^3$ for minor constituents up to 100-500 $\mu g/m^3$ for major species such as benzene and toluene (both concentrations are below the Threshold Limit Values). Total organic loadings were in the neighborhood of 2-3 mg/m^3. In analyzing the gas chromatograms of the samples, the compounds identified were placed in six subcategories under the broad headings of aliphatic and aromatic compounds. Most of the samples were similar in gross chemical composition. Representative results, obtained in the analysis of three samples collected at two different levels in the gasifier building and at two different stages of operation, are shown in Table 4.3. As in the case of Tenax-collected vapors, aromatic compounds predominate, accounting for 55-79% (average 63%) of the total sample. Cycloalkanes and alkenes account for most of the remainder. As anticipated, the quantities of sample components decrease with increasing molecular weight and number of aromatic rings. In contrast to the earlier result (Table 4.2), only small amounts of phenols were observed.

TABLE 4.3 Percentage Composition and Total Mass Loading of Organic Vapors Collected on XAD-2 Resin[a]

Compound Identified	Level 2 (Gasification Level)	Level 7 (Lockhopper Empty)	Level 7 (Lockhopper Refilling)	Average
Aliphatic, wt. %				
Alkanes	4.6	9.9	5.3	6.6
Cycloalkanes/olefins	16.5	27.8	35.5	26.6
Aromatic, wt. %				
Benzenes	55.4	15.7	20.2	30.4
Polycyclic HC	16.4	36.7	32.4	28.5
Heterocycles	2.6	1.4	2.5	2.2
Phenols	1.2	2.8	1.3	1.8
Total, $\mu g/m^3$	3400	1880	3500	2930

[a] Based on the proportionality of fractional flame ionization detector area to fractional mass.

Analysis of the size-fractionated particulates collected in October, 1981 indicate that particle morphologies resemble those of fly ash from coal combustion, including smooth spheres, vesicular spheres, and crystalline material. Trace element size distributions are bimodal and resemble data for ambient air. Lead particle sizes are predominantly submicron, while particles of Al, Fe, and other crustal species are mostly of supermicron size. Aluminum-based aerosol enrichment factors calculated from the lignite composition show that the composition of the aerosol resembles that of the coal, with the exception of modest enrichments of Mg, Na, As, and Pb in the submicron size range. More than 100 organic compounds were identified in the filtered extract of the combined particulate sample. The compounds ranged in size and volatility from toluene to a C_{31}-alkane. The composition of the sample, calculated in the same way as for the vapors collected on XAD-2 resin, is shown in Table 4.4. In contrast to the results obtained in collection of organic vapors, aliphatic rather than aromatic compounds predominate and, among the aliphatic compounds, open chain alkanes predominate over the cycloalkanes and alkenes. The reason for the large difference in composition of the organic vapors and the particulate-associated organic matter is not obvious, but it is clear that the organic vapors are much more representative of process oil and tar than are the particulate-associated organic compounds.

TABLE 4.4 Percentage Composition of Organic Matter Extracted from a Composite Particulate Sample[a]

Compound Type	Percent of Total
Aliphatic	
Alkane	51.0
Cyclane/alkene	11.4
Aromatic	
Benzenes	29.6
Polycyclic HC	6.5
Heterocycles	0.3
Phenols	1.1

[a] Based on the proportionality of fractional FID area to fractional mass.