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MASTER

LOW-BTU-GASIFIER EMISSIONS TOXICOLOGY

**STATUS REPORT
JUNE 1980**

EDITED BY
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EXECUTIVE SUMMARY

Natural gas is one of the United States' most important fossil fuels, accounting for about one-third of the total energy produced. Natural gas reserves are also limited and partly because of this and in part due to attempts to reduce dependence on foreign oil imports, coal gasification is scheduled for a significant role in our future energy options. Low Btu gas, commonly called "producer gas," derived from coal could supply some of our energy needs, especially in load following requirements for electrical power generation.

Uncertainties surrounding coal gasification range from economic viability and various processes to questions of environmental impact. Process streams in competing gasification processes are only partially characterized, making specific environmental problems difficult to pinpoint and plant waste treatment procedures difficult to define.

Since June 1977, a cooperative comprehensive multidisciplinary research effort between the Lovelace Inhalation Toxicology Research Institute (ITRI) and the Morgantown Energy Technology Center (METC) has been addressing basic human health risks associated with low Btu coal gasification. The major goal of this research effort is to assess inhalation hazards to plant workers and the general population that may be associated with low Btu coal gasification. Secondary goals are characterization of potential toxicants in liquid and solid process and waste streams. To these ends, the experimental low Btu gasifier at METC has been sampled to determine aerosol components in gaseous process streams and to assess potential toxicants in liquid and solid effluent streams with the most recent sampling effort in December 1979. Although this report concentrates on results obtained from December 1, 1979, to June 1, 1980, the following summary is intended to organize all data to date and draw tentative hypotheses which will be subjected to further testing in future sampling and analysis efforts.

- Diluting and/or cooling low Btu producer gas, as would happen in fugitive releases, produces a dense, respirable aerosol.
- Toxic element concentrations are higher in aerosols from clean gas than from raw gas streams at METC.
- Gasifier operating conditions have little effect on the elemental composition of cleaned gas aerosols.
- Gasifier bottom and cyclone ash are similar to coal combustion fly ash in elemental composition.
- Ba and Ge are enriched in large ($> 5 \mu\text{m}$) aerosol particles of the cooled and diluted coal gas aerosols.
- Sn, V, Cr, Mn, Fe and Pb are enriched in small aerosol particles ($< 5 \mu\text{m}$).
- Concentration of particle-associated organics is reduced by the METC cleanup system.
- The METC gas cleanup system partially removes high molecular weight organic compounds.
- High molecular weight organic compounds present in the gasifier effluent and process streams are primarily aromatic and alkyl-substituted aromatic compounds.

- Cooling and diluting low Btu producer gas preferentially transfers polynuclear aromatics heavier than 182 amu from the vapor to the particle phase.
- Most fractions of gasifier cleanup system tars are mutagenic in the Ames test.
- Producer gas aerosol particulate-phase material is mutagenic in the Ames test.
- Producer gas aerosol vapor-phase material is not mutagenic in the Ames test.
- Two tar fractions were both cytotoxic to rat and dog pulmonary alveolar macrophages and mutagenic in the Ames test.
- The most mutagenic samples of gasifier tar were basic subfractions of LH-20 fractions 3, 4 and 5.
- Representative polycyclic aromatic hydrocarbons (pyrene and benzo(a)pyrene) are widely distributed in soft tissue following inhalation exposure.
- Based on inhalation studies with benzo(a)pyrene and pyrene, polycyclic aromatic hydrocarbons are rapidly cleared from the body following inhalation.
- The major clearance route of inhaled polycyclic aromatic hydrocarbon is through the GI tract.
- Induction of lung aryl hydrocarbon hydroxylase is a sensitive indicator of polycyclic aromatic hydrocarbon presence in lung.
- A transient decrease in the molecular weight range of rat lung DNA is observed after instillation of a polynuclear aromatic hydrocarbon (4-nitroquinoline-1-oxide).
- Five separate sampling systems were employed at METC in December 1979 to emphasize different aspects of the toxicological assessment.
- A condenser train has provided sufficient mass of organic constituents of producer gas for biological testing.
- A high temperature, high pressure cascade impactor was designed, constructed, tested and used to obtain entrained fly ash samples at stream conditions (400°C and 8.7 atm.).
- Samples collected with a multicyclone train have been analyzed and tested for mutagenicity in the "Ames" test.
- Cleanup devices appear to be effective in removing mutagenic organics from the gasifier process stream.
- Water-soluble material from either condensers or the Venturi scrubber is not mutagenic in the Ames test.
- Methylene chloride-soluble bases are the only component of Venturi scrubber effluent processing mutagenic activity. Bases represent less than 0.001% of scrubber water, so overall environmental health hazards associated with scrubber water may be low.
- Tar from the Venturi scrubber is mutagenic, with most activity associated with components in LH-20 fraction 5. Tar in the Venturi scrubber effluent may represent a greater health and environmental hazard than do water soluble materials.
- Polar components of condenser LH-20 fractions 3 and 4 contribute significantly to the mutagenicity of these fractions.
- Phenanthridine (one of the bases found in condenser LH-20 fraction 5) inhaled by rats was metabolized in lung but did not induce aryl hydrocarbon hydroxylase activity in lung.

- Inhalation of benzo(a)pyrene aerosols by rats caused slight, if any, DNA damage to lungs and no detectable damage to other tissue during short-term studies.

STATUS OF LOVELACE INHALATION TOXICOLOGY RESEARCH INSTITUTE'S
LOW BTU GASIFIER HEALTH EFFECTS PROGRAM
DECEMBER 1, 1979 TO MAY 31, 1980

INTRODUCTION

This report is a summary of research activities at the Lovelace Inhalation Toxicology Research Institute (ITRI) concerning human health risk assessments for low Btu coal gasification and covers the period from 1 December 1979 through 31 May 1980. For more complete in-depth reports, one should refer to the ITRI Annual Reports (1976-1977, LF-58; 1977-1978, LF-60; 1978-1979, LF-69) and a previous status report on the low Btu gasifier research efforts (LF-75). During the six month period discussed herein, the major activities concerned a field sampling effort and preliminary analyses for physical, chemical and biological characterization of collected samples.

General

Low Btu coal gasification is scheduled for a significant role in this nation's future energy options. This is partly due to decreasing world-wide petroleum and natural gas reserves which tend to divert petroleum and natural gas from electrical generation to other vital fluid fuel uses. This would leave electrical utilities without sufficient peaking period capabilities. Low Btu coal gasification could supply some of this peak load requirement. It is of particular interest for use in combined-cycle electrical generation and also as a raw material in syngas production.

Process streams in coal gasifiers have been only partially characterized. This makes environmental assessment difficult to define. Since accurate characterization of process streams is also required for process modification and control technology, this has created considerable interest in improved process stream sampling. Because respirable aerosols from coal conversion technologies are a potential health hazard, we have designed our sampling system to have an upper size limit of about 10 μ m aerodynamic diameter. In addition to inhalation toxicity concerns, characterization of fine particle fractions in process streams is of great interest to those designing coal gasifiers since these particles cause blade erosion when low Btu gas is used to fire turbines. Fine particles may also cause methanation catalyst poisoning and increase gas distribution system maintenance costs if released from high Btu gasification plants.

Currently available gasifiers have two major restrictions: (1) they are restricted to non-caking coals and hence are unable to use large eastern USA coal reserves, and (2) they are limited to low operating pressures which result in limited throughput. A research and development program at the Morgantown Energy Technology Center (METC) in Morgantown, WV has been underway to overcome these restrictions. Program goals at METC include development of gas cleanup systems to enable use of combined-cycle low Btu gas-fired turbines.

The METC Low Btu Coal Gasifier

The METC coal gasifier is a pressurized version of the McDowell-Wellman (Wellman-Galusha) atmospheric pressure stirred-bed gasifier (Figure 1) and differs from commercial fixed-bed producers with respect to its smaller size (1.1 m ID) and various provisions for stirring the bed. A grate in the lower end of the pressure vessel supports the coal. The vessel bottom is sealed with lock hoppers through which spent ash is removed. The gasifier top is a hemispherical dome through which gas exits and also where coal is fed via a lock hopper. The gasifier uses the Lurgi process for low Btu coal gasification which requires heat, air, steam and coal. Inside the

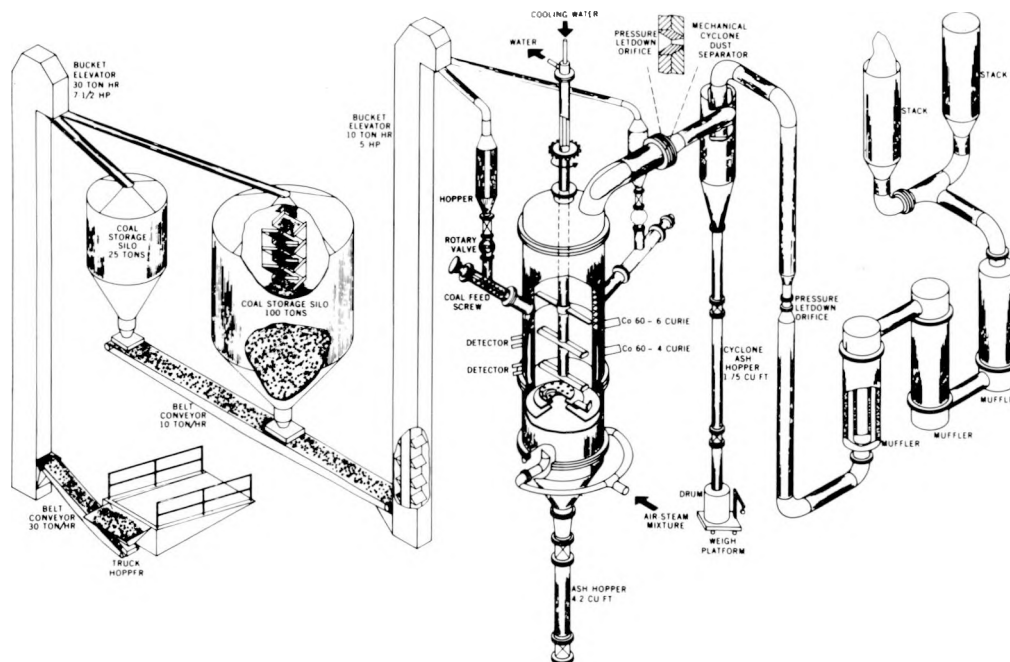


Figure 1. Schematic diagram of METC Low Btu Coal Gasifier.

gasifier, coal undergoes a complex series of reactions beginning with devolatilization which produces tars and oils and ending with combustion of coal char to CO. This mixture of vapors and gases with entrained ash particles exits the gasifier and passes through cleanup systems. Gas composition varies with fuel and operating conditions but generally consists of 15 to 20% CO, 5 to 15% CO₂, 55 to 60% N₂, 10 to 15% H₂, < 5% CH₄ and < 1% each of C₂H₆ and H₂S. Heat content of the gas is 3.7 to 7.4 x 10⁶ J/m³ at STP (100-200 Btu/SCF) and historically has been called producer gas.

Since June 1977, a cooperative comprehensive multidisciplinary research effort between METC and ITRI has been underway to address basic human health risks associated with low Btu coal gasification. The remainder of this report concentrates on a field sampling effort at METC in December 1979 and preliminary physical, chemical and biological characterization of samples obtained.

GOALS AND APPROACH

The major goal of this research effort is to assess human health risks to plant workers and the general population that may be associated with low Btu coal gasification. To this end the project is designed to determine the potential inhalation toxicity of gaseous process, effluent and combustion streams. Secondary goals are characterization of potential toxicants in liquid and solid effluent streams. Assessment of potential inhalation hazards requires determination of: (1) physical and chemical characteristics that influence inhalation, deposition and subsequent fate of airborne materials and (2) biological response to inhalation of potential airborne toxicants including responses in (a) early screening tests and (b) inhalation exposure of laboratory animals to representative materials. Early damage and screening tests are directed toward (1) defining cellular and molecular mechanisms for damage and repair of target cells and (2) determining dose distributions at the cellular and molecular level for polycyclic aromatic hydrocarbons (PAH), heterocyclic compounds and other low Btu gasifier effluents. Inhalation exposures of laboratory animals are used: (1) to assess early damage to cells and organs, (2) to determine

retention and fate of inhaled materials, (3) to determine short- and long-term health effects and (4) to determine the dose response associated with health risks. Long-term health effects of primary concern are delayed effects on critical organs and tissues, such as carcinogenesis, fibrosis and emphysema.

Sample Collection

The gas cleanup system at METC is experimental and consequently is evolving. This results in new conditions for most of the low Btu gasifier sampling efforts to date. Figure 2 is a schematic representation of the gasifier cleanup system as it existed in December 1979. Most (approximately 75%) of the total flow goes through the main stream cleanup system which consists of a cyclone, humidifier, tar trap, Venturi scrubber and several pressure reducing valves, a muffler and a final flare. A side stream is diverted after the Venturi scrubber and typically represents about 25% of the total output. The side stream is further cleaned with the devices schematically shown in the inset of Figure 2. To obtain combustion effluent samples, a small portion of the cleaned side stream was burned with an optimum amount of injected air. The remainder of the side stream was tested and reinjected into the main flow prior to the flare. All gas cleanup procedures tend to reduce temperature and pressure which transfers material from a vapor to a liquid state. Resultant tars and oils are removed by disengagement chambers and scrubbers. The purpose of gas cleanup is to remove fly ash, oils, tars and entrained metallic compounds to produce low Btu gas suitable for methanation or turbine combustion. During the gasifier run in December 1979, five separate sampling systems were used to obtain a larger number of samples.

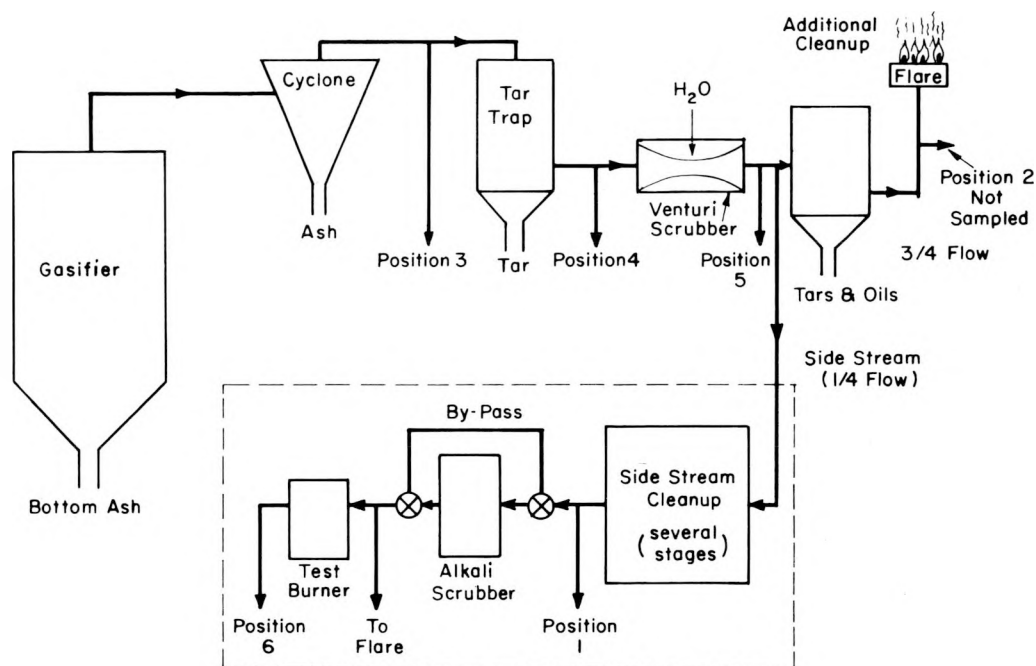


Figure 2. Schematic diagram of the gas cleanup on the METC Low Btu Gasifier during December 1979 tests.

In order to address the main programmatic goals in these projects, five different sampling systems were developed and used, sometimes simultaneously. The analytical system collects cooled and diluted samples of producer gas aerosol using extractive sampling techniques and is schematically shown in Figure 3. Extractive sampling, dilution and cooling results in formation of a dense producer gas aerosol consisting principally of tars and oils with small inclusions of fly ash. The resulting aerosol was sampled from a chamber (Figure 4) by filters, cascade impactors, electrostatic precipitators and a hydrocarbon vapor adsorbent trap. These instruments are listed in Table 1 along with the purpose of each type of sample. Samplers were chosen to (1) determine aerodynamic and real size distributions in the less than 10 μm range, (2) obtain samples for electromicroscopic examination and analysis (both SEM and TEM) and (3) obtain samples for chemical and biological characterization. Aerosol size distribution parameters and concentrations were determined from cascade impactor substrate and filter weights at METC and then returned to ITRI for further analyses. Inorganic composition is being determined on selected samples. Organic composition is being determined by gas chromatography and mass spectrometry of extracts of the organic fraction of the samples. The analytical system was used to obtain samples from positions 1, 3, 4 and 5 (Figure 2).

In order to obtain larger amounts of temperature-separated condensates, a series sampling train consisting of four modified Greenberg-Smith impingers, (GSI vapor traps) was used. Modifications consisted of increasing collecting surfaces (glass beads or steel wool) inside the main vessels, eliminating the jet and collector and adjusting sample flow to 20 L/min. Condensers were placed in temperature-controlled baths with Number 1 at ambient (-10° to 10°C), Number 2 in an ice water bath (approximately 0°C) and Numbers 3 and 4 in dry-ice acetone (-40°C). The GSI vapor traps sample undiluted producer gas. Samples were obtained from downstream of the cyclone (position 3) and after the Venturi scrubber (position 5).

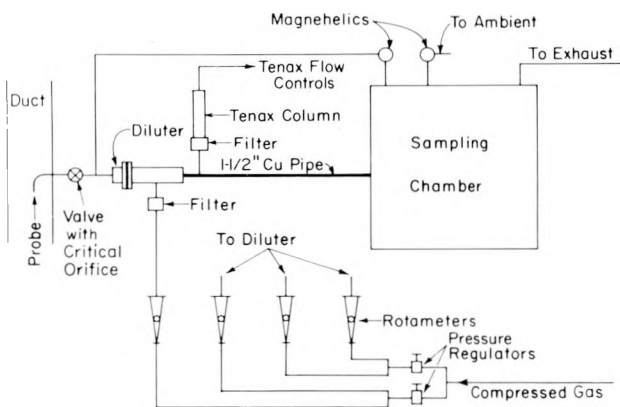


Figure 3. Schematic diagram of extractive aerosol sampling system used on METC Low Btu Coal Gasifier.

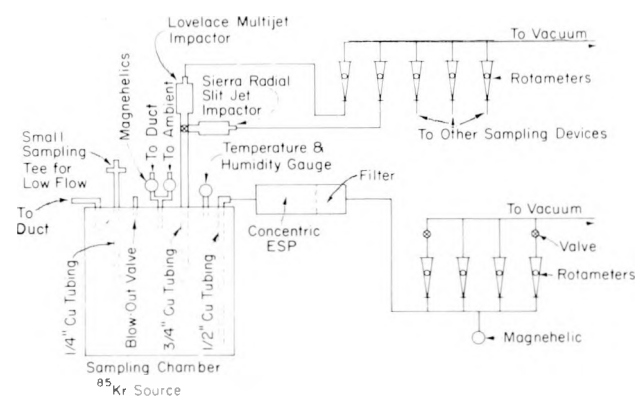


Figure 4. Schematic diagram of the analytical aerosol sampling system used on METC Low Btu Coal Gasifier.

Table 1

Analytical System Samplers Used on Gaseous Effluent Streams from METC Low Btu Coal Gasifier

Sampling Device	Flow Rate (l/min)	Total Sample Size		Comments
Lovelace Multi-Jet Cascade Impactor (LMJ)	21	400	mg	Eight aerodynamic size fractions 0.6 to 12 μ m
Sierra Radial Slit Jet Cascade Impactor (SRSJ)	21	500	mg	Seven aerodynamic size fractions 0.6 to 10 μ m
Filter (47, 90 mm)	25	~ 1	g	On glass fiber filters to help determine mass loading and provide unsized samples for inorganic analysis
Point-to-plane Electrostatic Precipitator	0.5	< 1	ng	Samples for transmission electron microscopy for geometric size analysis and samples for scanning electron microscopy for morphological and elemental analyses
Tenax Sampler with Prefilter	12.0	~ 10	mg	Samples for determination of vapor-phase and particle-associated polycyclic aromatic hydrocarbons above C ₆
Concentric Electrostatic Precipitator	100-125	~ 1	gram	Device is used as a sample chamber exhaust cleanup. Samples are used for major elemental analysis and particulate hydrocarbon analysis.

The third sampling system employed used a five-cyclone sampling train and also sampled undiluted producer gas. Samples were obtained from positions 1, 3, 4 and 5. This multicyclone train (MCT) was dimensionally and dynamically similar to one developed by the Southern Research Institute (SRI) and Table 2 lists SRI-determined cut points. This sampling device was used to obtain size-fractionated samples of producer gas aerosol in large enough quantities to enable chemical and biological characterization of the aerosol.

The fourth sampling system was designed to obtain samples of aerosol after combustion of low Btu producer gas. About 50 L/min of the cleaned side stream was burned and the combustion products sampled with filters, cascade impactors, electrostatic precipitators and Tenax[®] vapor-phase hydrocarbon adsorbent traps. Cleaned producer gas was diverted at position 6 and burned.

The fifth sampling system was designed to obtain particulate samples under stream conditions and was only used at position 3 (after the cyclone). A modified stainless steel version of the Lovelace Multi-Jet Cascade impactor was designed and built to function as a high temperature, high pressure (HTHP) cascade impactor. Knowledge of the particles entrained in the producer gas is required for engineering input for advanced control technology. Aerosol samples from cooled or cooled and diluted producer gas process streams consist primarily of condensed tars and oils with small amounts of entrained fly ash. Samples of these fly ash inclusions without contamination with tars and oils are required for several applications. In practice, the HTHP cascade impactor was placed in an electrically heated tube furnace and when temperatures were near stream

conditions, the high temperature (400°C) high pressure (130 psig) producer gas was passed through the cascade impactor. A schematic of this system is shown in Figure 5. Table 3 lists stage constants for the HTHP cascade impactor with effective cut-off diameters, $[ECD(\mu m)]$ for stream conditions and also for ambient conditions.

Table 2

Laboratory Calibration of the Five-Stage Cyclone Train^a

Cyclone Stage No.	1		2		3			4		5	
Particle Density g/cm ³	2.04	1.00	2.04	1.00	2.04	1.35	1.00	1.05	1.00	1.05	1.00
Flow Temp. (L/min) °C	D ₅₀ Cut Points (μm)										
7.1 25	-	-	-	-	-	-	-	2.5	(2.5)	1.5	(1.5)
14.2 25	5.9	(8.4) ^b	2.4	(3.5)	(1.7)	2.1	(2.4)	1.5	(1.5)	0.85	(0.87)
28.3 25	3.8	(5.4)	1.5	(2.1)	0.95	-	(1.4)	0.64	(0.65)	0.32	(0.32)
28.3 93	4.4	(6.3)	2.3	(3.3)	1.2	-	(1.8)	-	-	-	-
28.3 204	6.4	(9.1)	2.9	(4.1)	1.9	-	(2.8)	-	-	-	-

^aData from Southern Research Institute

^bD₅₀ cut points enclosed in parenthesis are derived values.

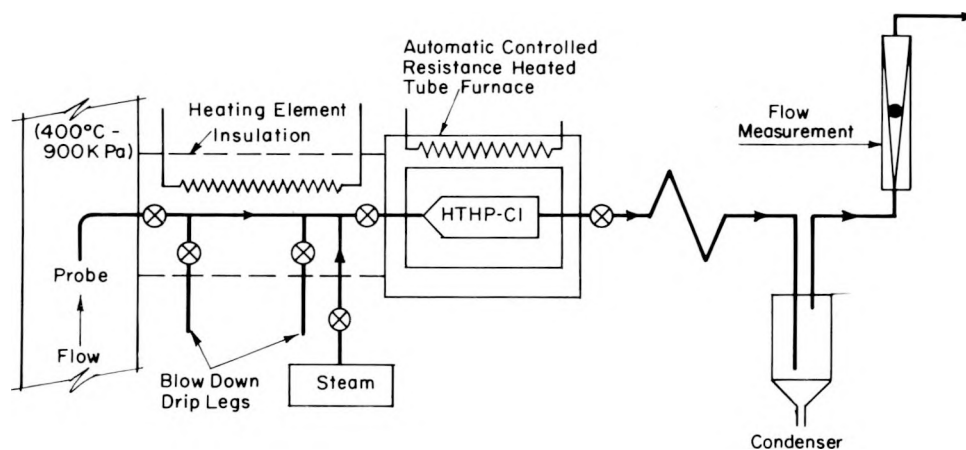


Figure 5. Schematic diagram of high temperature, high pressure cascade impactor sampling system used on the METC Low Btu Coal Gasifier (Position 3) during December 1979 tests.

Table 3

Stage Constants of the High Temperature, High Pressure Cascade Impactor

Stage Number	Number of Holes	W (Hole Diameter) (cm)	ECD ₅₀ (μm)	
			HTHP ^a	Ambient ^b
1	3	0.6350	10.8	8.8
2	3	0.5055	7.7	6.3
3	3	0.3988	5.4	4.4
4	5	0.2377	3.1	2.5
5	7	0.1702	2.3	1.9
6	10	0.1194	1.6	1.3
7	20	0.0584	0.76	0.62

^aT = 400°C, P = 8.73 atm, F = 16.5 L/min, $\eta = 2.77 \times 10^{-4}$ poise.

^bT = 0°C, P = 1.0 atm, F = 16.5 L/min, $\eta = 1.84 \times 10^{-4}$ poise.

RESULTS AND DISCUSSION OF PHYSICAL AND CHEMICAL CHARACTERIZATION

Physical and Chemical Characteristics

Aerosol size and mass loading were dependent on sampling location and apparently independent of operating conditions (Table 4). Although gas cleanup was different than used during previous sampling efforts, general trends are similar. The clean gas from the side stream was about 1.2 μm MMAD with a mass loading of about 0.04 g/m³. Raw gas exiting the first cyclone was smaller with a MMAD of 0.75 μm and a high mass loading of 14.3 g/m³. Mass loading was decreased to 4.6 g/m³ in passage through the tar trap. Further along the full flow cleanup, the MMAD was 1.05 μm entering the Venturi scrubber and only 0.33 μm exiting the scrubber. All aerosols as measured with the analytical system were in the highly respirable size range. It must be realized that much of these aerosols do not exist as such at stream conditions because of temperatures and pressures encountered within the process streams. The aerosol measured is the result of cooling and diluting processes and consists primarily of condensed tars and oils. The variations in particle size and mass loading at individual sampling locations are believed to be due to instability of the combustor. It is noteworthy that the combustion products (position 6) of low Btu gas were extremely small in size and all of the collected mass was found on the final filter in the cascade impactor samples. The small amount of both vapor phase and particle-associated hydrocarbons from the Tenax[®] traps at position 6 attests to the combustion efficiency of the test burner. These preliminary results indicate that clean low Btu producer gas can probably be used in many process heat applications and that environmental concerns for final-use, combustion effluents are probably not of major importance.

Collection of HTHP cascade impactor samples at stream conditions (position 3) of 400°C and 8.0-9.1 Atm. represents the first measurement of tar and oil-free, solid particles under such

Table 4

Preliminary Summary of Aerosol Characteristics of METC Low Btu Coal Gas Process Streams During December 1979 Tests

Position (Number)	Analytical System				Multi-Cyclone Train		GSI Vapor Traps	Tenax	
	n	MMAD (μm)	σ_g	Concentration (g/m^3)	MMAD (μm)	Concentration (g/m^3)	Concentration (g/m^3)	VP ^a (g/m^3)	Filter ^b (g/m^3)
Post cyclone (3)	12	0.75 ± 0.07	1.36 ± 0.07	14.3 ± 9.3	-	-	27.5	0.3	12 - 21
Pre Venturi scrubber (4)	4	1.05 ± 0.17	1.65 ± 0.10	4.6 ± 1.7	-	-	-	0.1 - 0.2	3.5 - 4.3
Post Venturi scrubber (5)	4	0.33 ± 0.16	2.13 ± 0.64	- ^c	-	-	-	-	-
Clean side stream (1)	4	1.22 ± 0.10	1.78 ± 0.21	0.04 ± 0.02	0.7	0.5	-	0.3	0.9
Combustion products (6)	4	< 0.6	-	0.004	-	-	-	0.005	0.001

^aVapor phase hydrocarbon C > 6^bParticle associated hydrocarbon (C > 6) collected on Tenax prefilter^cDilution ratio unknown

conditions. These measurements and future efforts to evaluate gas cleanup technology will be of interest to engineers designing gasifiers and gas cleanup systems. Figure 6 is a log-probability plot of the cumulative size distribution of one sample collected by the HTHP cascade impactor. The linear distribution indicates that it could be approximated by a log-normal function. The MMAD of this sample is $3.50\ \mu\text{m}$ with a σ_g of 2.92. Results of six HTHP samples from position 3 indicated a MMAD equal to 3.24 ± 0.53 (SD) with a σ_g of 2.48 ± 0.20 .

Organic Constituents

Samples of producer gas aerosols were obtained at positions 1, 3, 4, 5 and 6 to determine both particle-associated and vapor-phase hydrocarbons. These samples are of three types: (1) Tenax and prefilter samples from the analytical system at all sampling positions, (2) GSI vapor traps at positions 3 and 5 and (3) five stage cyclone train samples at positions 1, 3, 4 and 5 (cooled and undiluted aerosol). Samples of tars and oils from liquid process streams were also obtained. A combination of solvent extraction, several types of chromatography, fluorescence spectroscopy and mass spectrometry are being used for quantitation and identification of organic compounds.

Tenax filters were extracted with dichloromethane and the solvent was rotary evaporated to yield the residue. Tenax samples were Soxhlet extracted with n-pentane and also concentrated by rotary evaporation. The GSI samples were partitioned between water-acetone and dichloromethane and concentrated with rotary evaporation. Table 5 lists weights of Tenax trap samples.

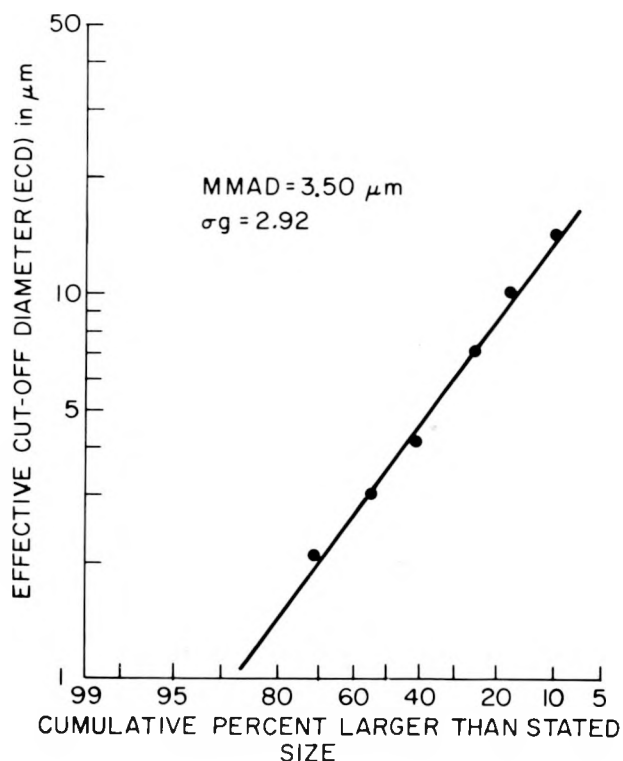


Figure 6. Typical log-probability plot of cumulative mass distribution as determined by the HTHP cascade impactor at position 3 on the METC Low Btu Coal Gasifier. Conditions: Temperature = 400°C , pressure = 8.73 atm and flow rate = 15 L/min.

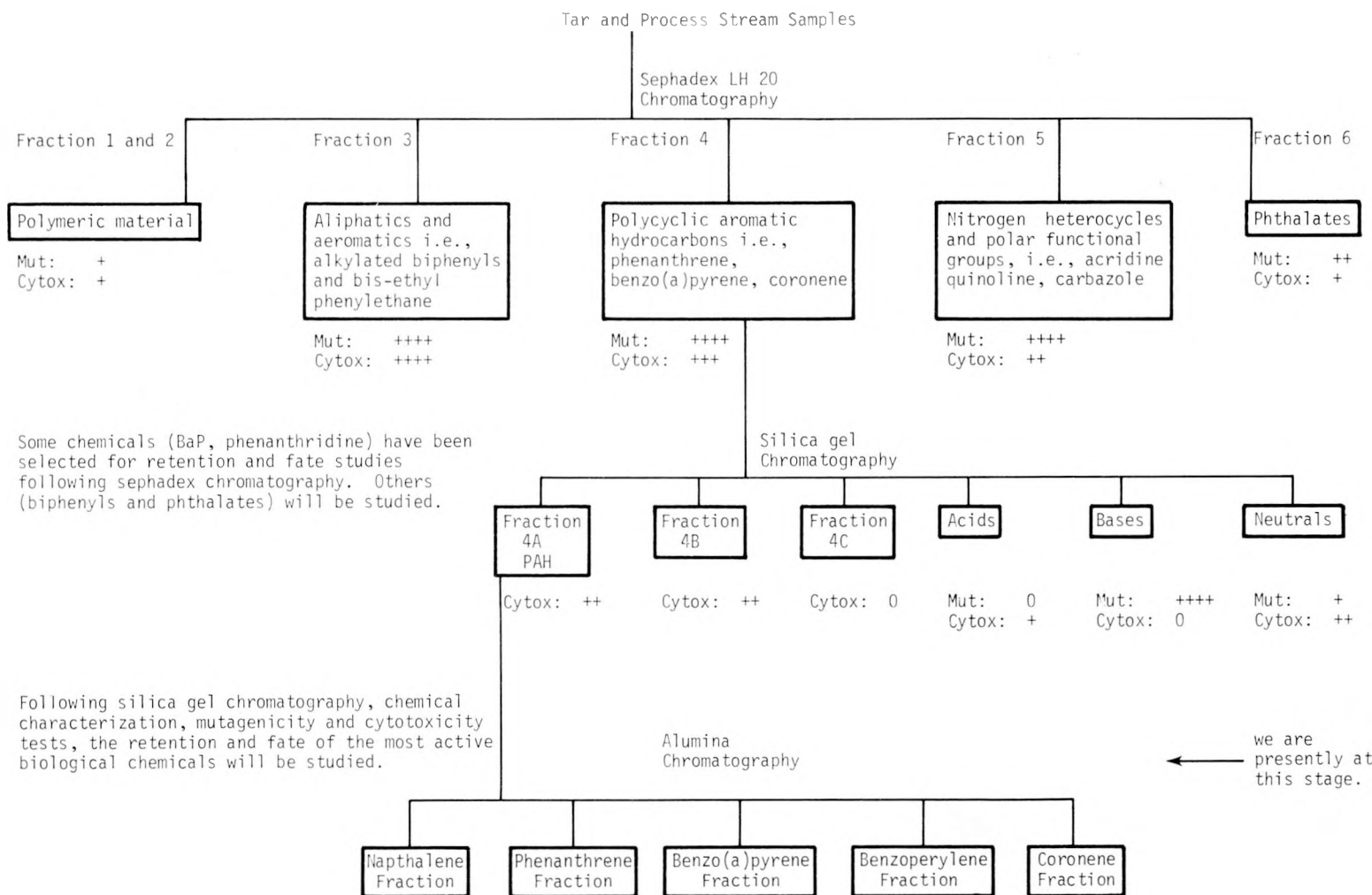
Table 5

Mass Loading of Hydrocarbons Extracted From Tenax Traps
on the METC Low Btu Coal Gasifier

Position (Number)	Total Hydrocarbon Concentration g/m ³	Particle-Associated Hydrocarbons g/m ³	Vapor-Phase Hydrocarbons g/m ³
Post cyclone (3)	12.354	12.070	0.284
Post cyclone (3)	21.460	21.148	0.312
Pre Venturi scrubber (4)	3.710	3.540	0.170
Pre Venturi scrubber (4)	4.460	4.349	0.111
Post Venturi scrubber (5)	-	-	-
Cleaned side stream (1)	1.224	0.891	0.333
Combustion products (6)	5.07×10^{-3}	0.44×10^{-3}	4.63×10^{-3}
Blank (6)	1.01×10^{-3}	0.000	1.10×10^{-3}

Samples from the different GSI vapor traps at a single position yielded similar appearing chromatograms. Lower collection temperatures collected more volatile compounds as expected. Although complete identification and separation of GSI vapor trap samples are not yet complete, it appears that there is adequate sample mass for biological studies.

A greater number of compounds were present in tar samples than were seen in either prefilter or Tenax samples. Gas chromatographable compounds ranged from 17 to 66% of the tar mass. Adequate fractions of tar samples have been obtained for biological characterization. Figure 7 illustrates the chemical fractionation scheme chosen and developed for separation, identification and selection of materials that will be used for biological characterization using inhalation exposure of laboratory animals. Tenax prefilter samples from positions 1 and 4 contained higher molecular weight compounds that were not found in the corresponding vapor phase samples. Samples from positions 1 and 4 were similar in composition (by GC) indicating that the side stream clean-up (position 1) does not change the type of hydrocarbon found in the producer gas. The total hydrocarbon concentration in the producer gas was reduced from 4.085 g/m^3 at the Venturi scrubber (position 4) to 1.224 g/m^3 exiting the side stream (position 1). Similar compounds were found at both positions ranging from trimethylbenzene (120 amu) to dimethylnaphthalene (282 amu). The range of molecular weight of hydrocarbons penetrating the cleanup system is summarized in Figure 8 along with ranges of size distribution parameters and mass loading. Chemical characterization of both organic and inorganic constituents is continuing on samples from the December 1979 gasifier run. With the addition of the GSI vapor traps and multi-cyclone train plus the Tenax samplers, we are now able to obtain sufficient mass of organic material for biological screening tests.



Following alumina chromatography and chemical characterization, a representative compound of the biological active fraction will be incorporated into retention and fate studies. Additional fractionation of active fractions will be done to isolate and identify the active compound or compounds. The fractionation and analysis of any fraction of interest can be done likewise.

Figure 7. Flow chart of LH-20 fractionation scheme used on METC low Btu Coal Gasifier Effluent streams with indications of cytotoxicity and mutagenicity.

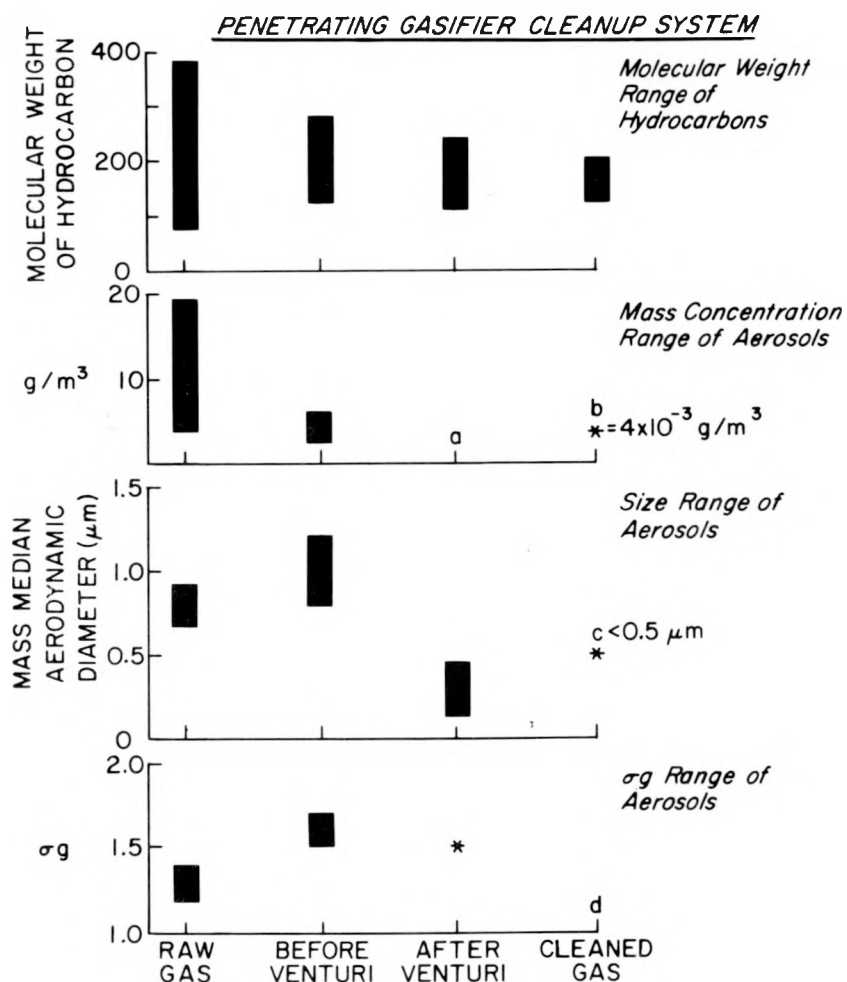


Figure 8. Molecular weight ranges of hydrocarbons, range of size distribution parameter and mass loading penetrating the cleanup systems on the METC Low Btu Coal Gasifier during December 1979 tests.

*Single measurement, ^b $4.0 \times 10^{-3} \text{ g/m}^3$, ^call mass collected on final filter of cascade impactor and $< 0.5 \mu\text{m}$ MMAD, ^dno measurement obtained.

RESULTS AND DISCUSSION OF BIOLOGICAL CHARACTERIZATION

General

Biological effects of solid, liquid and gaseous effluents from low Btu coal gasification are being studied using *in vitro* screening tests and *in vivo* early damage indicators. *In vitro* tests use bacterial mutagenicity assays (Ames) and pulmonary alveolar macrophage cytotoxicity tests. *In vivo* early damage indicators are induction of aryl hydrocarbon hydroxylase (AHH) and DNA damage and repair in laboratory animals following intratracheal instillation of suspected toxicants. Based on results of screening tests and chemical characterization, we will choose representative polynuclear aromatic hydrocarbons for inhalation studies in laboratory animals to determine deposition, retention, excretion and tissue distribution.

Mutagenicity of Low Btu Gasifier Effluents

During the past six months, mutagenicity studies on aza-arene standards were completed. Of eleven compounds tested, only quinoline and phenanthridine (3,4 benzoquinoline) were mutagenic in the "Ames test." Metabolic activation by rat liver supernatant was required in order for these compounds to exhibit a mutagenic effect whereas some tar fractions were direct acting mutagens. These results indicate that although aza-arenes may contribute to the mutagenicity of low Btu gasifier tar (LH-20 fraction 5 and its basic subfraction) other basic compounds such as aromatic amines may be important.

Preliminary tests were conducted on material collected by the multi-cyclone train to determine the optimum liver S-9 concentration to be used to assay gasifier samples. Table 6 shows the results of these tests. Considering the high background when using 6% and 9% S-9, 3% S-9 appears to be best for future assays. Also, due to the relatively high toxicity (Table 7) of the multi-cyclone train sample, a concentration range of 5 to 250 μg per plate will be used instead of the usual 10 to 500 $\mu\text{g}/\text{plate}$.

Table 6

Effect of Liver S-9 Concentration in the Ames Test on Multi-Cyclone

Train Sample "D" (0.65 μm) from Position 1

Sample μg Per Plate	TA-100 Revertants Per Plate			
	Saline	3% S-9	6% S-9	9% S-9
0 (DMSO)	120 \pm 6	108 \pm 8	157 \pm 26	340 \pm 72
10	97 \pm 15 (101) ^a	198 \pm 69 (198)	261 \pm 28	242 \pm 5
50	117 \pm 12 (177)	302 \pm 74 (347)	388 \pm 55	462 \pm 81
100	124 \pm 5 (413)	347 \pm 8 (475)	310 \pm 68	424 \pm 59
250	102 \pm 13	312 \pm 26 (709)	354 \pm 38	465 \pm 15
500	85 \pm 7	179 \pm 32 (688)	320 \pm 23	429 \pm 41

^aNumbers in parenthesis represent number of revertants per plate corrected for toxicity.

Table 7

Cytotoxicity of Low Btu Gasifier Sample from the 4th stage, "D", (0.65 μm)
of the Multicyclone Train from Position 1 (Clean Gas)^a

<u>$\mu\text{g}/\text{plate}$</u>	<u>Saline</u>	<u>3% S-9</u>
10	96	\approx 100
50	66	87
100	30	73
250	2.9	44
500	0	26

^aNumbers refer to colonies per histidine supplemented plate.

Materials collected at position 3 ("dirty gas") by the GSI condensers contained greater than 80% methylene-chloride-soluble components. Methylene-chloride solubles were highly mutagenic toward tester strains TA98 and TA100 (with metabolic activation) whereas water-solubles were not (Table 8). All LH-20 fractions of methylene-chloride solubles were mutagenic. Greatest mutagenic activity was associated with fraction 1, 3, 4 and 5, indicating alkane polymers, neutral and polar PAH derivatives were contributing to overall mutagenicity of the sample. Further fractionation and mutagenicity testing of LH-20 fractions 3 and 4 indicated that polar non-aromatic components of these fractions are also highly mutagenic (> 30 revertants/ μg). These polar components may be important compounds for future study. Work is currently being conducted to further characterize components of these fractions.

Multicyclone train samples from position 3 (dirty gas) and 1 (clean gas) were screened for mutagenicity. In general, crude material of all size fractions collected (5.4 to 0.32 μm aerodynamic diameter) was mutagenic toward TA100 (with metabolic activation only). Cytotoxicity of samples for TA100 was too great to allow for accurate comparison of mutagenicity of material collected from both positions. Material collected in the 0.32 μm aerodynamic diameter cut-off cyclone was fractionated (LH-20) and then screened for mutagenicity. Results on the most mutagenic LH-20 fractions indicate that cleanup devices were effective in removing most of the mass of mutagenic materials (especially polymeric alkanes and PAH) from the process stream. Although the mass loading of mutagenic material is decreased by the cleanup system, LH-20 fractions 1 through 5 exhibit similar patterns of mutagenicity independent of sampling position. On a per gram basis, position 3 (dirty gas), is the most mutagenic in all but fraction 4. Figure 9 compares the mutagenicity of LH-20 fractions 1 and 5 and Figure 10 compares the mutagenicity of fractions 2, 3 and 4 as a function of cleanup. Analyses are continuing to characterize mutagenicity of multicyclone samples obtained at intermediate positions in the process stream in order to assess the effectiveness of individual devices.

Table 8

Mutagenicity of GSI-Condenser Samples From Position 3 on the METC Low Btu Gasifier

Sample/Fraction	Revertants/Plate (n=3)			
	TA 98		TA 100	
	Saline	S-9	Saline	S-9
<u>Background</u>	36	48	123	119
<u>Crude-H₂O-Solubles (19%)</u>				
5 µg/plate	29	44	138	138
10	30	52	131	134
50	33	47	143	141
100	29	33	122	129
250	28	43	135	144
<u>Crude-CH₂Cl₂ Solubles (81%)</u>				
5 µg/plate	38	169	125	221
10	39	223	127	251
50	50	365	130	300
100	47	436	120	243
250	37	397	129	243
<u>LH-20 Fractions of CH₂Cl₂-Solubles</u>				
<u>LH-20, Fraction 1 (8%)</u>				
5 µg/plate	37	53	139	132
10	45	62	156	155
50	34	68	176	195
100	51	108	153	125
250	44	213	173	253
<u>LH-20, Fraction 2 (8%)</u>				
5 µg/plate	30	57	141	118
10	27	69	128	124
50	35	85	125	143
100	38	83	128	145
250	44	92	159	144
<u>LH-20, Fraction 3 (29%)</u>				
5 µg/plate	36	56	158	191
10	43	78	157	204
50	35	72	146	227
100	47	90	151	249
250	44	73	156	190
<u>LH-20, Fraction 4 (30%)</u>				
5 µg/plate	39	100	142	203
10	36	102	142	217
50	40	108	144	225
100	27	81	135	212
250	22	64	122	165
<u>LH-20, Fraction 5 (25%)</u>				
5 µg/plate	35	82	129	165
10	31	133	155	198
50	58	312	189	298
100	62	325	159	246
250	59	264	155	256

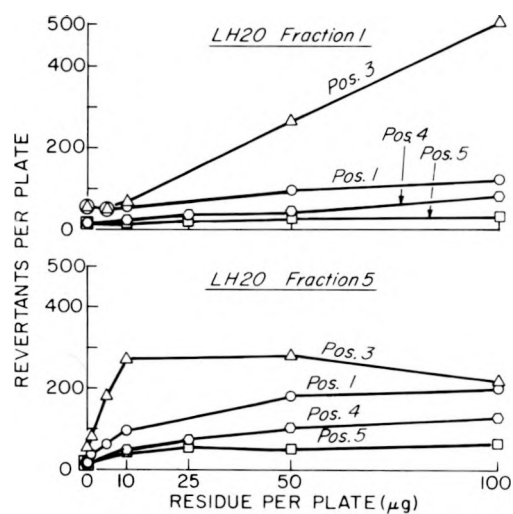


Figure 9. Comparison of the mutagenic activity of low Btu gasifier process stream material collected at positions prior to and after cleanup. Material collected (0.32 μm) using the multicyclone train was subfractionated by gel permeation chromatography. Mutagenicity of fractions 1 and 5 are shown above. Mutagenic activity is expressed as *Salmonella* tester strain TA98 revertants/plate ($n = 3$) when fractionated material was incubated with rat liver supernatant.

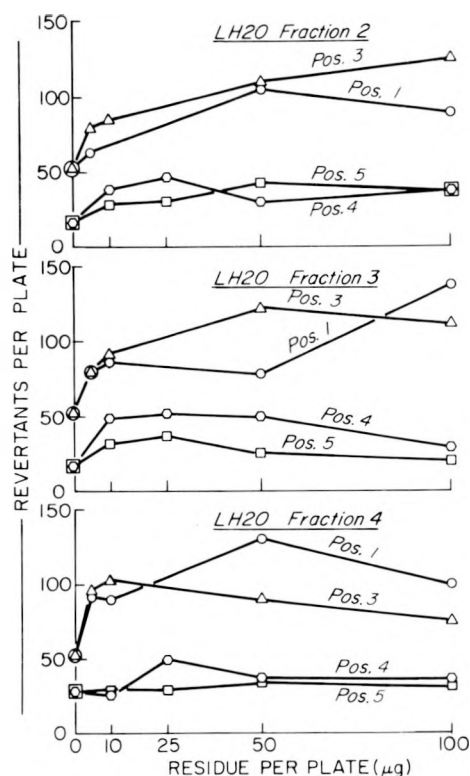


Figure 10. Comparison of the mutagenic activity of low Btu gasifier process stream material collected at positions prior to and after cleanup. Mutagenicity of LH-20 fractions 2, 3 and 4 are compared above.

Venturi scrubber effluents were separated into tar, methylene chloride and water-soluble fractions. Water solubles (96% of the mass) were not mutagenic, whereas methylene chloride soluble bases and the tar were (Table 9 and Figure 11). Mutagenic activity of the methylene-chloride solubles was attributable to the basic fraction (.001% of the mass) while activity in the tar was associated mostly with LH-20 fraction 5 (containing polar PAH components). The Venturi scrubber appears to be effective in removing polar mutagenic PAH's from the process stream.

Table 9

Mutagenicity of Venturi Scrubber Water-Tar Samples From the METC Gasifier

Sample/Fraction	Revertants Per Plate (N=3)				
	TA98		TA100		
	Saline	S-9	Saline	S-9	
<u>Background</u>	30	32	104	96	
<u>Crude-H₂O-Solubles (96%)</u>					
1 µg/plate	34	22	142	141	
5	32	35	157	137	
10	32	32	150	124	
25	36	36	173	126	
100	33	32	144	156	
<u>Crude-CH₂Cl₂-Solubles</u>					
1 µg/plate	17	25	110	98	
5	21	15	159	128	
10	19	25	159	139	
25	15	23	139	142	
100	27	23	153	142	
<u>CH₂Cl₂-Soluble Acids</u>					
1 µg/plate	16	25	148	140	
5	29	30	146	138	
10	29	28	134	143	
25	24	24	172	144	
100	28	23	169	159	
<u>CH₂Cl₂-Soluble Bases</u>					
1 µg/plate	28	20	157	139	
5	26	31	173	142	
10	31	43	161	155	
25	33	71	154	148	
100	30	258	-	-	
<u>CH₂Cl₂-Soluble Neutrals</u>					
1 µg/plate	23	26	145	121	
5	29	35	150	120	
10	31	38	145	131	
25	27	37	156	146	
100	38	50	156	146	

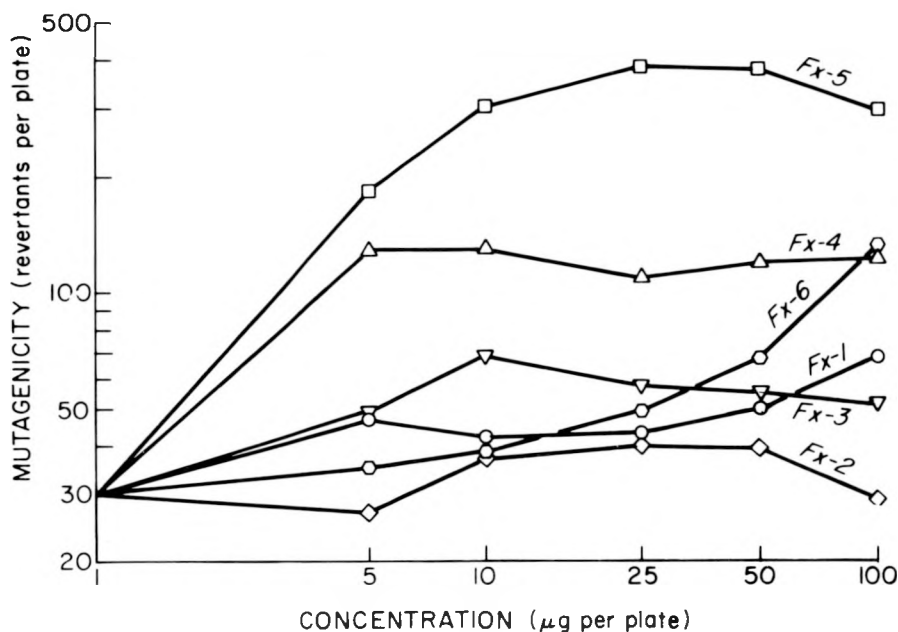


Figure 11. Mutagenicity of tars from the Venturi scrubber effluent on the METC low Btu gasifier. Tars were fractionated on Sephadex LH-20 and six (6) fractions were tested in the "Ames" assay.

In Vitro Cytotoxicity of Potential Effluents from Low Btu Coal Gasification

Toxicity testing of energy-related effluents in systems of cultured cells are useful. These systems can be used to screen a large number of materials rapidly. Generally the relative toxicity of compounds in cell cultures systems is similar to the toxicity in whole animals. As part of the low-Btu gasifier toxicology program, pulmonary alveolar macrophages were used to screen the chemical fractions of the disengagement chamber tar. We found that the test is very reproducible and served to target representative compounds for further characterization.

Low Btu coal-gasifier tar fractions are being tested for cytotoxicity using Beagle dog pulmonary alveolar macrophages (PAM). This represents a change from previous cytotoxicity tests where rat PAM's were used. Beagle dog PAM's are more plentiful and more easily harvested than are rat PAM's. Soluble tar fractions in DMSO are added to cultures so that the resultant DMSO concentration is about 1%. Various dilutions are tested for 24 hours, cells harvested and tested for trypan blue uptake and the supernatant analyzed for the cytoplasmic enzyme lactate dehydrogenase (LDH). Disengagement chamber tar was found to be toxic with 70% of all LDH released at 25 µg per 10⁶ cells. Ninety-five percent of the cells were killed at this level as determined by trypan blue exclusion studies. Using gel chromatography on Sephadex LH-20, the tar was fractionated into six fractions and further tested with the results summarized in Table 10. Toxicity was highest in fractions 3-6. Since fractions 3, 4 and 5 constitute the main mass (69%) of the crude tar, these fractions were further subfractionated for bioassay procedures.

Fractions 3 and 4 containing alkylated aromatic and polycyclic aromatic hydrocarbons were subfractionated on silica columns. Fraction 5 was further separated into acids, bases, neutrals and water soluble subfractions. Since neutral subfractions represent 48% of fraction 5 and 7% of the total crude tar and because results of cytotoxicity assays indicated that the neutral fraction was the most toxic, this subfraction has been selected for further study. Most

Table 10

Lactate Dehydrogenase Release as an Indicator of Cytotoxicity for
Disengagement Chamber Tar Fractions from the METC Low Btu Gasifier

<u>Fraction</u>	<u>Nature of Tentatively Identified Components</u>	<u>Percent of Crude</u>	<u>LDH Release^a</u>
Crude	-	100	164 ± 5
1,2	Polymeric material	28	17 ± 2
3	Compounds with both aromatic and aliphatic character	28	166 ± 8
4	Polycyclic aromatic hydrocarbons	18	129 ± 9
5	Aza-arenes and aromatic compounds with polar functional groups	21	114 ± 9
6	Phthalates and other hydrogen bonding organics	5	140 ± 5

^aIn international units per liter at 37°C at a concentration of 25 µg/10⁶ cells. Background release of LDH (6 ± 1 international units/10⁶ cells) in the presence of the solvent (1% DMSO) has been subtracted from the values given.

of the neutral subfraction of fraction 5 is gas chromatographable and further studies will concentrate on efforts to identify pure compounds or classes of compounds which are representative of those found in the low Btu gasifier effluent.

Soluble fractions of crude tar in a DMSO solvent from the gasifier's tar trap were added to cultures of Beagle dog PAM's at various concentrations. The final DMSO concentration was 1%. After 24-hours of exposure, the cell culture supernatant fluids were harvested and assayed for the presence of LDH, which is extracellular only if there is cell membrane damage. The results are expressed as an LC₅₀, the concentration of material in µg per ml which would effect the release of 50% of all the LDH which is detectable in mechanically (sonicated) disrupted cell cultures. Figure 12 summarizes the results of toxicity testing to date. The LC₅₀ for crude tar was approximately 45 µg/ml. Tar was fractionated by Sephadex LH-20 chromatography into 6 fractions, two of which (3,4) were later combined. The length of the bars in Figure 12 are proportional to the concentration in the combined tar or tar fraction. For example the most toxic fractions were 3-4 and 5 with LC₅₀'s of 40 and 32 micrograms per ml respectively. Fraction 3-4 was the largest subfraction comprising 49% of the total tar trap sample. Both of these fractions were further sub-fractionated by the methods shown and the sub-fractions tested. Fraction 5 sub-fractionated by aqueous-organic partitioning yielded ether soluble neutrals with the highest indicated toxicity of all subfractions tested. This subfraction was further reduced to collections of individual compounds by analytical and preparative gas chromatography. The LC₅₀'s of the compounds associated with this peak on the gas chromatograph ranged from 17 to greater than 40 µg/ml. Current efforts involve the identification of some of the compounds found in the most toxic sub-fractions.

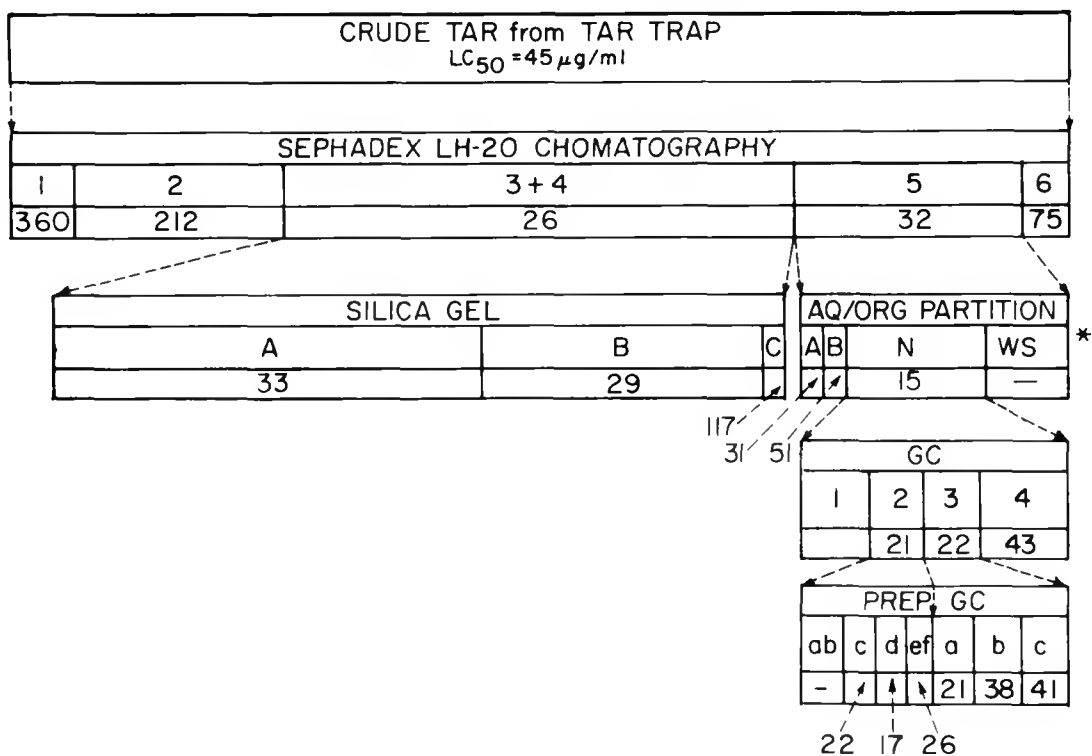


Figure 12. *In Vitro* cytotoxicity of crude tar from the tar trap and subfractions for Beagle dog alveolar macrophages in culture. The relative contribution (mass) of each subfraction is proportional to the length of the bar representing the parent fraction. Values of LC₅₀ are the concentrations (µg/ml) which result in the release of 50% of the cytoplasmic LDH and are given below each fraction and subfraction.

* In the AQ/Org position of fraction 5, A = acid organic fraction; B = basic organic fraction; N = neutral organic fraction; WS = water soluble fraction.

Generally, the macrophage cytotoxicity test system has been useful in evaluating fractionation schemes which may be useful in isolating representative toxic compounds found in gasifier effluents. During the next report period, the cytotoxicity test system will also be applied to the evaluation of samples from the various cleanup devices on line in the METC unit.

Inhalation Studies with Representative Compounds

An improved aerosol generating system has been developed for generating polynuclear aromatic hydrocarbon (PAH) aerosols (7 µg to 100 µg/L; MMAD, 1-2 µm) for 6 hours a day and for 5 days a week. This system will be used for short-term and subchronic inhalation studies. The PAH aerosol generating system has also been adapted to a nose-only exposure chamber for rodent exposures. This adaptation will be valuable for comparing retention and clearance patterns to those obtained using whole-body exposure systems.

Fischer 344 rats were exposed nose only to benzo(a)pyrene (BaP) aerosols (500 µg/L; MMAD, 1-3 µm) for 1 hour and, following serial sacrifice, a number of tissues were removed and assayed for ³H-BaP radioactivity. Although all of the tissue analyses have not been completed, the present data appear to confirm those obtained following whole-body inhalation exposure to BaP aerosol. BaP clears rapidly from the upper respiratory tract. A significant amount is cleared via mucociliary clearance and swallowed, resulting in a large G.I. tract burden. The remaining

material is cleared from the respiratory tract via the blood and lymph nodes and is found in a large number of tissues and organs during its metabolism and clearance from the body. It appears that it will be possible to classify the tissues investigated as having a "fast turnover rate" or "slow turnover rate" relative to the presence of BaP.

A follow-up study on the ability of phenanthridine to induce AHH activity in rat lung microsomes was conducted. Groups of 6 male rats were administered phenanthridine (5 mg/kg) by intratracheal instillation and sacrificed at 24, 48 and 72 hours post-exposure. No significant AHH induction was seen at any time period. Results are in agreement with earlier studies where lung supernatant, not microsomes were used and animals were sacrificed at 24 hours post-exposure only. Although phenanthridine is metabolized in the lung, it does not appear to induce AHH activity there. Demonstration of induction may require isolation of specific cell populations from lung, such as the Clara cell.

DNA Damage from Inhaled Representative Compounds

Fischer 344 rats were exposed to benzo(a)pyrene (BaP) aerosols (250 µg/L; MMAD, 1-3 µm) for 1 hour and a number of tissues were removed at different times and assayed for DNA damage using alkaline sucrose gradient chromatography. Although all data have not been analyzed, it appears that inhalation of BaP for 1 hour at this concentration did not result in measurable damage to the tissues assayed. Only slight damage, if any, appeared to have occurred in the lungs. A higher dose (50 mg BaP/kg) was intratracheally instilled into lungs of Fischer 344 rats, and lung, liver, kidney and brain were assayed for DNA damage at 6, 12 and 24 hours after instillation. Some lung DNA damage was found at this higher dose level where the DNA elution rate of the lungs from animals that received BaP was approximately 1.5 times that of the control. No detectable damage was found in any of the other tissues. Damage seen was slight when compared to direct acting mutagens such as methylmethane sulfonate (MMS). When MMS was instilled at the same dose, DNA damage was detected (2 hours post treatment) in every tissue assayed (i.e., tracheal cells, lung, liver, kidney, stomach, brain and testes). For some tissues, the DNA sucrose gradient elution rate was ten times that of controls.

DNA Damage from Instilled Representative Compounds

BaP was instilled into rat lung as a particulate material, as a particulate material attached to iron oxide and as a soluble material in corn oil. In addition, several other carcinogens and mutagens (nitroquinoline oxide and MMS) were also instilled in rat lungs in various forms. The DNA damage was determined by alkaline sucrose gradient chromatography. Benzo(a)pyrene did not damage lung DNA at 6 or 24 hours post instillation when instilled as a particulate alone, as a particulate associated with iron oxide or as a soluble form in corn oil. It appeared that the corn oil was retained in the lung for at least a day and it is likely that BaP is retained similarly in the oil whereby the oil is slowly releasing the BaP. Thus corn oil may be retaining the BaP similarly to the role played by iron oxide. Instillation of MMS did result in considerable lung DNA damage as early as 4 hours after administration. 4-nitroquinoline oxide was only slightly damaging to DNA when instilled; however, the DNA damage was highly noticeable when this compound was injected s.c., implying that the effects may be related to metabolism and/or rapid clearance from the lungs.

Rodents have been exposed (nose only) to ³H-BaP (20, 100 and 500 µg/L; AMAD, 1-2 µm) for 1 hour. Animals were sacrificed at various times after exposure and a number of tissues have been obtained for analyses. These studies will provide data on the kinetics of PAH clearance from various organs with time and on the effect of dose on clearance kinetics. Data will also be useful

for comparing clearance patterns to those obtained when rodents are exposed via whole-body routes. In addition, some rats were exposed by inhalation to ^3H -BaP (500 $\mu\text{g/g}$) following induction of xenobiotic metabolism by prior administration of 3-methylcholanthrene (3 nCi) or inhibition of xenobiotic metabolism by administration of L-ethionine. These animals were then exposed for 1 hour to inhaled ^3H -BaP (500 $\mu\text{g/L}$) and tissues obtained for the analysis of BaP. Clearance patterns from these studies will be compared with those obtained from animals that did not receive 3-MC or an enzyme inhibitor and the role of metabolism will be assessed.

APPENDIX I

Publications and Presentations

Gasifier Publications and Reports

1. Peele, E. R., R. L. Carpenter, G. J. Newton and M. M. Sturm, "Aerosol Sampling of An Experimental Stirred-Bed Lurgi Coal Gasifier," Lovelace Inhalation Toxicology Research Institute (1976-1977 Annual Report, LF-58, pp. 243-250), 1977.
2. Carpenter, R. L., S. H. Weissman, G. J. Newton, R. L. Hanson and R. E. Royer, "Chemical Characteristics of Aerosols of Cooled, Diluted Coal Gas from Cleaned and Uncleaned Low Btu Gas," Lovelace Inhalation Toxicology Research Institute (1976-1977 Annual Report, LF-58, pp. 251-256), 1977.
3. Mitchell, C. E. and K. Tu, "Distribution, Retention and Elimination of Pyrene in Rats Following Inhalation," Lovelace Inhalation Toxicology Research Institute (1976-1977 Annual Report, LF-58, pp. 350-355), 1977.
4. Mitchell, C. E., "A Rapid Spectrofluorometric Method for the Analysis of Polycyclic Aromatic Hydrocarbons in Animal Tissue," Lovelace Inhalation Toxicology Research Institute (1976-1977 Annual Report, LF-58, pp. 356-359), 1977.
5. Mitchell, C. E., "Induction of Aryl Hydrocarbon Hydroxylase in Rodent Tissue Following Intratracheal Instillation or Intraperitoneal Administration of Benzo(a)pyrene," Lovelace Inhalation Toxicology Research Institute (1976-1977 Annual Report, LF-58, pp. 360-364), 1977.
6. Weissman, S. H., R. L. Carpenter and G. J. Newton, "Inorganic Composition of Particles Collected from low Btu Gasifier Exhaust Streams," Lovelace Inhalation Toxicology Research Institute (1977-1978 Annual Report, LF-60, pp. 229-233), 1978.
7. Royer, R. E., C. E. Mitchell and R. L. Hanson, "Chemical Characterization and Mutagenicity of Potential Low Btu Gasifier Effluents," Lovelace Inhalation Toxicology Research Institute (1977-1978 Annual Report, LF-60, pp. 285-289), 1978.
8. Hill, J. O. and C. E. Mitchell, "*In Vitro* Cytotoxicity Testing of Potential Effluents from the Fluidized Bed Combustion and Low Btu Gasification of Coal," Lovelace Inhalation Toxicology Research Institute (1977-1978 Annual Report, LF-60, pp. 290-293), 1978.
9. Mitchell, C. E. and K. W. Tu, "Distribution and Retention of ¹⁴C-Benzo(a)pyrene in Rats Following Inhalation," Lovelace Inhalation Toxicology Research Institute (1977-1978 Annual Report, LF-60, pp. 332-336), 1978.
10. Benson, J. M., R. E. Royer and E. L. Pape, "Metabolism and Fate of Benzo(a)pyrene in Rats Following Pulmonary Exposure," Lovelace Inhalation Toxicology Research Institute (1977-1978 Annual Report, LF-60, pp. 338-391), 1978.
11. Mitchell, C. E., R. C. Pfleger and C. H. Hobbs, "Induction of Aryl Hydrocarbon Hydroxylase Activity in Lung Cells and Tissues of Syrian Hamsters," Lovelace Inhalation Toxicology Research Institute (1977-1978 Annual Report, LF-60, pp. 392-396), 1978.
12. Hanson, R. L., R. E. Royer, R. L. Carpenter and G. J. Newton, "Characterization of Potential Organic Emissions from a Low Btu Gasifier for Coal Conversion," in Polynuclear Aromatic Hydrocarbons, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, pp. 3-19, 1979.
13. Hobbs, C. H., R. O. McClellan, C. R. Clark, R. F. Henderson, L. C. Griffis, J. O. Hill and R. E. Royer, "Inhalation Toxicology of Primary Effluents from Fossil Fuel Conversion and Use," in Proceedings of ORNL CONF-780909, 25-28, September 1978, Potential Health and Environmental Effects of Synthetic Fossil Fuel Technologies, pp. 163-175, NTIS, Springfield, VA, 1979.
14. Newton, G. J., R. L. Carpenter, H. C. Yeh, S. H. Weissman, R. L. Hanson and C. H. Hobbs, "Sampling of Process Streams for Physical and Chemical Characterization of Respirable Aerosols," in Proceedings of ORNL CONF-780909, 25-28, September 1978, Potential Health and Environmental Effects of Synthetic Fossil Fuel Technologies, pp. 78-94, NTIS, Springfield, VA, 1979.
15. DeNee, P. B. and R. L. Carpenter, "Application of Heavy-Metal Staining (OsO₄)/Backscattered Electron Imaging Technique to the Study of Organic Aerosols," in Microbeam Analysis, San Francisco Press, Inc., San Francisco, CA, pp. 8-10, 1979.

16. Newton, G. J., Low Btu Gasifier Emission Toxicology Program, Status Report, Lovelace Inhalation Toxicology Research Institute, LF-75, 1979.
17. Mitchell, C. E., "A Method for the Determination of Polycyclic Aromatic Hydrocarbons in Animal Tissues," Bull. Envtl. Contam. and Toxicol. **23**: 669-676, 1979.
18. Mitchell, C. E. and K. W. Tu, "Distribution, Retention and Elimination of Pyrene in Rats Following Inhalation," J. Toxicol. Envtl. Health **5**: 1171-1179, 1979.
19. Mitchell, C. E., "Induction of Aryl Hydrocarbon Hydroxylase in Chinese Hamsters and Mice Following Intratracheal Instillation of Benzo(a)pyrene," Resch. Comm. in Chem. Path. and Pharm. **28**: 65-78, 1980.
20. Benson, J. M. and R. F. Henderson, "Isolation and Characterization of a Low Molecular Weight Cd-Binding Protein From Syrian Hamster Lung," Toxicol. Appl. Pharmacol. (in press).
21. Green, D. A., P. B. DeNee and R. G. Frederickson, "The Application of Heavy Metal Staining (O_5O_4) and Backscattered Electron Imaging for Detection of Organic Material in Gas and Oil Shale," Scanning Electron Microscopy (1979) I SEM Inc., AMF O'Hare, Ill., pp. 495-500, 1979.
22. Dahl, A. R. and T. J. Briner, "Biological Fate of a Representative Lyophilic Metal Compound (Ferrocene) Deposited by Inhalation in the Respiratory Tract of Rats," Toxicol. Appl. Pharmacol. (in press).

Presentations

1. Mitchell, C. E., "Induction of Aryl Hydrocarbon Hydroxylase in Rodent Tissue Following Intratracheal Instillation of Intraperitoneal Administration of Benzo(a)pyrene," Society of Toxicology Meeting, San Francisco, CA, March 12-16, 1978.
2. Benson, J. M. and C. R. Clark, "Use of Rat Lung Homogenates in Microbial Mutagenesis Testing," presented at Joint Meeting of American Society for Pharmacology and Experimental Therapeutics and Society of Toxicology, Houston, TX, August 13-17, 1978.
3. Hobbs, C. H., "Inhalation Toxicology of Primary Effluents from Fossil Fuel Conversion and Use," Life Sciences Symposium on Potential Health and Environmental Effects of Synthetic Fossil Fuel Technologies, Gatlinburg, TN, September 25-28, 1978.
4. Newton, G. J., R. L. Carpenter and H. C. Yeh, "Sampling Process Stream for Physical and Chemical Properties of Respirable Aerosols," Life Sciences Symposium on Potential Health and Environmental Effects of Synthetic Fossil Fuel Technologies, Gatlinburg, TN, September 25-28, 1978.
5. Hanson, R. L., R. E. Royer, G. J. Newton and R. L. Carpenter, "Characterization of Organic Emissions from a Low Btu Gasifier for Coal Conversion," Third International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, OH, October 25-27, 1978.
6. Carpenter, R. L. and G. J. Newton, "Sampling Methods for Fluidized Bed Coal Combustors and Low Btu Coal Gasifiers," presented at the 1978 DOE Contractors' Workshop, Boca Raton, FL, November 1978.
7. Weissman, S. H., "Chemical Characterization of Effluents Collected from Fluidized Bed Coal Combustion and Low Btu Gasification," DOE Contractor Meeting-Workshop on Review and Development of Biotesting Programs for Energy Utilization, Boca Raton, FL, November 1978.
8. Clark, C. R. "Mutagenic Survey of Effluents Collected from the Low Btu Gasification and Fluidized Bed Combustion of Coal," Review and Development of Biotesting Programs for Energy Utilization, Boca Raton, FL, November 11-14, 1978.
9. Bice, D. E., C. T. Schnizlein and C. E. Mitchell, "Effects of Acute Lung Exposure to BaP on Immunity Induced by Lung Immunization," Amer. Rev. Resp. Dis. **119**: 207, 1979.
10. Mitchell, C. E., R. C. Pflieger and C. H. Hobbs, "Induction of Aryl Hydrocarbon Hydroxylase Activity in Lung Cells and Tissues of Syrian Hamsters," Seventieth Annual Meeting of the American Association for Cancer Research Abstract **98**: 25, 1979.

11. Royer, R. E., C. E. Mitchell and R. L. Hanson, "Fractionation, Chemical Analysis and Mutagenicity Testing of a Low Btu Coal Gasifier Effluent," Fall Meeting of the American Chemical Society, Washington, DC, September 1979 (Abstract).
12. Newton, G. J., R. L. Carpenter, Y. S. Cheng and H. C. Yeh, "Design and Performance of Cascade Impactor for Both Ambient and High Temperature-High Pressure Applications," Presented at the 89th Annual Meeting of the ASME, San Francisco, CA, August 10-21, 1980.
13. Green, D. A., P. B. DeNee and R. G. Frederickson, "The Application of Heavy Metal Staining (OsO₄) and Backscattered Electron Imaging for Detection of Organic Material in Gas and Oil Shale," Annual Meeting of SEM Inc., April 16-20, 1979, Washington, DC.
14. DeNee, P. B. and R. L. Carpenter, "Application of Heavy-Metal Staining (OsO₄)/Backscattered Electron Imaging Technique to the Study of Organic Aerosols," 14th Annual Conference of the Microbeam Analysis Society, San Antonio, TX, August 12-17, 1979.
15. Benson, J. M. and R. F. Henderson, "Evidence for Metallothionein in Syrian Hamster Lung." 18th Annual Meeting, Society of Toxicology New Orleans, LA., March 1979. Abstract #153.
16. Benson, J. M. and R. Kubrick, "Mutagenicity of Quinolines and their Effect on Rat Lung and Liver Aryl Hydrocarbon Hydroxylase," 19th Annual Meeting, Society of Toxicology. Washington, DC, March 1980, Abstract #313.

APPENDIX II

CONTRIBUTING PROFESSIONAL STAFF

A major effort of the type described in this report requires input from a number of individuals with diverse skills. The listing below identifies the major contributors to the program at the Inhalation Toxicology Research Institute. It by no means includes all who are contributing to the effort. In the unnamed category are many highly skilled technical, animal care, maintenance, shop, administrative and secretarial personnel whose efforts are essential to a productive and meaningful research program.

Rogene F. Henderson, PhD	Chemist, Program Manager
Charles H. Hobbs, DVM	Toxicologist, Assistant Director
Janet M. Benson, PhD	Toxicologist
Robert L. Carpenter, PhD	Biophysicist
	Coordinator, Biological Characterization Project
C. Richard Clark, PhD	Toxicologist
Alan R. Dahl, PhD	Toxicologist
Raymond L. Hanson, PhD	Chemist
Joseph O. Hill, PhD	Microbiologist
George M. Kanapilly, PhD	Aerosol Scientist
Charles E. Mitchell, PhD	Molecular Biologist
	Coordinator, Early Damage and Fate of Inhaled PAH Projects
George J. Newton, BS	Aerosol Scientist
Robert E. Royer, PhD	Chemist
Suzanne H. Weissman, PhD	Chemist
	Coordinator, Organometals Project