

**INDUSTRIAL HYGIENE STUDY OF  
COAL GASIFICATION PROCESSES**

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A STUDY OF COAL LIQUEFACTION  
AND GASIFICATION PLANTS:  
AN INDUSTRIAL HYGIENE ASSESSMENT,  
A CONTROL TECHNOLOGY ASSESSMENT,  
AND THE DEVELOPMENT OF SAMPLING  
AND ANALYTICAL TECHNIQUES

VOLUME II  
INDUSTRIAL HYGIENE STUDY OF COAL  
GASIFICATION PROCESSES



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## ABSTRACT

Comprehensive industrial hygiene surveys designed to characterize employee exposures to suspected hazardous chemicals were conducted at three coal gasification plants. Air sampling was carried out for simple aromatics (benzene, toluene, and xylene), phenolics, anilines, polynuclear aromatic compounds (PNA) including polycyclic aromatic hydrocarbons, polycyclic aromatic amines, and aza-arenes, and toxic gases (carbon monoxide and hydrogen sulfide). Sampling for PNAs was accomplished through the use of a silver-membrane filter followed by Chromosorb 102; analysis for up to 36 individual PNA compounds was performed by gas chromatography and mass spectrometry.

Area and personal air sampling indicated that workers are exposed at low microgram per cubic meter concentrations to light molecular weight 2- and 3-ring PNA compounds. In some cases limited quantities of 4- through 7-ring compounds were detected. Highest exposures to PNAs were found to be associated with maintenance activities being carried out in the process area during plant operation.

Air sampling for phenolics, anilines, and polycyclic aromatic amines may have been affected by high humidity conditions at the sites during the surveys, because water vapor interferes with the standard NIOSH sampling method for these classes of compounds. Air sampling data for these classes of compounds therefore indicates qualitatively the presence of detected compounds, but the data is not qualitative and some compounds not detected may have been present. Simple aromatic compounds were present occasionally and at very low levels of personal exposure, i.e., maximum concentrations of 0.2 PPM for benzene.

Nonquantitative wipe sampling for PNAs revealed the presence of up to 5-ring PNA compounds on most surfaces sampled, indicating that dermal exposure to higher ring PNAs may present a health hazard.

Information was obtained on the occupational health programs of the plants involved in this study. Components of their medical surveillance, industrial hygiene, and other program components are reviewed.

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## 1. INTRODUCTION

### AUTHORITY

The Williams-Steiger "Occupational Safety and Health Act of 1970" was passed into law "to assure safe and healthful working conditions for working men and women...". This Act established the National Institute for Occupational Safety and Health (NIOSH) in the Department of Health, Education, and Welfare (presently the Department of Health and Human Services) and the Occupational Safety and Health Administration (OSHA) in the Department of Labor. The Act provides for research, informational programs, education, and training in the field of occupational safety and health and authorizes the enforcement of standards.

NIOSH has been given the authority and responsibility under the Act to conduct field research studies in industry, to evaluate findings, and to report on these findings. Section 20(a)(1) of the Act mandates NIOSH to "conduct (directly or by grants or contracts) research, experiments, and demonstrations relating to occupational safety and health...". Section 20(c) provides the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for the purpose of conducting studies relating to responsibilities under the Act. Under this mandate, NIOSH established a contractual agreement with Dynamac Corporation/Enviro Control Division (Enviro) to study worker exposures to potential health hazards in coal gasification plants.

### PURPOSE AND NEED FOR STUDY

In the 1970s the United States accelerated its effort to research, develop, and exploit energy sources to supplement or replace traditional petroleum and natural gas supplies. The technical feasibility of producing gaseous and liquid fuels and chemical feedstocks from coal had long been known. Although small-scale commercial coal gasification plants had operated successfully

until the 1940's, these plants were typically low tonnage gasifiers designed to provide a low-Btu gas for in-plant use, town gas, or chemical feedstock. The Federal Government established the Department of Energy to explore technologies for producing synthetic fuel from coal.

In 1976 the Department of Energy (then, the Energy Research and Development Administration) estimated that by the year 2000 coal gasification products would be supplying  $8.6 \times 10^{15}$  Btu/year toward the national energy demand and that the industry might employ up to 140,000 workers.

In an effort to develop an industrial hygiene data base for coal gasification plants as one basis for the prevention of occupationally induced disease in the anticipated industry, NIOSH began in 1978 the industrial hygiene characterization of selected coal gasification plants. At the time that the study was initiated, there were about 20 commercial or pilot demonstration plants operating or planned.

#### SCOPE OF STUDY

The overall scope of the study was to develop a catalog of worker exposures; to determine the composition of product and by-product streams; to identify process areas that may present high exposure potential; to determine whether selected carcinogens are being concentrated in any process area; to identify and evaluate controls which have been implemented to reduce worker exposure; and to review industrial hygiene and medical surveillance programs implemented at the gasification plants.

The National Institute for Occupational Safety and Health (NIOSH) has published a criteria document for a recommended standard for coal gasification plants (NIOSH, 1978). That document recommends standards for each of three types of processes; high-Btu product coal gasification; low- or medium-Btu product gasification utilizing bituminous coal or lower ranked feedstocks, and low- or medium-Btu product gasification utilizing anthracite feedstock or very high temperatures. No attempt has been made in the criteria document to develop permissible levels of exposure to toxic chemicals inherent to coal

gasification. The current study concerns each of the three generic types of low or medium-BTU gasifiers: fixed bed, fluidized bed, and entrained bed. These three types of gasification involve significantly different process conditions, resulting in significantly different types and quantities of byproducts or wastes, with subsequently different potential occupational health hazards.

No satisfactory method for sampling a large number of individual polynuclear aromatic hydrocarbons (PNAs) existed which was compatible with the requirements for personal sampling. Conventional collection devices using large packed columns of solid polymer sorbents had been used in environmental studies, but these require powerful vacuum pumps with non-portable electric motors. In order to conduct personal sampling programs for a large number of individual PNAs, a sampling device was developed which could be adapted to a standard, battery-powered personal sampling pump.

Walk-through surveys were conducted early in the project for the purpose of determining concentration ranges of chemical and physical agents identified in the literature as potential health hazards. The sampling conducted in the walk-through surveys was also used to test the sampling assembly and analytical methods for PNAs.

This study concentrated on those chemical agents which appeared to present the most significant health hazard, or which were less well documented in the coal gasification industry.





## 2. BACKGROUND

### COAL GASIFICATION PROCESS DESCRIPTIONS

#### Introduction

The coal gasification facilities surveyed in this study utilize different technologies to produce similar industrial fuel gases. The product of coal gasification is a low- or medium-Btu gas composed primarily of carbon monoxide, carbon dioxide, hydrogen, water vapor, nitrogen (if air is used as the oxidant), and hydrogen sulfide. Gas treatment systems can remove hydrogen sulfide and other contaminant gases and particulates to low levels. Low-Btu gas is suitable for various industrial purposes. Plant processes differ in terms of the design and operation of the gasifier unit itself, and in downstream treatment of the gas. Although there are numerous significant design variations for gasifier units, most may be categorized generically as fixed bed, entrained bed, or fluidized bed units. These major design differences result in significantly different levels of by-product coal tars; thus, they pose different potential exposure hazards.

The basis of low- and medium-Btu coal gasification is the incomplete combustion of coal to form CO and H<sub>2</sub>. This is accomplished by oxidation of part of the organic material to provide heat to reduce the remaining organic material to fuel gases, oils, and tars. When coal is heated, oil and tar vapors are distilled from it. The type of gasification process design determines the extent to which the oils and tars are further reduced to fuel gases. The use of air as the oxidant results in a low-Btu gas containing much nitrogen and with a heating value of from about 100 to 150 Btu/scf. Using oxygen yields a medium-Btu, low-nitrogen gas with a higher methane and hydrogen content; its heating value ranges from 250 to 350 Btu/scf.

Undesirable gases which are produced include hydrogen sulfide, ammonia, and limited quantities of other sulfur or nitrogen gases. By-product hydrocarbon solvents, oils, and tars can pose health and safety problems, and their

removal and handling are important aspects of the gasification process. Ash is mainly mineral matter but may be enriched in heavy metals and contaminated with tars; and thus may present an industrial hygiene problem during handling.

#### Process Details

A simplified gasification process schematic is presented in Figure 2-1.

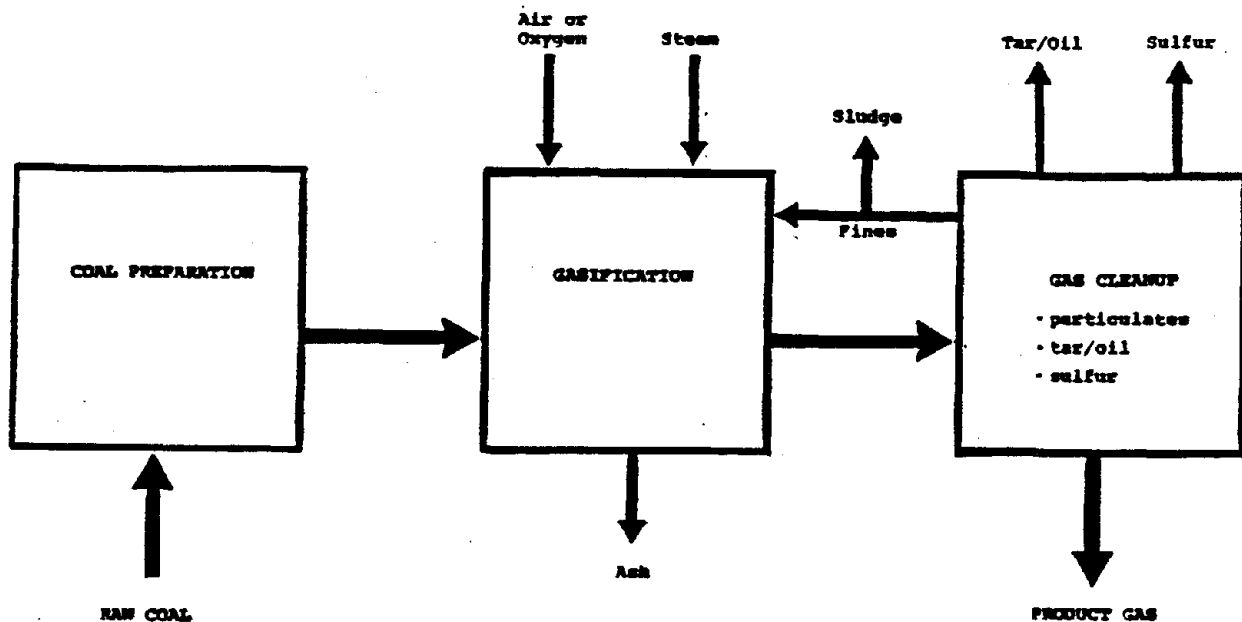


Figure 2-1. Simplified Coal Gasification Schematic  
(low- and medium-Btu)

Raw coal is prepared for gasification by crushing and drying to an optimal condition specific to the technology involved. Prepared coal may be stored or fed directly to the gasifier system. Preparation and storage present dust and explosion hazards comparable to those in coal fired power plants. Coal dust levels may be controlled by closed conveyance systems, baghouses, and wet methods. Explosion-proofing is typically achieved by purging storage bins and conveyances with nitrogen. In some instances a process gas that is low in oxygen is used.

Prepared coal is sent to the gasifier. Modern gasifiers are designed for continuous operation and production of gas. Optimal gasification conditions result in maximum CO and H<sub>2</sub> yields, and in minimal formation of carbon dioxide (CO<sub>2</sub>).

Gas exiting the gasifier may require removal of contaminants and by-products. Contaminants include ash, entrained fines, and char which may be carried over in the process stream, and sulfur and nitrogen bearing gases.

These particulates are typically removed by separators, such as cyclones, and some may be recycled to the gasifier for further energy production. Alternately, particulates may be removed with wet scrubbers.

Sulfur compounds can be removed by a number of commercially available processes. A typical one uses water and diethanolamine (DEA) scrubbing, producing sour water and a concentrated hydrogen sulfide (H<sub>2</sub>S) stream. Further treatment of these sulfur-containing streams by systems such as Stretford units yields elemental sulfur. Potential exposure hazards associated with downstream sulfur removal systems were not addressed in this study.

Significant quantities of oil or tar by-products may be produced, dependent on the type of gasifier used. These may be retained in the fuel gas if it is to be directly combusted. For some gas uses, the condensible hydrocarbon oils and tars must be separated. Some of these contain mutagenically active materials, and thus may present occupational health hazards on handling.

A checklist of process units used in the three plants surveyed in this study is presented in Table 2-1. The major operating parameters specific to each gasifier are presented in Table 2-2. A more detailed description and schematic of each facility is presented in Appendix A.

Table 2-1. A CHECKLIST OF MAJOR PROCESS UNITS  
at Coal Gasification Plants

PROCESS UNIT	PLANT A	PLANT B	PLANT C
Coal Preparation	/	/	/
Gasification	/	/	/
Gas Quench	/	/	/
Ash Removal	/	/	/
Particulate Removal	/	/	/
Tar/Gas Separation	-	/	-
Sulfur Removal	/	/	-

Table 2-2. Major Operating Parameters of Coal Gasification Plants

PARAMETER	PLANT A	PLANT B	PLANT C
Plant Capacity	120 ton/day	65 ton/day	15-30 ton/day
Process	Entrained bed	Fixed bed	Fluidized bed
Combustion Gas	Air or oxygen	Air	Air or oxygen
Product Gas	Low- or medium-Btu	Low-Btu	Low- or medium-Btu
Temperature, °C *	900-1700	100-1200	700-1100
Pressure, psig	-0.02	+0.5	215

\* Two temperatures shown are gas exit temperature (first) and  
combustion zone temperature (second).

#### Process Specifics of Plant A--

The gasifier configuration used at Pilot Plant A is an entrained-bed system which can be fired with either air or oxygen to produce low- or medium-Btu gas. The process uses pulverized coal which is gasified in a two-stage

sequence. The gasifier is approximately 90 feet tall, and 11 feet in internal diameter(see Figure A-1, p.A-2.). Temperatures inside the gasifier are high, ranging approximately from a maximum of 1,700°C (3,200°F) in the combustion zone (combustor), to a minimum of about 900°C (1,700°F) as the product gas exits the gasifier at the outlet. The gasifier operates at a slight negative pressure, -0.02 psig. Approximately one-third of the coal is fired in the gasifier combustor, and the remaining two-thirds in the lower portion of the reductor called the diffuser.

Heat from the combustor causes distillation and gasification of coal in the diffuser. Thus, the reductor produces the major quantity of product gas. The high combustor temperature produces a slagged ash which passes through a taphole located at the bottom of the combustor and collects in a quench tank. The slagged ash from the combustor collects in an ash hopper and is dumped when necessary into a dewatering bin. The dewatered slag is periodically disposed of by landfilling.

The gas cleanup system for particulates removes unburned carbon and fly ash present in the product gas stream. Major equipment in this system consists of a spray dryer, two cyclone collectors, and a venturi scrubber and thickener. Product gas cleaning begins in the spray dryer using a recycled slurry of organic sludge and water. From the dryer, the product gas enters a cyclone separator where entrained particulates and char are removed. These particulates collect in the char receiving bin and are recycled to the combustor for burning.

Char and unburned carbon passing through the cyclone separator are removed by a venturi scrubber and separator. The suspended particulates collect in the sludge thickener where they settle to the bottom. Water is removed at the top of the thickener and recycled to the venturi scrubber; the slurry at the bottom of the thickener is recycled to the spray dryer. The product gas exiting the separator enters the induced-draft fan at a pressure of minus 35 inches of water.

Sulfur present in the gas, as  $H_2S$ , is removed from the stream with DEA absorption and treated in a Stretford system. The Stretford system yields impure elemental sulfur as a by-product of the gasification process. Oil and tars are not significant waste products of this technology.

## Process Specifics of Plant B--

Plant B uses a set of two fixed-bed, two-stage gasifiers for production of low-Btu gas which is used in a manufacturing process(see Figure A-3, p. A-10). Coal for the process is crushed only, since the gasifiers will not accept pulverized coal or fines.

The gasifiers have a normal operating temperature of about 1000 to 1,200°C (1,800 to 2,100°F) in the combustion-char reduction zones of the bed. The heat content of the gas distills tars from the coal in the top zone of the bed at substantially lower temperatures. Two product gas fractions are taken off: a bottom gas with an exit temperature of approximately 400 to 500°C (800 to 1,000°F); and a top gas with an exit temperature of approximately 100 to 150°C (200 to 300°F). Operating pressure for the gasifiers is slightly above atmospheric with a maximum of 0.75 psig. Ash from the gasification process is deposited into a water-filled ash pan at the bottom of the gasifier. The cooled, wet ash is then transported by belt conveyor to the ash dumpster for disposal.

The top gas, which contains tar and oil, is passed through an electrostatic precipitator (detarrer) before entering the tubular cooler. The collected tars have a viscosity equivalent to that of No. 6 bunker fuel and contain measurable amounts of high molecular weight polynuclear aromatics compounds (PNAs). Tars are stored in a tar tank.

The bottom gas and entrained dust is passed through a wash column before entering the tubular cooler. The two gas fractions are combined in the cooler, and exit the cooler at a temperature of approximately 50°C (125°F). Water for the wash column is passed through a settling tank to remove particulates, then recycled.

The combined product gas from the cooler passes through an electrostatic precipitator (deoiler) for removal of oil and liquor. The liquor contains phenols and is burned in a thermal oxidizer. The gas is further treated in a Stretford unit for removal of hydrogen sulfide, and the cleaned product gas is distributed for in-plant use.

## Process Specifics of Plant C--

Pilot Plant C utilizes a fluidized-bed process which is fired with oxygen to produce a medium-Btu gas(see Figure A-6, p. A-17). Crushed coal is introduced into the gasification process through a series of pressurizing lockhoppers. The gasifier itself operates at high pressures of about 215 psig, and at temperatures of approximately 850-1,100°C (1,600-1,950°F). Bed fluidization in the gasifier is maintained by radially introduced recycle gas. Ash produced in this system agglomerates, drops out of the bed, and is removed through depressurizing lockhoppers.

The product stream with entrained fines exits the top of the gasifier and moves to a set of cyclones. The cyclones remove most of the fines and deliver them to lockhoppers. Fines are recycled to the gasifier with part of the product gas.

The product stream then passes to a quench scrubber unit which eliminates the remaining fines and cools the gas. Further cooling is accomplished by a packed-bed gas cooler. Both units use water which is cleaned of sludge and recycled. Clean product gas is used for transport gas and for bed fluidization. A gas compressor is employed to repressurize the gas.

This facility operates with low-sulfur coal and does not utilize a sulfur treatment system.

## Potential Health Implications of the Coal Gasification Process

Coal gasification processes present several health concerns. The exact extent of each hazard may be expected to change with the scale of a large commercial size operation. A list of potential occupational health hazards associated with each process unit is presented in Table 2-3.



Table 2-3. Potential Occupational Health Hazards in Coal Gasification

Unit Process	Potential Hazard
Coal Handling and Preparation	Coal dust, noise, fire
Coal Feeding	Coal dust, noise, gaseous toxicants
Gasifier Operation	Coal dust, high-pressure hot raw gas, high-pressure oxygen, high-pressure steam, fire
Ash Removal	High-pressure steam, high-pressure oxygen, hot ash, and dust
Quenching	High-pressure hot raw gas, hot tar, hot tar oil, hot gas liquor, fire
Gas Cooling	High-pressure hot raw gas, hot tar, hot tar oil, hot gas liquor, fire
Sulfur Removal	Hydrogen sulfide, other sulfides, and sulfur oxides
Gas-Liquor Separation	Tar oil, tar, and gas liquor with high concentrations of phenols, ammonia, hydrogen sulfide
By-product Storage	Tar, tar oil, phenols, ammonia, fire

#### WORK FORCE ACTIVITIES

Coal gasification plant workers with potential exposure to process emissions, byproducts, and waste products on a routine basis fit generally into three categories: plant operators or process technicians, maintenance staff, and laboratory technicians.

A total of about 250 workers were employed at the three gasification plants studied in this project. In the future, a large commercial scale high-Btu gasification plant may employ up to 600 workers, a combination of operators and maintenance personnel.

## Operators/Process Technicians

Operators or process technicians work on 8- or 12-hour shifts and have the responsibility for the operation of one or more unit processes of the pilot plant. In a commercial facility, several operators are projected for each process unit. In most cases, operators' and process technicians' duties are clearly defined and include a significant amount of time spent in relatively routine activities, such as reading gauges, checking valve positions, and monitoring process operating parameters. During normal plant operations, up to 80 percent of their time may be spent in the control room where exposure can be expected to be less than in the process area. Depending upon the particular operation involved, extended periods (up to a full shift) are frequently required in the process area where exposure potentials are greater. These operations involve routine activities such as blowing down vessels, taking process stream samples, handling chemicals, loading waste materials for disposal, and general housekeeping chores such as cleaning the baghouse filters. These activities vary with the type of plant and may be reduced in a commercial scale operation. Upset conditions require the operator to assist the maintenance crew in such high-exposure situations as clearing plugged valves and lines, and repairing steam leaks.

## Maintenance Personnel

Shift and nonshift maintenance personnel, belonging to several crafts, are responsible for maintaining, repairing, and remodeling all equipment in the facility. The greater part of this work occurs during plant turnarounds or upset conditions. These workers may be regular plant employees or outside contractors. At a pilot plant, both the jobs performed by the maintenance personnel and the areas of the plant frequented vary unpredictably on a day-to-day basis. In a commercial facility, exposure situations are expected to be normalized by detailed maintenance instructions which outline the frequency of maintenance work and detail procedures for decontamination of equipment. Jobs with a high potential for exposure include removing pumps or equipment containing process material, breaking into process lines, and entering tanks or vessels. In general, field exposure is minimized whenever possible by performing maintenance work in offsite shops rather than on-line.

## Laboratory Technicians

Laboratory technicians analyze process stream samples; however, job responsibilities vary widely. In one plant, these technicians are also responsible for securing process stream samples (a high-exposure operation) and, therefore, spend substantial time in the process area of the plant. In another plant, laboratory technicians are responsible only for testing of the samples and, consequently, do not experience any significant exposure.

## HEALTH EFFECTS OF EXPOSURE TO COAL GASIFICATION MATERIALS

Workers in the coal gasification industry are chronically exposed by skin contact, inhalation, and inadvertent ingestion to unknown levels of potentially toxic (but as yet incompletely characterized) liquid, gaseous, and particulate emissions and/or solid products and wastes. Acute exposure to high levels of these materials can also occur during maintenance and repair operations, startup and shutdown periods, as well as during accidents.

Concern over health hazards associated with exposure to these materials is based on two types of information. Epidemiological studies have long shown an increased risk of mortality and morbidity in workers exposed to coal-derived materials in related industries. In addition, experimental laboratory findings in whole animals, animal cells, and bacteria have demonstrated the potential toxicity and carcinogenicity of certain coal-derived materials, as well as of individual components of these materials.

Chemical analysis of materials produced from bench- or pilot-scale gasification plants is incomplete. However, tars and oils produced as a by-product of some processes have been found to have a higher degree of aromaticity and more condensed ring compounds than petroleum crudes. In addition, the heteroatomic content of coal liquids is increased primarily due to increased amounts of nitrogen and oxygen. High condensed ring content and heteroatomic content result in materials boiling at greater than 370° C (700°F). A correlation exists for increased mutagenic/carcinogenic activity with increased boiling point (Mobile, 1976; Pelroy and Wilson, 1981). In addition, some lighter,

lower-boiling oil fractions (315-425°C; 600-800°F) exhibiting minimal direct carcinogenic activity have been shown to possess promoting and/or cocarcinogenic activity. Comparison with petroleum industry material properties has demonstrated that coal liquid fractions are generally more mutagenic than are petroleum fractions of comparable boiling ranges (Kimball and Munro, 1981). Further, synthetic coal liquids, in contrast to petroleum, possess higher levels of acidic components, such as phenols and cresols, which appear in the lower-boiling distillates. These fractions, too, represent a potential for adverse health effects.

A detailed discussion of the known health effects of coal-derived materials is presented in Appendix C.

#### COMPARISON WITH SOME STUDIES OF SIMILAR INDUSTRIES

An industrial hygiene monitoring survey of PNA concentrations in petroleum refineries was conducted by Enviro Control, Inc. (Futagaki, 1981). Sampling and analytical methods for PNAs were identical to those used in this coal gasification survey.

A comparison of results shows that worker exposure to unsubstituted PNAs, as measured in three different types of process units at nine petroleum refineries, was higher than that of coal gasification workers monitored in this study. In both studies, the lighter molecular weight 2- and 3-ring PNAs were found in the highest concentrations, with only minimal amounts of the heavier 4-, 5-, 6-, and 7-ring compounds detected. In the petroleum study, the levels of PNAs showed a positive correlation with the age of the facility and with the crude petroleum utilized. No correlation was found for production capacity of the plant, duration since last major turnaround, or environmental conditions during sampling.

In a closely related study conducted by Enviro in five coal liquefaction plants (Vol. I), area and personal sampling was conducted for PNAs, anilines, simple aromatics, phenolics, and toxic gases (Cubit and Tanita, 1982).

Additional discussion and comparison of the results of this study with the petroleum refinery and coal liquefaction studies are presented in the Analysis and Discussion of Results chapter of this document.

In another industrial hygiene monitoring survey in the literature quantifying PNA concentrations in air samples, PNA compounds in coke oven emissions were measured at 20 different coke plants using a gas chromatographic/ultraviolet procedure (Smith, 1971), the mean concentrations of the measured PNAs decreased in the following order: fluoranthene, benz(a)pyrene, benz(a)anthracene, pyrene, chrysene, benz(e)pyrene. Benz(a)acridine and benz(a)anthrone were not found. Since air volumes and sampling times were not included in the report, direct comparison with other studies is not possible.

### 3. METHODS OF STUDY

#### FACILITY SELECTION

Plants were selected to provide representatives of each of three generic types of gasification units - fixed bed, entrained bed, and fluidized bed.

Two of the plants (Plants A and C) are DOE-sponsored pilot test plants operated by DOE contractors; Plant B is a commercial low-Btu, fixed-bed gasifier.

The dates of the walk-through and comprehensive surveys at the respective plants were:

- . Plant A: January 1979 (walk-through); April 1981 (comprehensive)
- . Plant B: August 1979 (walk-through); April 1981 (comprehensive)
- . Plant C: (no walk-through survey); May 1981 (comprehensive)

#### WALK-THROUGH SURVEYS

Walk-through surveys were conducted in Plants A and B for the purposes of:

- . conducting range-finding sampling for species identification and determining concentration and exposure ranges of chemical and physical hazards;
- . field testing of sampling assembly for collection of polynuclear aromatic hydrocarbons (PNAs);
- . obtain samples for evaluation of analytical protocols for PNAs; and
- . developing generic sampling protocols for the comprehensive surveys to be conducted at the three gasification plants.

The sampling programs during the walk-through surveys consisted primarily of "high-volume" area sampling to collect adequate quantities of PNAs, anilines, and simple aromatic hydrocarbon species for analysis. Table 3-1 shows the species of chemicals collected at each of the plants during the surveys (walk-through and comprehensive). Table 3-2 shows the results of PNA screening conducted on samples collected during the walk-through surveys. Quantitative results of sampling conducted in the walk-through surveys are presented in Appendix B.

Table 3-1. Classes of Samples Collected at Coal Gasification Plants

SAMPLES	PLANT A		PLANT B		PLANT C
	WT <sup>a</sup>	CS <sup>b</sup>	WT	CS	CS
<b>AIR SAMPLES</b>					
<u>Organics</u>					
PNAs	✓	✓	✓	✓	✓
Aro. Amines/Anilines	✓	-	✓	-	✓
Phenolics	✓	-	-	-	✓
Benzene/Toluene/Xylene	✓	✓	✓	✓	✓
<u>Gases</u>					
Carbon monoxide (CO)	✓	-	✓	✓	✓
Hydrogen sulfide (H <sub>2</sub> S)	✓	-	✓	✓	-
Hydrogen cyanide (HCN)	✓	-	✓	✓	-
Mercaptans	✓	-	✓	✓	-
Sulfur dioxide (SO <sub>2</sub> )	✓	-	✓	-	-
Ammonia	✓	-	✓	-	-
Arsine	✓	-	✓	-	-
Carbon disulfide (CS <sub>2</sub> )	✓	-	✓	-	-
Ozone	-	-	✓	-	-
Nitrogen oxides (NO <sub>x</sub> )	✓	-	✓	-	-
<u>Trace Metals</u>	✓ <sup>c</sup>	-	✓ <sup>c</sup>	-	-
<b>BULK SAMPLES</b>					
<u>Organics</u>					
PNAs	-	-	-	✓	-
Phenolics	-	-	-	✓	-
<u>Trace Metals</u>	-	-	✓ <sup>c</sup>	-	-
<b>WIPE SAMPLES</b>					
<u>Organics</u>					
PNAs	-	✓	-	✓	✓

<sup>a</sup>WT = walk-through survey.

<sup>b</sup>CS = comprehensive survey.

<sup>c</sup>Arsenic, beryllium, cadmium, copper, mercury, manganese, nickel, strontium, tellurium, magnesium.

✓ = "looked for"      - = "not looked for"



Table 3-2. PNA Compounds Screened in Walk-Through Surveys of Two Coal Gasification Plants

COMPOUND	Sample Type: Location:	PLANT A				PLANT B					WIFE						
		AIR				AIR											
		Gasifier	Cyclone/ Scrubber	Induced- Draft Fan	Sludge Thickener	Top of Gasifier	Poke Hole	Day Tar Tank	Between Cooler and Deciler	Between Washer and Detarrer	Rubber Glove Outside Surface	Rubber Glove Outside Surface	Rubber Glove Inside Surface	Rubber Glove Inside Surface	Stair Rail	Control Room Desk	Side of Gasifier
Indene		-- <sup>a</sup>	--	--	--	-- <sup>b</sup>	"	"	"	"	"	"	"	"	"	"	"
1,2,3,4-Tetrahydro- naphthalene		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Naphthalene		--	°	•	•	•	•	•	•	•	--	--	--	--	--	--	--
2-Methylnaphthalene		•	•	•	•	--	--	•	•	•	--	--	--	--	--	--	--
1-Methylnaphthalene		--	--	--	--	•	•	•	•	•	--	--	--	--	--	--	--
Quinoline		--	--	--	--	•	•	--	--	--	--	--	--	--	--	--	--
Acenaphthene		"	"	"	"	•	•	•	•	•	--	--	--	--	--	--	--
Acenaphthalene		--	--	--	--	--	•	•	--	--	--	--	--	--	--	--	--
Fluorene		--	•	--	--	•	•	•	•	•	--	--	--	--	--	--	--
Phenanthrene/Anthracene		•	•	•	•	•	•	•	•	•	•	•	•	--	•	•	•
Acridine		--	--	--	--	--	--	•	--	--	--	--	--	--	--	--	--
Carbazole		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Fluoranthene		--	--	--	--	•	•	•	•	•	--	--	--	--	--	--	--
Pyrene		•	•	•	--	--	•	•	•	•	•	•	--	--	--	--	--
Benzo(a)fluorene		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(b)fluorene		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benz(a)anthracene/ Chrysene/Triphenylene		--	--	--	--	--	--	--	--	--	•	--	--	--	--	--	--
Naphthacene		--	--	--	--	"	"	"	"	"	"	"	"	"	"	"	"
Benzo(e)pyrene/ Benzo(a)pyrene		--	--	--	--	--	--	--	--	--	•	•	--	--	--	--	•
Perylene		--	--	--	--	--	--	--	--	--	•	•	--	--	--	--	--
Dibenzanthracene		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(g,h,i)perylene		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Anthanthrene		--	--	--	--	"	"	"	"	"	"	"	"	"	"	"	"
Coronene		"	"	"	"	--	--	--	--	--	--	--	--	--	--	--	--
Dibenzpyrene		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,j)acridine		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,i)carbazole		--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

<sup>a</sup>--" indicates compound not detected.<sup>b</sup>" indicates sample not analyzed for this compound.<sup>°</sup> indicates compound detected.

## SELECTION OF PNA COMPOUNDS FOR SAMPLING AND ANALYSIS

From the analytical results obtained for the samples collected during the walk-through surveys, it was decided to delete some specific analytes or groups from the sampling protocols in the comprehensive surveys. These were eliminated primarily because they were not detected in the range-finding sampling or because measured concentrations were far below levels considered to have health implications. These walk-thru surveys were based on plants A and B only. Monetary considerations ruled out sampling during walk-thru surveys of the last plant. The PNAs were included in all comprehensive survey protocols even though initial monitoring suggested that air concentrations in process areas were low.

Analysis of PNAs showed the presence of many PNA species and homologs. The selection of individual PNAs that would be routinely quantitated in subsequent analytical protocols was based on these requirements:

- . availability of analytical standards to permit quantitation of exposures;
- . selection of a distribution of PNA species in each of the 2-, 3-, 4-, 5-, 6-, and 7-ring groups;
- . inclusion of as many of the known or suspected carcinogens as possible.

The final group of PNAs which were routinely quantitated on all personal, area, wipe, and bulk samples is listed in Table 3-3. More information on these chemicals including structure, ring number, boiling point, and carcinogenicity rating is given in Appendix C (Table C-4).

Table 3-3. PNAs Routinely Quantitated by GC/MS

Order of Elution	Compound
1	Naphthalene
2	1-Methylnaphthalene
3	2-Methylnaphthalene
4	Quinoline
5	Acenaphthalene
6	Acenaphthene
7	Fluorene
*8	Phenanthrene/Anthracene
9	Acridine
10	Carbazole
11	Fluoranthene
12	Pyrene
*13	Benzo (a) fluorene/Benzo (b) fluorene
*14	Benz (a) anthracene/Chrysene/Triphenylene
*15	Benzo (j) fluoranthene/Benzo (b) fluoranthene/Benzo (k) fluoranthene
*16	Benzo (e) pyrene/Benzo (a) pyrene
17	Perylene
18	Dibenz (a, j) acridine
19	Dibenz (a, i) carbazole
20	Indeno (1, 2, 3-cd) pyrene
21	Dibenz (a, h) anthracene
22	Benzo (g, h, i) perylene
23	Coronene
24	Dibenz (a, i) pyrene
25	Dimethylbenz (a) anthracene
26	3-Methylcholanthrene
27	6, 13-Dimethyldibenz (a, h) anthracene

\*Compounds not separated with 6' 3% OV-17 column.

## SAMPLING AND ANALYTICAL METHODS

The industrial hygiene sampling and analytical protocols used for these studies were standard NIOSH methods, except, in the case of PNAs, sampling procedures were those developed by Enviro, and analytical procedures developed and validated by the University of Iowa's University Hygienic Laboratory under a subcontract to Enviro.

A complete description of all procedures including the validation testing for PNA sampling and analysis is presented in a companion volume to this document, "A Method for Sampling and Analysis of Polynuclear Aromatic Compounds in Coal Conversion Plants and Petroleum Refineries" (Vol. IV).

Prior to the survey, all sampling pumps were calibrated to a primary standard with the appropriate sampling train in line. Correct sampling rates were confirmed by periodic checks with a precision rotameter throughout the sampling period. Sampling devices were checked periodically for overloading of sampling media, pump performance, and functioning of the sampling train.

Each sample was given a unique identification number at the start of the sampling period. Sample data sheets were prepared for each sample and identified by a corresponding sample number. Meteorological data taken at the plant were supplemented by data from the local weather bureau or station.

The following sampling procedures were followed as closely as possible at each of the gasification plants surveyed.

- . Sampling was conducted during each of the three shifts during the survey period, which was about 5 days for each plant. The surveys at Plants A and C were interrupted for several days due to plant shutdown. When the plants came back on stream, the sampling programs were resumed.
- . Full-shift sampling was conducted on each worker selected for monitoring. At least two full-shift samples were taken for each job category.

- Two or three area samples were collected during the survey at equipment or process areas suspected to have the highest concentrations of PNAs, hydrocarbon vapors, and gas emissions.
- Plant boundary, or upwind, area samples were collected for all agents sampled within the process area to determine the contribution of extra-plant sources.

After sampling, samples were immediately sealed and protected from light to prevent accidental contamination or sample losses. Samples were packed in dry ice in styrofoam containers specially designed for the shipment of materials under refrigeration. Filters, charcoal tubes, silica gel tubes, and bulk samples were packed in separate containers with styrofoam packing material to prevent breakage and contamination.

#### Polynuclear Aromatic Hydrocarbons (PNAs)

The general principle for collection of PNAs and their aza-analogs from air involves the use of a sampling device consisting of a 37-mm silver-membrane filter with a solid adsorbent backup. The silver-membrane filter is only able to trap particulate phase PNAs. The Chromosorb 102 (C-102) backup captures the vapor phase PNAs.

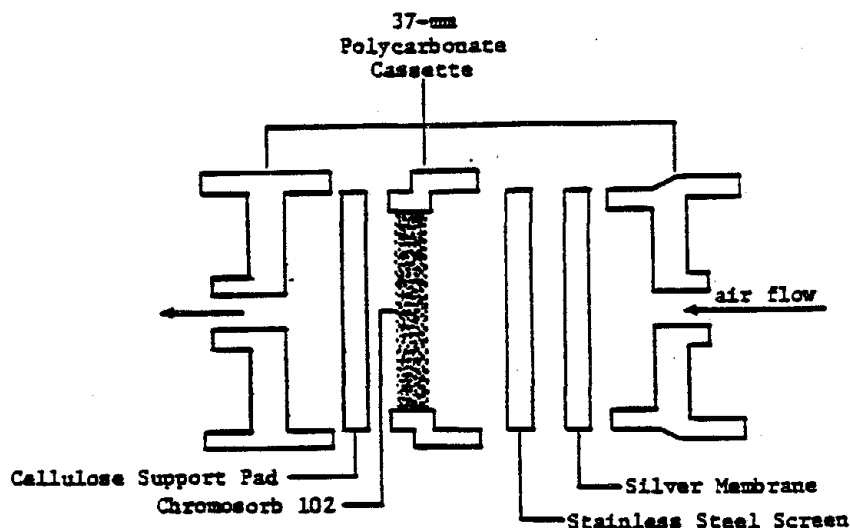


Figure 3-1. Area Monitoring Device for PNAs

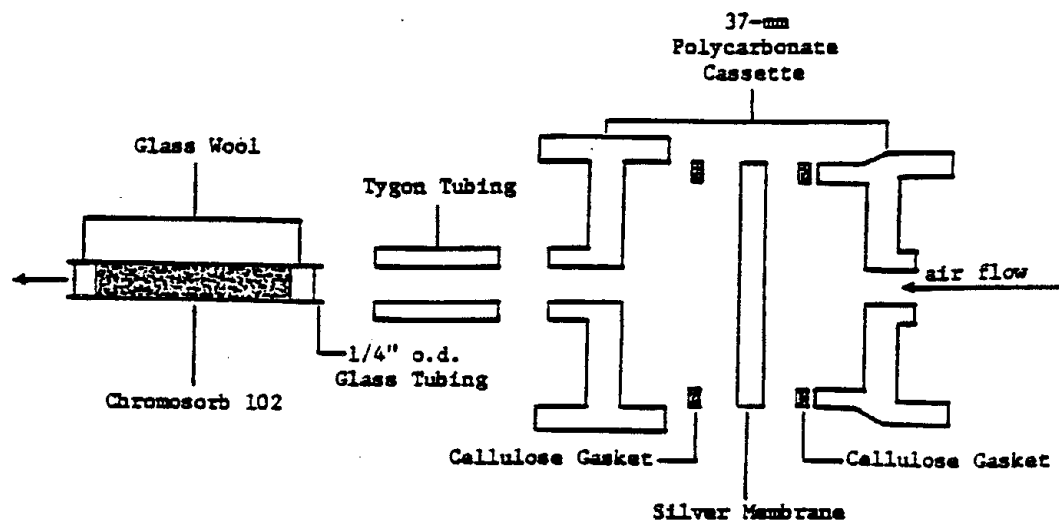


Figure 3-2. Personal Monitoring Device for PNAs

Sampling for airborne PNAs was performed by drawing air through the two-stage sampling unit consisting of a silver-membrane filter followed by Chromosorb 102 (C-102), a porous polymer adsorbent. The commercially available C-102 used for this study was contaminated and required pre-extraction prior to use. The C-102 cleanup scheme is presented in Table 3-4.

Table 3-4. Chromosorb 102 Cleanup Protocol

Solvent	No. of Solvent Changes	Soxhlet Extraction Time (hr)
Methylene chloride	4	48
Methanol	2	24
Methylene chloride/methanol (1:1; v/v)	2	48

The area sampling cassette contained a silver-membrane filter followed by 3 to 4 grams of C-102 sandwiched in the middle section of a three-piece cassette. A modified sampling unit was used for personal monitoring. Approximately 150 mg of C-102 was packed in a glass tube following the silver-membrane-containing cassette, rather than in the cassette itself. The intent of the

larger quantity of solid sorbent in the area cassettes was to minimize the possibility of sample breakthrough in high-concentration areas. The NIOSH method (P&CAM 183) recommended the use of a glass-fiber filter in front of the silver-membrane filter to prevent clogging; since this was not a problem in this study, the glass-fiber filter was not used. NIOSH no longer recommends glass fiber filters for PNA sampling.

After collection of personal or area samples, the sampling assemblies were covered with foil and stored at  $-20^{\circ}\text{C}$  in the dark until analyzed.

The C-102 solid sorbent and the silver-membrane filter were extracted separately. After extraction and concentration, the extracts were either analyzed separately or combined. The extraction procedure is shown in Figure 3-3.

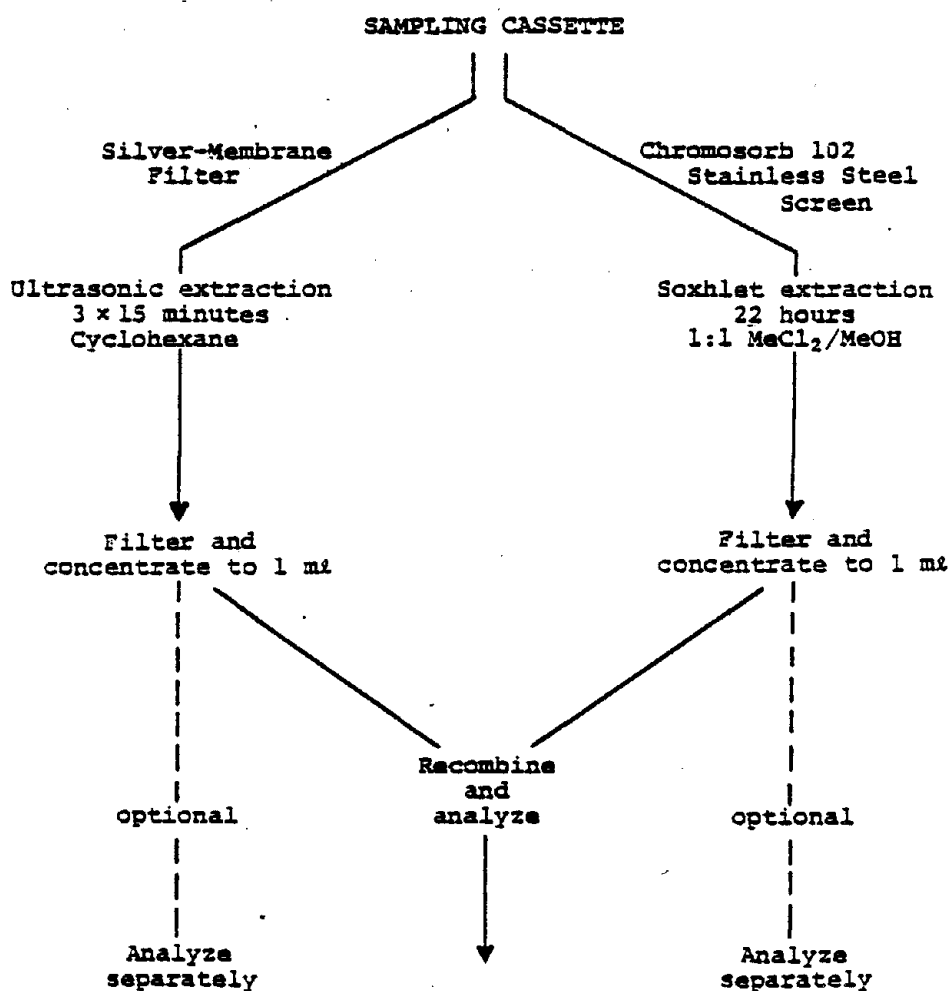


Figure 3-3. Sample Preparation Procedure

The C-102 adsorbent (and stainless steel backup screen for the two-stage area samples) were placed in a foil-wrapped soxhlet extractor fitted with a 500-mL round-bottom flask and extracted with 300 mL of glass-distilled methylene chloride/methanol (1:1, v/v) for 22 hours (Phillips, 1977). The extracts were processed by concentrating to approximately 10 mL in a round-bottom flask fitted with a 3-ball Snyder column. The concentrate was then filtered through a Millipore sample clarifier (0.45-µm Teflon filter) in a 15-mL serum vial fitted with Teflon-lined rubber septum and crimp cap and stored at -20°C (-4°F) in the dark until analyzed.

The extraction procedures used for the silver-membrane filters is a modification of the NIOSH-validated method P&CAM 217 (NIOSH, 1977). The modification includes multiple extractions instead of a single extraction, and cyclohexane in place of benzene.

The silver-membrane filters were ultrasonically extracted in a 200-watt Bransonic 52 bath for 15 minutes with 5 mL of glass-distilled cyclohexane. The extracts were then placed in a 15-mL centrifuge tube. The process was repeated two additional times, and the extracts were combined, filtered, and then placed in a heating block regulated at 63°C and concentrated to approximately 1 mL.

PNAs were identified and quantified by the use of two internal standards -- d<sub>10</sub>-anthracene and d<sub>12</sub>-chrysene. All GC analyses of the referenced PNA compounds produce symmetrical Gaussian peaks, with the exception of quinoline which tails slightly.

Each batch of samples included field blanks and reagent blanks to check for contamination. Desorption efficiencies were determined on each batch of Chromosorb 102.



The GC/MS parameters used for the separations and quantitation of PNAs were as follows:

- . GC Column: 6' x 0.079" i.d. glass column packed with 3% OV-17 on 80/100 mesh Supelcort (purchased from Supelco, Inc.)
- . Column Temperature: 8°C/min to 260°C, then held at 260°C for 50 min
- . Injector Temperature: 240°C
- . GC/MS Interface Temperature: 320°C
- . Carrier Gas (helium) Flow Rates: 30 mL/min
- . MS Ionizer Block Temperature: 250°C
- . MS Electron Multiplier Voltage: 1800 V
- . MS Electron Energy: 70 eV
- . MS Emission Current: 500 mA

The isomers not resolved by this GC column (i.e., numbers 8, 13, 14, 15, and 16 in Table 3-3) but found to be present in quantifiable amounts were quantitated as isomeric groups. If multiple isomers were suspected of contributing to a single peak, additional analysis by either high-pressure liquid chromatography (HPLC) (Thomas and Lao, 1977) coupled with a fluorescence detector (Das and Thomas, 1978) or capillary column gas chromatography was used. These methods were found to separate isomers not resolved with the 6-ft, 3% OV-17 column.

The capillary GC parameters are as follows:

- . GC Equipment: Varian Model 3700 equipped with an auto-integrator and dual flame-ionization detectors
- . GC Column: 15m x 0.2495-mm i.d. glass capillary column packed with 0.34-µm film thickness of SE-52 (from J&W Scientific)
- . Column Temperature: 50°C to 250°C at 2°C/min

- . Injector Temperature: 300°C
- . Detector Temperature: 320°C
- . Carrier Gas (helium) Pressure: 20 psig

#### Aromatic Hydrocarbons

Air samples were collected on 600-mg charcoal tubes and analyzed for: benzene, toluene, and xylene. Sampling and analysis followed the NIOSH-recommended procedures described in Method No. P&CAM 127 (NIOSH, 1977).

#### Aromatic Amines

Separate samples collected on 800-mg silica gel tubes were analyzed for the two groups of aromatic amines listed below:

1. Anilines: aniline  
N,N-dimethylaniline  
o-toluidine  
2,4-dimethylaniline  
o-anisidine  
p-anisidine  
p-nitroaniline
2. Naphthylamines: 1-naphthylamine  
2-naphthylamine

Analyses followed recommended NIOSH (1977) procedures described in P&CAM 168 for aromatic amines and P&CAM 264 for the naphthylamines. Field experience has demonstrated that sampling using silica gel tubes is adversely affected by relative humidities greater than 75 percent. Therefore, the aromatic amine results published in this report are considered to be underestimated. Almost all sampling campaigns had relative humidity conditions in excess of 75 percent. NIOSH is researching other methods for aromatic amine sampling but these methods were not available for this study.

## Phenols

Samples were collected on 800-mg silica gel tubes and analyzed using NIOSH (1977) procedures in S167 for the following phenolics: phenol, o-cresol, m-cresol, p-cresol, o-ethylphenol, p-ethylphenol, 2,3-xyleneol, and 2,4-xyleneol. Since phenols are collected on silica gel, collection efficiency due to water interference must be considered. Therefore, phenol results reported may be underestimated.

## Gases

Sampling for gases such as CO, H<sub>2</sub>S, and SO<sub>2</sub> was done by grab sampling techniques using length-of-stain indicator tubes or direct-reading monitoring devices. Because of the intermittent nature of gaseous emissions in the facilities, grab sampling and real-time monitoring were preferred because full-shift personal sampling did not pinpoint emissions sources or measure peak concentrations.

## DATA ANALYSIS

All analytical results were corrected for desorption efficiencies as determined on each batch or lot of C-102, charcoal tubes, and silica gel tubes. Corrections were also made for the mean field blanks values taken during the respective surveys.

The data for sets of samples were analyzed using the following statistical method:

- . Lognormal distribution of the measured concentrations in the samples sets was assumed (NIOSH, 1977).
- . The geometric mean (GM) and the geometric standard deviation (GSD) were determined using the formulas:

$$GM = \text{antilog}_{10} \left[ \frac{\sum_{i=1}^n \log_{10} X_i}{n} \right]$$

$$GSD = \text{antilog}_{10} \sqrt{\frac{n \sum \log_{10}^2 X_i - \left( \sum \log_{10} X_i \right)^2}{n(n-1)}}$$

- . The value of  $X_i$  for all samples less than the limit of detection was assigned the number equal to the lower limit of detection. This statistical manipulation will shift threshold values to the right with bias towards the onset of human effect. The lower limit of detection was used for all values of 0.
- . The upper and lower confidence limits (UCL and LCL) were calculated from the GM, GSD, and the Student's t test according to the formulas:

$$UCL = \text{antilog}_{10} \left[ \log_{10} GM + t_{.05} \frac{\log_{10} GSD}{n^{1/2}} \right]$$

$$LCL = \text{antilog}_{10} \left[ \log_{10} GM - t_{.05} \frac{\log_{10} GSD}{n^{1/2}} \right]$$

- .  $t_{.05}$  was used from the standard table.

<u>(n-1)</u>	<u>t.05</u>
1	12.7
2	4.3
3	3.2
5	2.6
6-7	2.4
8-9	2.3
10-13	2.2
14-27	2.1
28	2.0

The broad confidence limits were found on the group means of PNAs. This can be attributed to two factors. First the data were widely dispersed; concentration ranges routinely varied over four orders of magnitude within a

given population of samples. This probably resulted from the unsteady operating conditions at the plants and from inherent variability in the sampling and analytical methods. Second, the number of samples in each category or group was low due to the high cost for analysis of individual samples of PNAs.

#### 4. RESULTS

##### RESULTS OF AREA AND PERSONAL SAMPLING

This chapter summarizes the results of all sampling conducted at the three coal gasification plants. More than 90 personal or area samples were collected and analyzed for up to 26 individual PNAs or groups of PNAs. In order to present the data in an understandable format, "total PNA" values only are reported. When groups of data are combined, the geometric means (GM) are used along with the geometric standard deviation (GSD) and the 95% upper and lower confidence limits (UCL and LCL). In some cases statistical manipulations were performed on sets of samples with small  $n$  values; therefore, UCL's were extremely large. Individual sample results with the measured concentrations of each PNA species are presented in Appendix B.

One of the objectives of the study was to determine which of the unit processes contributed substantially to worker exposures. To accomplish this, area samples were collected, when possible, adjacent to equipment in each of the process units which were expected to be the source of highest emissions. Sampling data from these points were then combined for comparison to other process areas (Table 4-1). Similarly, personal sampling data collected from workers with equivalent job responsibilities at the three plants were combined for comparison (Table 4-2).

When grouped data are pooled, geometric means (GM) are listed along with the geometric standard deviation (GSD) and the 95% upper and lower confidence limits (UCL and LCL). Pooled data for 2 or 3 samples are described by GM and range.

In most PNA samples, the 2-ring PNAs, primarily naphthalene and its methyl derivatives, comprised the largest contributing mass to the total concentration. In order to include this information, the percent distribution of PNAs by ring number is also given (Tables 4-1 and 4-2).

Table 4-3 shows qualitative results of the wipe samples collected at the coal gasification plants.

Other samples were collected to assess worker exposures to aromatic amines, simple aromatics such as benzene, toluene, and xylene, and the gases carbon monoxide and hydrogen sulfide. The results displayed in Tables 4-1 to 4-7 are discussed in Chapter 5.

Table 4-1. Total PNA Concentrations for Area Samples of Coal Gasification Plants/% Distribution of PNAs by Weight

Plant	Area Sampled	N <sup>a</sup>	GM <sup>b</sup> (µg/m <sup>3</sup> )	GSD <sup>c</sup>	LCL <sup>d,j</sup> (µg/m <sup>3</sup> )	UCL <sup>e,j</sup> (µg/m <sup>3</sup> )	% Distribution of PNAs by Weight				
							2-Ring	3-Ring	4-Ring	5-Ring	6- and 7-Ring
A	Gasifier Combustor	4	0.4	4.9	<0.1 <sup>f</sup>	4.7	100	0	0	0	0
	Gasifier Reductor	1	0.4	N/A <sup>g</sup>	N/A	N/A	100	0	0	0	0
	Gas Duct	2	<0.1	<0.1	<0.1	<0.1	N/A	N/A	N/A	N/A	N/A
	Induced-Draft Fan	2	0.3	6.1	0.07	0.9	100	0	0	0	0
	Sludge Thickener	1	<0.1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Cyclone Scrubber	1	0.2	N/A	N/A	N/A	100	0	0	0	0
	Control Room	2	0.2	3.5	<0.1	0.6	100	0	0	0	0
	Total In-Plant	13	0.2	3.2	0.1	0.5	100	0	0	0	0
	Plant Perimeter	2	0.3	4.7	<0.1	0.9	100	0	0	0	0
B	Top of Gasifier	3	22.7	1.5	16.4	35.6	97.4	2.6	0	0	0
	Poke Hole	3	17.3	2.7	5.5	35.6	96.2	3.8	0	0	0
	Detarrax/Deciler	4	18.1	2.4	2.1	152.6	97.4	2.6	0	0	0
	Oil/Liquor Separator	1	74.2	N/A	N/A	N/A	97.4	2.2	0.4	0	0
	Ash Pan	1	42.1	N/A	N/A	N/A	96.4	3.6	0	0	0
	Day Tar/Oil Tank	2	20.6	2.2	11.9	35.7	96.4	3.0	0.6	0	0
	Tar Pump	2	72.4	1.1	68.7	76.4	97.2	2.8	0	0	0
	Gas Compressor	1	69.6	N/A	N/A	N/A	98.7	1.3	0	0	0
	Control Room	2	20.5	1.8	13.4	31.3	92.8	7.2	0	0	0
	Total In-Plant	19	26.8	2.2	18.3	39.1	96.7	3.2	0.1	0	0
	Plant Perimeter	2	1.8	4.7	0.6	5.4	73.3	25.0	1.7	0	0
C	Gasifier - 5th Level	3	0.6	2.6	0.2	1.1	73.9	26.1	0	0	0
	Gasifier - 6th Level	4	5.4	7.6	0.2	138.8	99.2	0.8	0	0	0
	Gas Compressor	4	1.7	3.0	0.3	9.7	69.9	21.4	6.8	1.9	0
	Filter/Strainer	2	0.9	2.4	0.5	1.8	91.3	4.3	4.3	0	0
	Control Room	4	2.9	3.7	0.3	23.6	96.5	3.5	0	0	0
	Total In-Plant	17	2.0	4.3	0.9	4.1	95.8	3.4	0.6	0.2	0
	Plant Perimeter	3	1.1	2.6	0.4	2.8	83.7	16.3	0	0	0

<sup>a</sup> Number of samples collected. <sup>b</sup> Geometric mean of concentrations. <sup>c</sup> Geometric standard deviation.

<sup>d</sup> Lower 95% confidence limit of geometric mean. <sup>e</sup> Upper 95% confidence limit of geometric mean.

<sup>f</sup> " indicates value below detection limit. <sup>g</sup> N/A = not applicable.

Table 4-2. Total PNA Concentrations for Personal Samples of Coal Gasification Plants/% Distribution by Weight

Plant	Personnel Sampled	N <sup>a</sup>	GM <sup>b</sup> (µg/m <sup>3</sup> )	GSD <sup>c</sup>	LCL <sup>d,h</sup> (µg/m <sup>3</sup> )	UCL <sup>e,h</sup> (µg/m <sup>3</sup> )	% Distribution of PNAs by Weight					
							2-Ring	3-Ring	4-Ring	5-Ring	6-Ring	7-Ring
A	EQUIPMENT OPERATORS	8	2.6	3.6	0.9	8.1	95.8	4.2	0	0	0	0
	MAINTENANCE PERSONNEL											
	Welder/Boilermaker	4	6.8	1.9	2.4	19.5	100	0	0	0	0	0
	Pipefitter	2	6.5	3.4	2.6	10.2	96.9	3.1	0	0	0	0
	Laborer	2	0.4	7.7	<0.2	1.8	100	0	0	0	0	0
	TOTAL Maintenance	8	3.4	5.1	0.8	13.4	97.4	2.6	0	0	0	0
	CHEMICAL TECHNICIAN	2	0.4	7.4	<0.2	1.7	100	0	0	0	0	0
B	INSTRUMENT TECHNICIAN	1	1.9	N/A <sup>g</sup>	N/A	N/A	100	0	0	0	0	0
	OPERATORS	4	19.3	1.5	9.7	38.4	96.2	3.8	0	0	0	0
	MAINTENANCE PERSONNEL											
	Millwright	2	58.0	2.5	30.5	110.3	97.9	2.1	0	0	0	0
	Utility Helper	2	15.3	1.1	14.8	15.9	97.1	1.3	1.6	0	0	0
	Maintenance	2	88.5	1.3	72.8	107.5	99.0	1.0	0	0	0	0
	Electrician	1	389.4	N/A	N/A	N/A	98.2	1.8	0	0	0	0
C	Foreman	1	35.1	N/A	N/A	N/A	92.9	7.1	0	0	0	0
	TOTAL Maintenance	8	55.1	3.0	21.4	141.5	98.0	1.9	0.1	0	0	0
	LOWER LEVEL TECHNICIAN	7	4.2	1.3	1.3	13.8	67.8	18.5	10.9	2.8	0	0
	UPPER LEVEL TECHNICIAN	5	5.3	11.3	0.3	110.7	67.8	18.4	8.9	4.9	0	0
	MAINTENANCE PERSONNEL	1	60.4	N/A	N/A	N/A	94.7	5.3	0	0	0	0

<sup>a</sup> Number of samples collected.

<sup>b</sup> Geometric mean of concentrations.

<sup>c</sup> Geometric standard deviation.

<sup>d</sup> Lower 95% confidence limit of geometric mean.

<sup>e</sup> Upper 95% confidence limit of geometric mean.

<sup>f</sup> "<" indicates value below detection limit.

<sup>g</sup> N/A = not applicable.

<sup>h</sup> for n=2 or 3 minimum and maximum value shown (not LCL and UCL)



Table 4-3. Wipe Sample PNA Analytical Results (Qualitative)  
for three Coal Gasification Plants

Plant	Site Sampled	PNAs					
		2-Ring	3-Ring	4-Ring	5-Ring	6-Ring	7-Ring
A	Maintenance tools	<sup>a</sup>	•	•	<sup>b</sup>	—	—
	Gloves of welder	•	•	•	—	—	—
	Hands of welder	•	•	—	—	—	—
	Gasifier	•	•	—	—	—	—
	Induced-draft fan	•	•	•	—	—	—
	Sludge thickener	•	•	•	—	—	—
	Cyclone scrubber rail	•	•	•	—	—	—
	Control room	•	•	—	—	—	—
	Lunchroom	•	•	—	—	—	—
	Lunchroom	•	•	—	—	—	—
B	Tools for tar pump	•	•	•	•	—	—
	Tools stored in control room	•	•	•	•	—	—
	Tools for gas compressor	•	•	•	•	—	—
	Rubber glove, outside surface	—	•	•	—	—	—
	Rubber glove, outside surface	—	•	•	—	—	—
	Rubber glove, inside surface	—	—	—	—	—	—
	Rubber glove, inside surface	—	—	—	—	—	—
	Gloves of millwright at tar pump	•	•	•	•	•	•
	Trousers under coveralls of tar pump worker	•	•	•	•	—	—
	Oil/liquor separator weir handle	•	•	•	—	—	—
	Handrail above compressor	•	•	•	—	—	—
	Handrail below Stretford unit	•	•	•	—	—	—
	Handrail on top of gasifier	•	•	•	—	—	—
	Side of gasifier	—	•	—	—	—	—
	Control room - desk top	•	•	•	—	—	—
	Control room - desk top	—	•	—	—	—	—
	Control room - stair rail	—	—	—	—	—	—
	Control room - bathroom handles	•	•	•	—	—	—
C	Wrench at ground sample port	—	—	—	—	—	—
	Wrench at filter	•	—	—	—	—	—
	Wrench at top of gasifier	—	•	•	—	—	—
	Gloves of lower level technician	•	•	•	•	—	—
	Coveralls of upper level technician	•	•	•	•	—	—
	Coveralls of lower level technician	•	•	•	•	—	•
	Lift truck steering wheel	—	—	—	—	—	—
	Sample port, 5th level	•	—	•	—	—	—
	Separator pit	•	•	•	•	—	—
	Filter housing	•	•	•	—	—	—
	Pipe duct between gasifier and cyclone	•	—	—	—	—	—
	Control room - desk top	—	—	•	—	—	—
	Work platform, gasifier	•	•	•	—	—	—

<sup>a</sup>• indicates compound detected.

<sup>b</sup>— indicates compound not detected.

Table 4-4. Maximum Concentrations (ng/m<sup>3</sup>) of Aromatic Amines Measured in Area Samples at Coal Gasification Plants<sup>h</sup>

Plant	Process Area	Aromatic Amines							
		Aniline	N,N-Dimethyl-aniline	2,4-Dimethyl-aniline	o-Toluidine	o-Anisidine	p-Anisidine	p-Nitro-aniline	Naphthyl-amine <sup>a</sup>
A	Gasifier	-- <sup>b</sup>	--	" <sup>a</sup>	"	--	--	"	"
	Cyclone Scrubber	--	--	"	"	--	--	"	"
	Induced-Draft Fan	--	--	"	"	--	--	"	"
B	Gasifier	--	--	--	--	--	--	--	--
	Poke Hole	--	--	--	--	--	--	--	--
	Detarrer/Deoiler	"	"	"	"	"	"	"	--
	Washer	"	"	"	"	"	"	"	--
C	Makeup Pumps <sup>d</sup>	--	--	--	--	--	--	"	"
	Separator Pit <sup>e</sup>	--	--	0.01	--	0.04	--	"	"
	Sampling Port <sup>e</sup>	--	--	--	--	--	--	"	"
	Cyclone - 5th Level <sup>e</sup>	--	0.01	0.01	--	0.01	--	"	"
	Gasifier - 6th Level <sup>e</sup>	0.01	0.01	0.01	--	--	--	"	"
	Compressor Pump Filters <sup>f</sup>	--	--	--	--	--	0.09	"	"
	Control Room <sup>g</sup>	--	0.1	--	--	--	--	"	"

<sup>a</sup> Includes 1- and 2-naphthylamine.

<sup>b</sup> "--" indicates compound not detected.

<sup>a</sup> "n" indicates sample not analyzed for this compound.

<sup>d</sup> Four samples collected.

<sup>e</sup> Three samples collected.

<sup>f</sup> Five samples collected.

<sup>g</sup> Six samples collected.

<sup>h</sup> note: sampling method inadequate under high humidity conditions compromised this data as discussed in the text.

Table 4-5. Maximum Concentrations (mg/m<sup>3</sup>, expressed in ppm) of Simple Organics Measured in Air Samples at Coal Gasification Plants

Plant	Process Area	Organics						
		Benzene	Toluene	Xylene	Xylenol	Phenols <sup>a</sup>	Cresol	Mercaptans <sup>b</sup>
A	Gasifier	0.02	— <sup>c</sup>	—	— <sup>d</sup>	—	—	—
	Char Bin	—	—	—	—	—	—	—
	Cyclone Scrubber	0.02	—	—	—	—	—	—
	Induced-Draft Fan	0.02	—	—	—	—	—	—
	Sludge Thickener	0.02	—	—	—	—	—	—
	Gas Dust	—	—	—	—	—	—	—
	Stretford Unit	0.01	—	—	—	—	—	—
	Control Room	—	—	—	—	—	—	—
B	Gasifier	—	—	—	—	—	—	—
	Detarrer/Deciler	—	—	—	—	—	—	—
	Oil/Liquor Separator	—	—	—	—	—	—	—
	Day Tar Tank	—	—	—	—	—	—	—
	Compressor	—	—	—	—	—	—	—
	Sump Blowdown	—	—	—	—	—	—	—
	Stretford Unit	—	—	—	—	—	—	—
	Control Room	—	—	—	—	—	—	—
	Wash Settling Tank	—	—	—	—	—	—	—
C	Gasifier	0.02	—	—	—	—	—	—
	Char Sample Port	0.01	—	—	—	—	—	—
	Filter	8.2	—	—	—	—	—	—
	Makeup Pump	—	—	—	—	—	—	—
	Compressor	0.05	—	—	—	—	—	—
	Separator Pit	—	—	—	—	—	—	—
	Control Room	0.5	—	0.01	—	—	—	—

<sup>a</sup>Includes ethylphenol.

<sup>b</sup>Includes n-propyl, n-butyl, and n-amymercaptan.

<sup>c</sup>— indicates compound not detected.

<sup>d</sup>— indicates sample not analyzed for compound.

Table 4-6. Maximum Concentrations (ppm) of Simple Organics Measured in Personal Samples at Coal Gasification Plants

Plant	Job Category	No. of Samples	Organics		
			Benzene	Toluene	Xylene
A	Equipment Operator	12	0.01	0.01	— <sup>a</sup>
	Maintenance Personnel	8	0.05	0.02	—
	Instrument Technician	2	0.01	0.02	—
	Chemical Technician	4	0.01	—	—
B	Operator	4	—	—	—
	Utility Helper	4	—	—	—
	Maintenance Personnel	3	—	—	0.1
C	Operator	13	0.03	—	—
	Maintenance Personnel	2	0.1	0.01	0.06

<sup>a</sup>— indicates compound not detected; detection limit for benzene, toluene, and xylene was 0.01 ppm assuming an average sample volume of 100 liters.

Table 4-7. Area Sampling Analytical Results (ppm) for Carbon Monoxide and Hydrogen Sulfide at Three Coal Gasification Plants

Plant	Location Sampled	Compound (ppm)	
		Carbon Monoxide	Hydrogen Sulfide
A	Gasifier	n <sup>a</sup>	--- <sup>b</sup>
	Induced-Draft Fan	n	---
	Cyclone Scrubber	n	---
	Sludge Thickener	n	---
	Stretford Unit	n	---
B	Coal Conveyor to Coal Bunker	5-21 <sup>c</sup>	n
	Top of Gasifier	0-10 <sup>c</sup>	---
	Poke Hole	0-10 <sup>c</sup>	---
	Stretford Unit	---	---
	Deoiler, Washer, Cooler	5-60 <sup>c</sup>	n
	Detarrer	0-55 <sup>c</sup>	n
	Deoiler/Detarrer	---	---
	Wash Settling Tank	n	2
	448 Level (Including Stretford)	0-5 <sup>c</sup>	---
	Ash Pan	0-5 <sup>c</sup>	---
	Ground Level	0-5 <sup>c</sup>	n
C	Top of Gasifier	n	---
	Top of Gasifier - Lid Off	27	---
	5th Level, Near Cyclone	16	---
	Separator Pit	2-5 <sup>c</sup>	---
	Recycle Gas Compressor/Filters	13-14 <sup>c</sup>	---
	Recycle Gas Compressor/Filters During Process Stream Sampling	50	---
	Filter Unit During Filter Replacement	n	120
	Filter Unit During Filter Replacement	5-1,745 <sup>c</sup>	160

<sup>a</sup> "n" indicates not sampled.

<sup>b</sup> "---" indicates not detected.

<sup>c</sup> Range of multiple samples or continuous monitoring.

## INDUSTRIAL HYGIENE AND MEDICAL SURVEILLANCE PROGRAMS

The industrial hygiene/medical surveillance programs reviewed here are divided into those elements designed to minimize physical contact between the worker and the plant environment (personal hygiene and educational programs), those aimed at the detection of health changes caused by the industrial environment (medical surveillance and epidemiological studies), and industrial hygiene monitoring programs designed to measure chemical pollutants in the plant environment. In general, the gasification plants included in this survey maintained generalized industrial hygiene programs; however, the monitoring programs were inadequately designed to fully define the potential hazards associated with coal conversion. The elements of the individual programs at each plant are summarized in Table 4-8.

### Personal Hygiene and Educational Programs

Personal hygiene procedures designed to protect coal gasification plant workers against dermal, inhalational and accidental ingestive exposures to hazardous chemicals include four major elements:

- . protective clothing/equipment programs
- . clean clothing programs
- . shower facilities with clean/dirty area separation
- . barrier creams and cleansing agents.

The range of protective clothing required or provided by the surveyed plants for protection against dermal exposure to coal-derived materials includes:

Table 4-8. Industrial Hygiene/Occupational Medicine Programs at Coal Gasification Plants

PROGRAM ELEMENT	PLANT A	PLANT B	PLANT C
<b>PERSONAL HYGIENE AND SAFETY</b>			
Protective Clothing/Equipment Program			
coveralls	✓	✓	✓
shoes/boots	✓	✓	✓
underwear	-	-	-
rainsuits/coats	-	✓	✓
gloves	✓	✓	✓
safety glasses	✓	✓	✓
hardhats	✓	✓	✓
earmuffs	-	✓	✓
respirators	✓	✓	✓
Clean Clothing Program			
clean coveralls	-	3 pairs	daily
protective shoes	-	-	-
clean underwear	-	-	-
Hygiene Facilities (Shower Room)	✓	✓	✓
single locker	-	✓	-
dual lockers	-	-	✓
clean/dirty separation	-	-	-
barrier creams/agents	-	-	-
<b>EDUCATIONAL PROGRAM</b>			
Prejob training	✓	✓	✓
Brochures/manuals	-	-	-
Continuing education	-	informal	classroom
Posted signs	-	-	-
Respirator training	✓	✓	✓
<b>WORK PRACTICES AND PERMIT SYSTEM</b>	-	✓	-
<b>INDUSTRIAL HYGIENE MONITORING</b>			
Informal schedule	-	-	-
Uniform program	-	-	✓
<b>MEDICAL SURVEILLANCE</b>			
Clinical monitoring	✓	✓	✓
Epidemiological program	-	-	-

- . shoes -- oil-resistant leather or rubber coverings required and provided by some plants
- . coveralls -- provided by all plants
- . raincoats, rainsuits, aprons, hoods -- provided by all plants on an "as-needed" or assigned basis for high-exposure jobs in the process area
- . gloves: cotton, asbestos, leather, rubber -- variously available or required in all plants for specific jobs

Safety equipment required for everyone entering the process areas of all plants includes safety glasses and hardhats; earmuffs were usually available as well.

Protection from inhalation of potentially dangerous gases and airborne particulates is provided by disposable respirators and full-face respirators with acid gas/organic vapor cartridges. In addition, supplied-air respirators include 5-minute, self-contained escape packs, and 30-minute, pressure-demand, self-contained breathing apparatus (SCBA).

The effectiveness of this part of the personal hygiene program depends upon the ready availability of this mandatory and nonmandatory equipment, as well as on the attitudes of supervisors and those responsible for using the equipment.

The clean clothes programs have as their goals the minimization of exposure to coal-derived materials and the prevention of their spread outside the dirty areas of the plant. The gasification plants provide several sets of clothing with changes left to the discretion of the worker. All plants provide laundering service for this clothing, either on the premises or at commercial laundries. No systematic programs for cleaning nonlaunderable articles, such as gloves and rubber items, were evident in any plant, and worker contact with heavily soiled articles of this nature was noted frequently.



All of the gasification plants provide shower facilities and recommend daily showers. In addition, dual lockers are available in the shower room of one plant for separation of work and nonwork clothing. Barrier creams and cleansing agents were not generally available.

The UV fluorescent examination of skin surface before and after showering or washing, of clothing after laundering, and of tools for the detection of PNA contamination has been done on an experimental basis only at two of the sites. No plant provides routine spot-checking of this nature for monitoring the efficiency of personal hygiene programs.

Educational programs for employees include prejob training by supervisors (on an as-needed basis) and formal training in the use and care of respirators. One plant also holds formal classroom sessions on first aid, accident prevention, and safety rules covering equipment, emergencies, materials, machinery, and fire prevention.

#### Medical Surveillance and Epidemiological Studies

Industrial medical surveillance protects the health of the individual by detection of incipient health problems, and the health of all workers by the provision of long-term health information which may identify plant and industrial hazards requiring process or work practices modifications. It should, therefore, include a program of medical monitoring of individual workers for immediate evaluation, and a system for continuous recording of both medical and exposure data for future study.

Table 4-9 lists the medical surveillance procedures utilized by each plant included in this study. All currently operating plants provide at least periodic history and physical examinations and one or more auxiliary tests, including pulmonary function tests, chest X-rays, electrocardiograms, audiograms, and visual acuity tests. They also provide special visual skin examinations by a physician.

Table 4-9. Medical Programs in Effect at Coal Gasification Plants

	PLANT A	PLANT B	PLANT C
No. of Employees: <sup>a</sup>	35	13 <sup>b</sup>	50
<b>MINIMAL WORK-UP</b>			
Preplacement History and Physical	✓	✓	✓
Annual Follow-up	✓	✓ <sup>c</sup>	✓
Urinalysis	-	✓	✓
Blood Count	✓	-	✓
<b>ROUTINE WORK-UP</b>			
Blood Chemistries	-	✓	serum glucose
<b>AUXILIARY TESTS</b>			
Chest X-ray	✓ <sup>d</sup>	✓	✓
Pulmonary Functions	✓ <sup>d</sup>	✓	✓
EKG	✓ <sup>d</sup>	-	✓ <sup>e</sup>
<b>SPECIALIZED TESTS</b>			
Audiogram	-	-	✓ <sup>e</sup>
Sputum Cytology	-	-	-
Urine Cytology	-	-	-
Skin Examination	-	✓	✓
<b>MISCELLANEOUS</b>			
Medical Work-up	-	-	visual acuity testing
Epidemiological Program	-	-	-

<sup>a</sup> Not all tests given to all personnel.<sup>b</sup> Does not include part-time maintenance personnel.<sup>c</sup> Semiannually after 5 years.<sup>d</sup> Every 3 years.<sup>e</sup> Every 2 years.

/ = annual exam unless otherwise noted.

long-term effects on nearly all major organ systems of the body have been attributed to constituent chemicals in various coal conversion process streams. Table C-6 (page C-30) lists the specific chemicals sampled in this study and the major organ systems at risk following exposure. Also included in the table are specialized blood and urine tests which can provide an index of exposure to certain of these chemicals. They are useful monitoring tests during periods of increased exposure such as during maintenance and cleanup operations and in emergencies.

No epidemiology programs are being undertaken at any of the surveyed gasification plants.

#### Industrial Hygiene Monitoring Programs

Each of the three coal gasification plants surveyed conducts limited air sampling for chemical pollutants. Table 4-10 summarizes these chemicals by individual plant. In one plant, hydrogen sulfide, carbon monoxide, and ammonia readings are taken each shift at four grade level sites. In another, CO levels are continuously monitored in certain areas of the plant; in other areas, readings are taken before entrance into the area. All three plants have conducted benzene-soluble (CTPV) analyses of air samples, and one has measured individual benzo(a)pyrene (BaP) and naphthalene levels.

Table 4-10. Summary of Industrial Hygiene Monitoring Programs at Coal Gasification Plants

Monitoring Program	Plant A	Plant B	Plant C <sup>a</sup>
Coal Dust/Respirable Particulates	-	-	✓
Aromatic Hydrocarbons	Benzene solubles	Benzene solubles	Benzene solubles Naphthalene Benzo(a)pyrene
Gases	-	Carbon monoxide	Hydrogen sulfide Carbon monoxide Ammonia
Benzene, Toluene, Xylene	✓	-	Benzene
Phenolics	-	✓	✓
Noise	-	-	✓

<sup>a</sup> A one-time survey.

Most results are considered proprietary information and therefore unavailable for outside publications. However, the following fragmentary results have been verbally reported:

- . Of the two plants regularly monitoring CO levels, one has reported levels greater than 1,500 ppm when the recycle gas compressor filters and strainers are changed.
- . All benzene levels have been below 1 ppm.
- . All benzo(a)pyrene and naphthalene levels measured in one plant were less than  $2 \mu\text{g}/\text{m}^3$  for air volumes ranging from 0.6 to  $4 \text{ m}^3$ .
- . Some of the personal samples taken on technicians in one plant and analyzed for benzene solubles and total dust were inexplicably high and exceeded current standards. Conditions concerning these samples are not known. Therefore the samples may be considered an anomaly.

#### WORK PRACTICES AND CONTROLS

Modern coal gasification plants are basically closed-system operations designed to contain process constituents within the system. In a properly maintained system, worker exposure to process constituents can occur:

- . at product/by-product entry and exit points within the system,
- . during upset conditions,
- . during activities that circumvent the closed system, as a result of catastrophic equipment failure, and
- . during maintenance and turnaround activities.

Supplemental engineering controls, such as local exhaust ventilation, have been employed at entry and exit points to control some emissions. However, in most coal gasification facilities, worker protection is provided by the use of

personal protective clothing and respirators. For upset conditions and for activities that circumvent the closed system, work practices and personal protective clothing and equipment are relied upon to provide workers with additional protection.

#### Work Practices

The principal objective of work practices observed at the three coal gasification plants is to minimize skin contact with process constituents encountered during upset conditions or in the performance of routine activities which are outside the closed system or in the handling of contaminated tools or equipment. These situations were identified by plant management and safety personnel as being related primarily to maintenance activities, process stream sampling, and emergency situations.

Chemical compounds which the plants' management and safety staffs considered to present the greatest hazard to workers in these special situations were used as models to develop the correct work practices procedures to control exposures. These compounds include PNAs, hydrogen sulfide, and carbon monoxide. The PNAs were selected because of the carcinogenic properties of a number of PNA species. The need for management concern regarding bodily contact with PNAs is supported by information obtained in this study which showed the presence of PNAs on work surfaces, tools, and clothing (shown in Table 4-3).

Hydrogen sulfide is considered a hazard because of its presence in the process streams in concentrations approaching 0.5 percent by volume; at these levels, hydrogen sulfide can be an acute hazard in enclosed areas (e.g., a vessel) or in emergency situations involving major process leaks. Carbon monoxide, a major component of the product gas, is also an acute hazard in similar situations in gasification facilities.

Maintenance workers run a higher risk of being exposed to process materials than workers in other job categories at gasification facilities. Maintenance activities are related to work on on-line equipment such as breaking into process lines, repairing and removing process equipment, and entering vessels. Sampling at the three gasification facilities indicated that workers engaged in such activities had the highest exposures of all worker groups.

Work practices for maintenance activities by the gasification plants are: isolation of the system, draining the system of process material, and cleaning of the work site. Only Plant B had these three elements formalized in its safety manual. The other two plants reportedly follow these procedures, but they did not have written procedures available at the time of the surveys.

Plant operators generally performed the pre-maintenance activities of isolation, draining, and cleaning because they are more familiar than the maintenance crew with the process design and dismantling of equipment. This presumably transfers the risk of highest exposure to process materials from the maintenance crew to the operators; however, sampling results did not substantiate this. Protection of the operators can be accomplished by the use of safe work procedures for these three activities, by the use of a permit system to monitor these procedures, and by the use of personal protective equipment and clothing.

Isolation. In the isolation step, the flow of process material into the process segment being repaired is stopped by blanking-off all process lines entering and leaving the segment. Blanking-off of the process segment is accomplished by the use of valves, caps, or blinds. Valving is the simplest and most common technique; it involves the closing of valves on all lines entering and leaving the segment under repair. Valving is also the least reliable method of isolation because of the possibility of valve failure or accidental opening. Where valving is used as an isolation technique, its reliability has been improved by adding refinements such as mechanical

lockouts. Caps and blinds are more reliable because they involve the actual removal of a segment of piping, physically isolating the vessel or equipment from the rest of the process.

Draining and Flushing. Once the system is isolated, it is drained or flushed of process material to reduce the potential for skin contact with the process material during maintenance work. Drained solid or liquid materials are routed to receptacles such as covered containers or drains for disposal; vapor and gases are vented to the atmosphere or flared. Workers are required to open valves slowly in order to prevent an explosive ejection of the process material from lines or vessels under high temperatures. Where pressurized systems exist, bleed valves are used to reduce pressures to atmospheric levels. This procedure was observed at Plant C where emissions were vented by piping to areas away from the workers.

Cleaning. Cleaning operations are used to remove surface contamination, primarily coal tars, from work surfaces. Steam-cleaning is the most common method, and was observed in Plant B where coal tars are formed as a by-product of the operation. Plants A and C do not include cleaning operations as part of their pre-maintenance procedures because of negligible tar formation in the gasification processes.

Vessel Entry. Maintenance work involving vessel entry requires additional precautionary measures besides isolation, draining, and cleaning. It was observed that all the gasification facilities have vessel entry procedures which were patterned after NIOSH recommendations. These procedures follow the cleaning step and involve:

- . purging the vessel with air,
- . checking combustible gas and oxygen levels,
- . measuring concentrations of toxic gases, such as hydrogen sulfide and carbon monoxide, likely to be present, and
- . employing the buddy system, whereby one person fully equipped with the necessary protective clothing and equipment is stationed outside the vessel to provide assistance in an emergency.

## Housekeeping--

The technique most commonly employed is to conduct cleanup activities on an as-needed basis. Plant B has the assigned staff clean the process area on a daily basis; there is a daily schedule in which operators on all three shifts are allotted time at the end of their shift to clean their assigned area. This procedure permits the daily cleaning of all areas. The presence of an epoxy coating on the concrete floor (at one plant) facilitates cleaning by minimizing the absorption of tars by the concrete flooring.

Plants A and C have no special procedures for cleanup of spills because tars are not a by-product of their process. However, at Plant C the process area is cleaned by the operators at each plant shutdown period.

Steam-cleaning for the removal of tar deposits was observed only at Plant B where tar formation was a problem; it was used primarily to remove old tar deposits. Fresh tar spills were cleaned up using a clay absorbent and then scrubbing with soap and water. This technique has been proved to be effective at Plant B because of the epoxy coating mentioned earlier. Plants A and C, where tars are not produced, used only detergent and water in their cleaning operations.

## Administrative Controls

The gasification plants studied on this project do not consider administrative controls to be a major technique for controlling worker exposures, preferring the use of protective clothing and equipment and the use of safe work practices procedures. Where administrative controls are used, they serve as supplements to protective clothing/equipment and work practices requirements.

The most commonly used form of administrative control observed was barricading, whereby an individual's movement into a specific area is physically restricted by barriers. Entry to the area is allowed based on the



individual's training in recognizing and handling hazards within the area. In temporary situations where process upsets or the performance of specific activities such as repair can create hazardous conditions, colored barrier tapes are used to erect a temporary barrier to keep untrained personnel out of the particular area (Plant C).

In Plant C entry into the process area was prohibited during operations. This system is considered effective because a warning light was also used in combination with the entry restriction. The warning devices used at this facility included a flashing red light signifying that the gasifier was in operation, and a sign listing the precautions that must be taken to safely enter the area. The presence of these warning devices reinforces worker training by serving as a reminder of the safety requirements needed during the operation of the gasifier.

Plants B and C are designated as "limited access" areas. Visitors entering the facility are assumed to be untrained and unfamiliar with the plant safety measures. A sign-in/sign-out system is used in these plants to monitor visitors while they are in the facility. In this system, a visitor entering the facility must sign a logbook, noting time of arrival; upon departure, the visitor must sign out, logging his time of departure. While in the facility, visitors are provided with company escorts who are familiar with plant safety policies. This provides an effective means of keeping track of visitors and their location in the facility and ensures that visitors are not endangered by unknowingly violating safety procedures.

An unusual situation exists at Plant B, in which the gasification facility accounts for only a fraction of the people employed at the plant. Since there is some interchange of personnel between the gasification facility and other plant operations, a certification system has been developed to keep track of the training status of workers in relevant safety matters, such as respirator training. At Plant B, any company employee entering the gasification facility must present his certification card for review by the supervisor in charge of the gasification facility. If the worker does not have the requisite training, he is provided with an escort.

## 5. ANALYSIS AND DISCUSSION OF RESULTS

### POLYNUCLEAR AROMATIC HYDROCARBONS (PNAs)

PNA samples collected at each of the three gasification facilities were divided into area samples and personal samples. Personal samples were combined into two major worker groups, operators and maintenance. These worker groups were identified on the basis of job descriptions obtained at the individual plants and observations of the workers made at the time of the surveys. Group selections were made to ensure that the workers placed in each group had similar functions at all three facilities. The combined area samples for each plant represent the mean of all area samples collected at each of the plants except the plant perimeter samples which were taken to determine extra-plant sources of PNAs. For each of the four groups, the geometric mean (GM), geometric standard deviation (GSD), and 95% confidence limits have been determined (Table 5-1). When reviewing this data one should note that the sample set size ranged from 1 to 19.

In each of the three gasification plants, five major process areas were identified, and all samples collected in the respective areas were grouped for interplant comparison. Table 5-2 shows the mean value (GM) and confidence limits of the process areas.

Statistical comparison of the GMs for both intraplant and interplant groups were made utilizing the equation (Sokal and Rohlf, 1969; p. 374):

$$|t'_s| = \text{antilog} \left| \frac{\log GM_1 - \log GM_2}{\sqrt{\frac{\log S_1^2}{n_1} + \frac{\log S_2^2}{n_2}}} \right|$$

where "n" represents sample size. This equation assumes the variances ( $S^2$ ) of the groups are different. The  $t_s$  value is then compared with the  $t'$  value at  $P = 0.05$  obtained through extrapolation using the following equation:

$$t'_{.05} = \frac{t_{.05}[n_1-1] \left( \frac{S_1^2}{n_1} \right) + t_{.05}[n_2-1] \left( \frac{S_2^2}{n_2} \right)}{\frac{S_1}{n_1} + \frac{S_2}{n_2}}$$

where "n-1" represents the degree of freedom.

Table 5-1. Total PNA Concentrations for Area and Personal Sample Groups Collected at Three Coal Gasification Facilities

Group	Plant	N <sup>a</sup>	GM <sup>b</sup> ( $\mu\text{g}/\text{m}^3$ )	GSD <sup>c</sup>	LCL <sup>d</sup> ( $\mu\text{g}/\text{m}^3$ )	UCL <sup>e,g</sup> ( $\mu\text{g}/\text{m}^3$ )
Combined Area Samples	A	13	0.2	3.2	0.1	0.5
	B	19	26.8	2.2	18.3	39.1
	C	17	2.0	4.3	0.9	4.1
Operator (Personal Samples)	A	8	2.6	3.6	0.9	8.1
	B	4	19.3	1.5	9.7	38.4
	C	12	4.6	5.8	1.5	14.2
Maintenance (Personal Samples)	A	9	3.2	4.7	1.0	10.3
	B	8	55.1	3.0	21.4	141.5
	C	1	60.4	N/A <sup>f</sup>	N/A	N/A
Laboratory Technician (Personal Samples)	A	2	0.4	7.4	<0.2	1.7
	B	0	N/A	N/A	N/A	N/A
	C	0	N/A	N/A	N/A	N/A

<sup>a</sup>Number of samples collected.

<sup>b</sup>Geometric mean of concentrations.

<sup>c</sup>Geometric standard deviation.

<sup>d</sup>Lower 95% confidence limit of geometric mean.

<sup>e</sup>Upper 95% confidence limit of geometric mean. <sup>f</sup>N/A = not applicable.

<sup>g</sup>If n less than or equal to 3 then UCL = highest value.

Table 5-2. Total PNA Concentrations at Process Areas of Three Coal Gasification Plants

Plant	Process Area Sampled	N <sup>a</sup>	GM <sup>b</sup> (ug/m <sup>3</sup> )	GSD <sup>c</sup>	LCL <sup>d</sup> (ug/m <sup>3</sup> )	UCL <sup>e</sup> (ug/m <sup>3</sup> )
A	Gasifier	5	0.4	4.0	0.1	1.9
	Gas Cleanup	2	0.1	1.6	<0.1 <sup>f</sup>	11.5
	Clean Product Gas	4	0.2	3.2	<0.1	1.0
	Control Room	2	0.2	3.6	<0.1	0.6
	Total In-Plant	13	0.2	3.2	0.1	0.5
	Perimeter	2	0.3	4.7	<0.1	0.9
B	Gasifier	7	22.1	2.0	11.7	41.7
	Gas Cleanup	9	29.7	2.5	14.9	59.2
	Clean Product Gas	1	69.6	N/A <sup>g</sup>	N/A	N/A
	Control Room	2	20.5	1.8	0.1	31.3
	Total In-Plant	19	26.8	2.2	18.3	39.1
	Perimeter	2	1.8	4.7	<0.1	5.4
C	Gasifier	4	5.4	7.6	0.2	138.8
	Gas Cleanup	3	0.6	2.6	0.1	6.5
	Clean Product Gas	6	1.4	2.7	0.5	4.0
	Control Room	4	2.9	3.7	0.3	23.6
	Total In-Plant	17	2.0	4.3	0.9	4.1
	Perimeter	3	1.1	2.6	0.1	12.0

<sup>a</sup>Number of samples collected.

<sup>b</sup>Geometric mean of concentrations.

<sup>c</sup>Geometric standard deviation.

<sup>d</sup>Lower 95% confidence limit of geometric mean.

<sup>e</sup>Upper 95% confidence limit of geometric mean.

<sup>f</sup>"<" indicates below detection limit. <sup>g</sup>N/A = not applicable.

## Intraplant Analysis

### Plant A--

A comparison of the three job categories at Plant A (Figure 5-1) showed no significant difference in the means for the operators and maintenance workers ( $P > 0.05$ ).

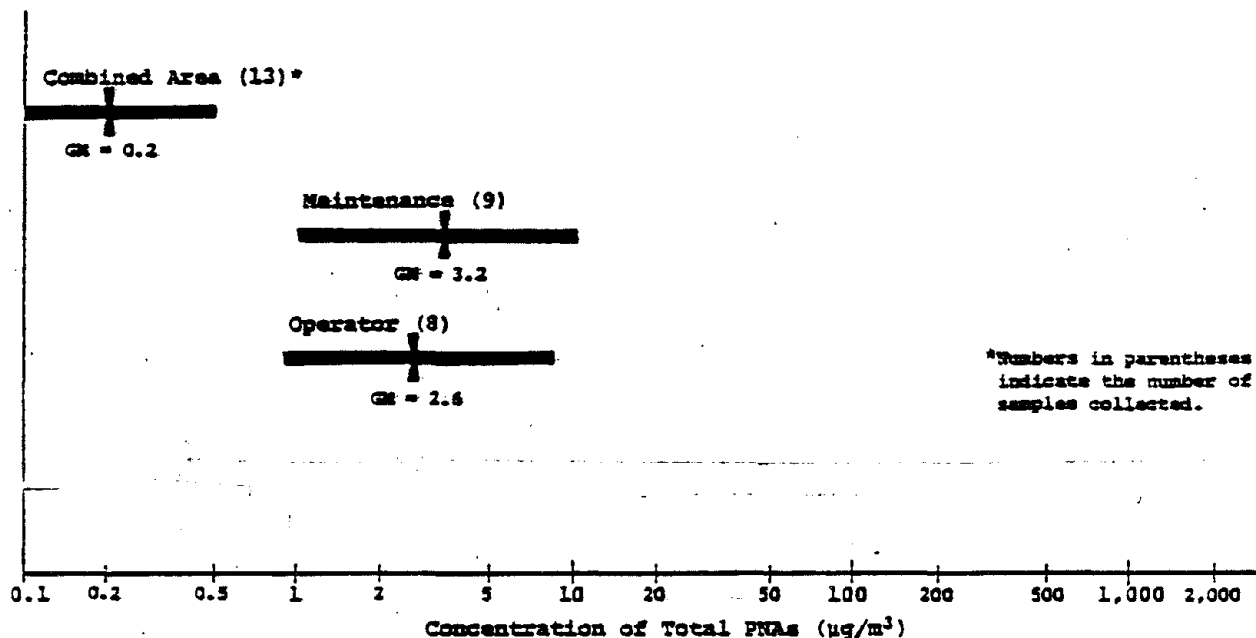


Figure 5-1. Geometric Mean PNA Concentrations with 95% Confidence Limits for Samples Collected at Plant A

This can probably be attributed to the sharing of duties which was the general practice at Plant A. Each group frequently assisted the other in repairing and cleaning the gasifier. The maintenance group ( $\text{GM} = 3.2 \text{ } \mu\text{g}/\text{m}^3$ ) and the operators ( $\text{GM} = 2.6 \text{ } \mu\text{g}/\text{m}^3$ ) were 15 times that of the combined area sample mean. Since sampling was carried out during repair and cleaning of the gasifier and other onstream process equipment which required dismantling of equipment and vessel entry, these activities rather than fugitive emissions appear to account for the higher PNA exposures. Exposure of laboratory

personnel was equivalent to that of the background PNA concentration, but the limited number of samples (2) and the wide divergence in the values do not permit clear evaluation of the laboratory personnel data.

A comparison of mean PNA concentrations of samples collected at each of the major unit operations at Plant A with those of the plant perimeter showed no significant differences (Table 5-2). Levels noted at each of the unit operations cannot be differentiated from background levels, indicating no significant emissions of PNAs by the process. The presence of a negative-pressure system and the up-and-down operational status of the plant are believed to be the two major contributing factors to this finding.

The significantly higher PNA levels recorded for the operators and maintenance workers must therefore be due to sources other than fugitive emissions from the gasification process. During the survey of Plant A, it was noted that when these workers were sampled they were repairing and cleaning the gasifier and other onstream process equipment. Their activities involved dismantling of the equipment and, in the case of the gasifier, entering the vessel. These activities may be responsible for the higher PNA values.

#### Plant B--

A comparison of the two worker groups at this plant with the area samples revealed no significant difference ( $P > 0.05$ ) between the operators ( $GM = 19.3 \mu\text{g}/\text{m}^3$ ) and the combined area samples ( $GM = 26.8 \mu\text{g}/\text{m}^3$ ) (Table 5-1; Figure 5-2).

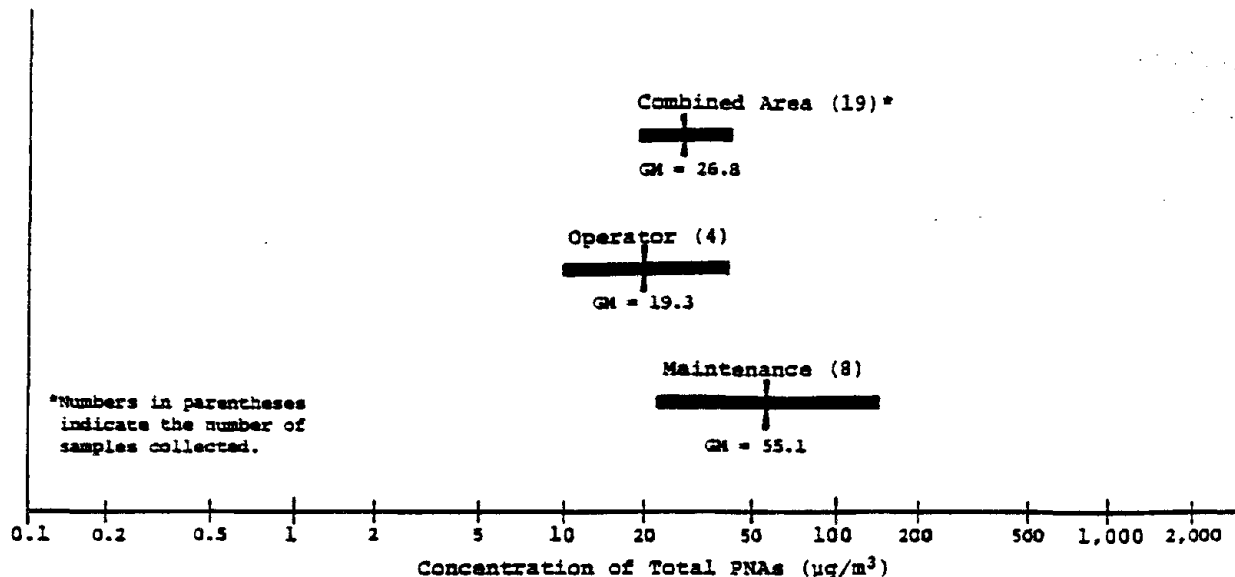


Figure 5-2. Geometric Mean PNA Concentrations with 95% Confidence Limits for Samples Taken at Plant B

The maintenance group, on the other hand, had a mean exposure of PNAs (GM =  $55.1 \mu\text{g}/\text{m}^3$ ) that was significantly higher ( $P < 0.05$ ) than that determined for the operators and the mean concentration of the area samples. The mean exposure of the maintenance group was about two times higher than either the operators or the area sample means. Since the operators and maintenance personnel work in the same general area, the difference in exposures appears to be due to the different specific activities performed by members of the two groups. From observations made at the time of the survey at Plant B, the key activities causing higher exposures of maintenance personnel are related to work on on-line equipment, especially that related to the tar-liquor separator system.

A significant difference ( $P < 0.01$ ) exists between the mean of PNA concentrations measured at the individual unit operations and the plant perimeter samples (Table 5-2); calculated GM values were 10 to 15 times those determined for the perimeter. No significant differences were noted between the individual unit operations ( $P > 0.05$ ). The complete enclosure of the gasification facility is considered the primary reason for the significantly high levels of PNAs measured relative to the background (perimeter) mean of  $1.8 \mu\text{g}/\text{m}^3$ .

The control room at Plant B has been enclosed and provided with its own air-conditioning system designed to maintain a positive-pressure environment to isolate it from the process area. Although the control room had an overall average PNA concentration ( $GM = 20.5 \mu\text{g}/\text{m}^3$ ) lower than the other three process areas (Table 5-2), the difference was not statistically significant. Although not conclusive from the data obtained, indications are that the system may not be effective in reducing PNA concentrations below general process area levels.

Area samples for PNAs taken at the gasification fire-bed-depth measurement ports indicate that this activity does not measurably contribute to the operators' overall level of exposure to PNAs. The absence of any appreciable contribution is an indication of the effectiveness of the present steam venturi system to control emissions from the port holes.

#### Plant C--

There was a significant difference ( $P < 0.001$ ) between mean PNA concentrations for operators ( $GM = 4.6 \mu\text{g}/\text{m}^3$ ) and for combined area samples ( $GM = 2.0 \mu\text{g}/\text{m}^3$ ), with the operators being 130% higher (Table 5-1; Figure 5-3). Comparison of operators with individual unit operations listed in Table 5-2 showed no significant difference ( $P > 0.05$ ) in the mean of the operator group and the samples collected at the gasifier. A significant difference was found between the operators and all other process areas ( $P < 0.05$ ), with operator levels ranging from 55% to 670% higher. No comparisons were made between the maintenance group and other groups because the single sample precluded any statistical analysis.

This plant had the only area samples which contained five ring PNAs. These samples were taken in an area containing coal fines. If coal fines were to accumulate in the sampling device, then the PNA analysis procedure could extract high molecular weight PNAs from these coal fines.



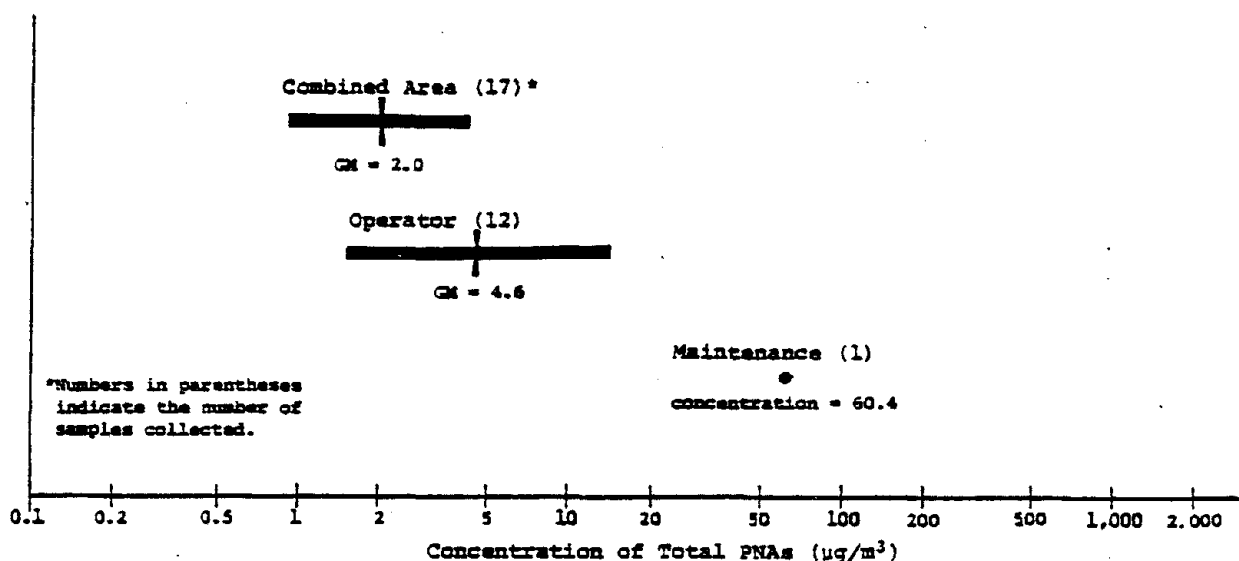


Figure 5-3. Geometric Mean PNA Concentrations with 95% Confidence Limits Geometric for Samples Taken at Plant C

Mean PNA concentrations of area samples collected at Plant C showed significant differences ( $P < 0.05$ ) among the four unit operations and perimeter samples (Table 5-2). The gasifier had the highest recorded mean PNA concentration ( $\text{GM} = 5.4 \mu\text{g}/\text{m}^3$ ) with the control room 40% lower at  $2.9 \mu\text{g}/\text{m}^3$ .

The perimeter level or background was 80% higher than the mean concentration for samples collected at the gas cleanup area ( $\text{GM} = 0.6 \mu\text{g}/\text{m}^3$ ). Variability of the sampling and analytical procedures probably account for this result. Indications are that the open structure of the gasification plant prevents accumulations of gaseous and vapor emissions.

The foregoing discussion showed the variability in personal exposures within individual plants based on differences in job activities and process areas. Higher exposures to PNAs were consistently found for employees, primarily

maintenance workers, engaged in activities which required them to work on, disassemble, or enter process equipment. As an example: Plant A had the lowest levels of PNAs in the process area of the three plants with an average area concentration of  $0.2 \mu\text{g}/\text{m}^3$  (GM). The higher average levels measured for operator and maintenance workers,  $2.6 \mu\text{g}/\text{m}^3$  and  $3.2 \mu\text{g}/\text{m}^3$  respectively, were markedly influenced by five samples (#034, #083, #013, #037, and #085, Table B-3, Appendix B) taken on plant employees engaged in activities which required "breaking into" process equipment. Although the concentrations of PNAs measured on these workers were low, they were significantly higher than the average of all other area or personal samples collected at Plant A.

Also serving to illustrate this point is an example from Plant B. The three highest personal exposure levels to PNAs were measured on employees directly involved in working on tar-contaminated process equipment or inspecting open vessels containing process stream materials (samples #1-020, 1-061, and 3-039, Table B-12, Appendix B).

#### Interplant Analysis

One objective of this study was to compare the different coal gasification processes in terms of the exposure potential of employees to PNAs. This would be used to identify those processes or unit operations which present a greater health risk.

Significant differences ( $P < 0.001$ ) exist in the mean PNA concentrations of combined area samples collected at the three facilities. The fixed-bed gasification unit (Plant B) had the highest level ( $\text{GM} = 26.8 \text{ ug}/\text{m}^3$ ) (Table 5-1; Figure 5-4). The average PNA concentration at Plant B was 13 times that recorded for Plant C which has a fluidized-bed gasifier ( $\text{GM} = 2.0 \text{ ug}/\text{m}^3$ ) and 130 times the concentration measured at Plant A ( $\text{GM} = 0.2 \text{ ug}/\text{m}^3$ ), an entrained-bed gasifier. The level at Plant C was 10 times that of Plant A.

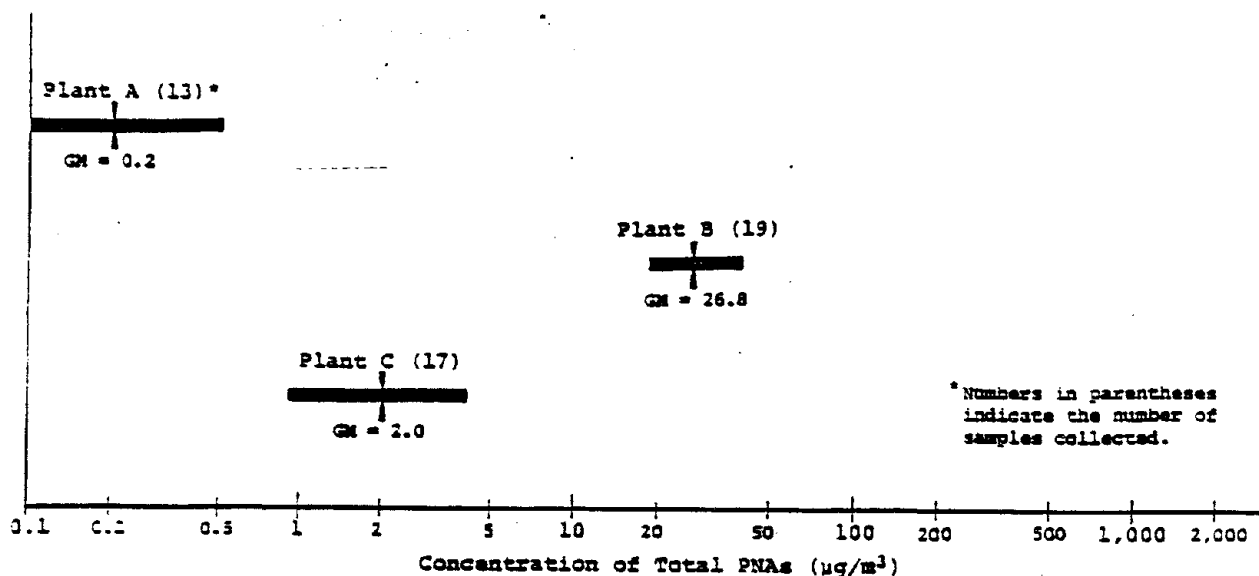


Figure 5-4. Geometric Mean PNA Concentrations with 95% Confidence Limits for Combined Area Samples at Three Gasification Plants

The highest PNA concentration at Plant B is partially attributable to the enclosed nature of the facility and partially to the low temperature (427°C, 800°F) of the product gas stream and the dynamics of fixed bed gasification processes in which tars distilled from coal near the top of the reaction bed are promptly carried out of the reactor in the fuel gas. Plants A and C have their gasification facilities in open structures which reduces the potential for accumulation of process emissions.

The low gasification temperature used at Plant B to form the top gas product stream favors PNA formation. Conversely, the high gasification temperature (982°C, 1,800°F) used at Plants A and C presents an unfavorable environment for PNA formation. As a result, tars are a major by-product of Plant B requiring the presence of special tar cleanup and handling systems.

High operating temperature, which precludes tar formation, and operating the system under negative pressure are both contributing factors to the low PNA values recorded at Plant A.

Comparisons of PNA levels measured for personal samples showed generally the same pattern as the area samples. Figures 5-5 and 5-6 show the mean (GM) of

samples collected on operators and maintenance personnel at the three plants except for Plant C where only one maintenance person was sampled.

#### Operators--

The mean value of PNA exposures of the operators at the three facilities differed significantly ( $P < 0.001$ ) from one another. Plant B operators had the highest recorded mean value ( $GM = 19.3 \mu\text{g}/\text{m}^3$ ). This exposure level was four times that recorded at Plant C ( $GM = 4.6 \mu\text{g}/\text{m}^3$ ) and more than seven times that at Plant A ( $GM = 2.6 \mu\text{g}/\text{m}^3$ ). The GM of Plant C operators was 75% higher than that calculated for operators at Plant A.

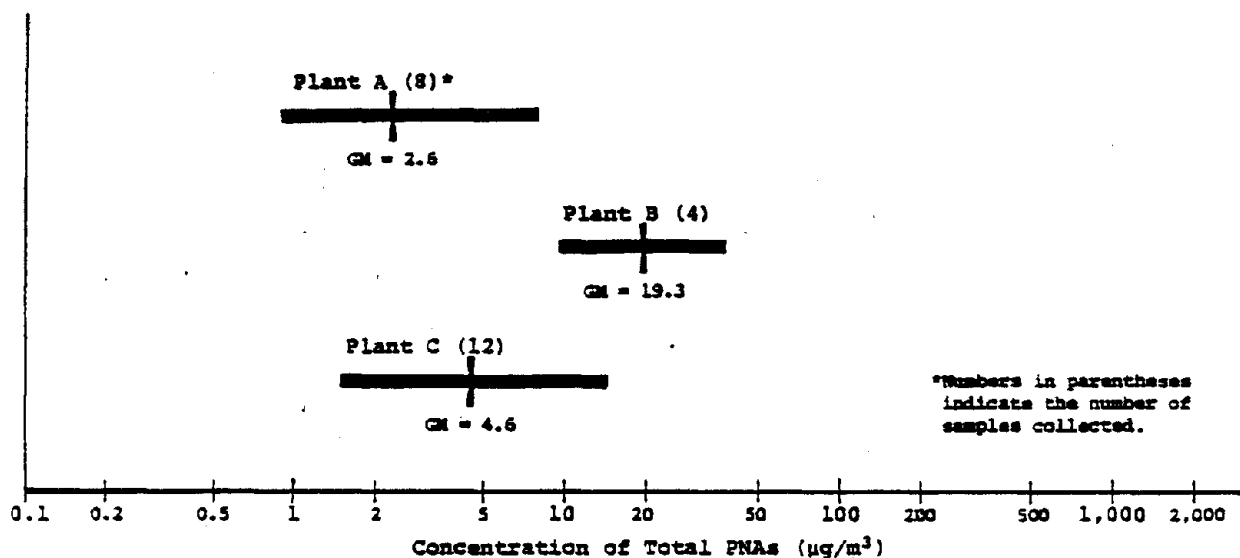


Figure 5-5. Geometric Mean PNA Concentrations with 95% Confidence Limits for Operators at Three Gasification Plants

#### Maintenance--

A significant difference ( $P < 0.001$ ) exists for the maintenance personnel at Plant A and Plant B, with Plant B having PNA levels 20 times higher. Since the maintenance operations at these facilities are similar, the differences in exposures can be considered a reflection of differences in the work environments of these facilities. The two major differences in the work environments

are the presence of an enclosed structure at Plant B versus an open structure at Plant A, and the higher tar production of the Plant B process relative to Plant A.

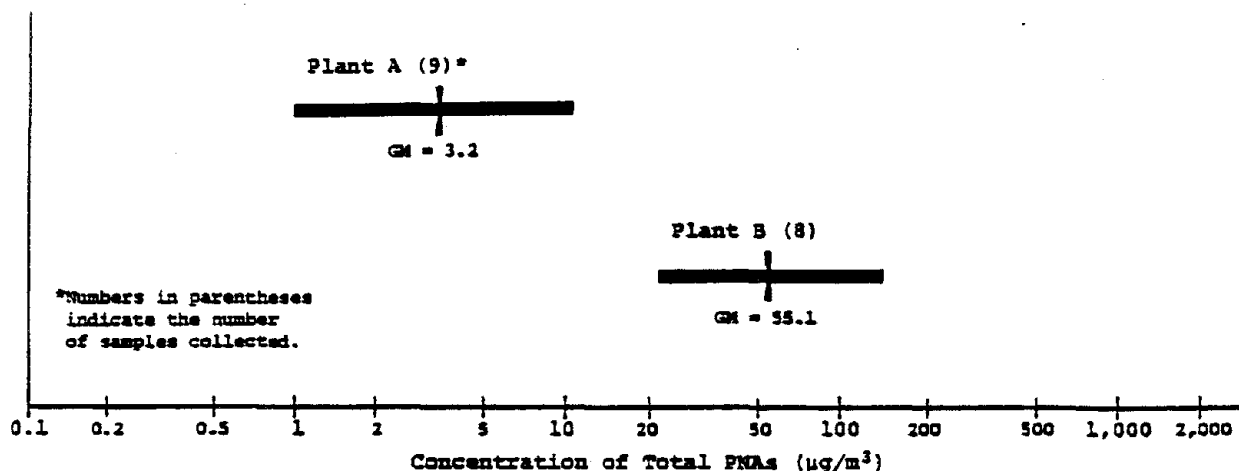


Figure 5-6. Geometric Mean PNA Concentrations with 95% Confidence Limits for Maintenance Workers in Two Gasification Plants

The ranking of the three facilities by PNA exposure was the same for operators and maintenance personnel as for area samples. Results indicate that workers in Plant B had higher exposures to PNAs relative to their counterparts in the other plants; Plant A workers had the lowest exposures.

Table 5-3 represents the GM and 95% confidence limits for the five major unit processes common to each of the plants. The data for these five groups were obtained by pooling sampling results for similar operations from all three facilities. Analysis showed no significant differences ( $P > 0.05$ ) between the means of the gasifier and the gas cleanup system, and between the means of the product gas areas and perimeter area samples.

Table 5-3. Combined Unit Operation Total PNA Concentration  
for Three Coal Gasification Plants

Process Area Sampled	N <sup>a</sup>	GM <sup>b</sup> ( $\mu\text{g}/\text{m}^3$ )	GSD <sup>c</sup>	LCL <sup>d</sup> ( $\mu\text{g}/\text{m}^3$ )	UCL <sup>e</sup> ( $\mu\text{g}/\text{m}^3$ )
Gasifier	16	4.3	8.9	1.4	13.1
Gas Cleanup	14	4.5	2.7	1.2	16.4
Clean Product Gas System	11	0.9	7.6	0.2	3.5
Control Room	8	2.5	7.1	0.5	13.4
Perimeter	7	0.9	3.7	0.3	2.8

<sup>a</sup>Number of samples collected.

<sup>b</sup>Geometric mean of concentrations.

<sup>c</sup>Geometric standard deviation.

<sup>d</sup>Lower 95% confidence limit of geometric mean.

<sup>e</sup>Upper 95% confidence limit of geometric mean.

The gasifier (GM =  $4.3 \mu\text{g}/\text{m}^3$ ) and gas cleanup system (GM =  $4.5 \mu\text{g}/\text{m}^3$ ) had the highest values and appear to represent the major sources of PNAs within the three facilities. Control rooms (GM =  $2.5 \mu\text{g}/\text{m}^3$ ) were significantly lower ( $P < 0.01$ ) than the gasifier value. The clean product gas systems (GM =  $0.9 \mu\text{g}/\text{m}^3$ ) and perimeter samples (GM =  $0.9 \mu\text{g}/\text{m}^3$ ) had the lowest PNA concentrations.

In order to provide a point of reference in the evaluation of employee exposures to airborne particulates and vapor phase PNAs in the three coal gasification plants, the results of the personal sampling conducted in this study are compared in Figure 5-7 with the similar sampling programs conducted in five coal liquefaction plants (Cubit and Tanita, 1982) and the delayed coker units and fluid catalytic cracker units (FCCUs) in nine petroleum refineries (Futagaki, 1981). The graphs represent the combined personal sampling data taken at each of the installations, using identical sampling and analytical methods.

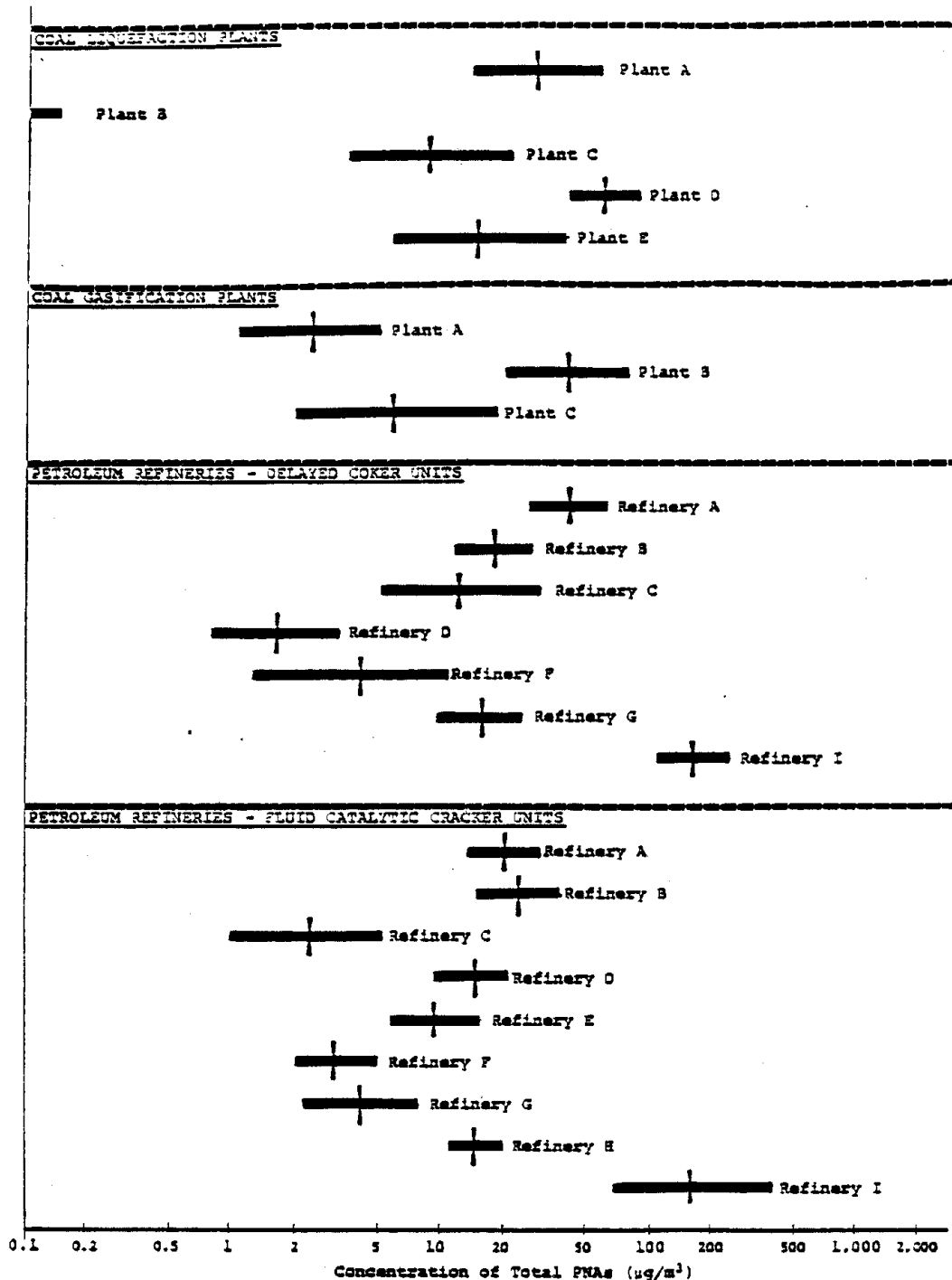


Figure 5-7. Geometric Mean PNA Concentrations with 95% Confidence Limits for Personal Samples Collected at Coal Liquefaction and Coal Gasification Plants, and Petroleum Refineries

In general, gasification plants A and C had lower mean exposure to PNAs for all groups of workers sampled than most of the refinery or coal liquefaction plant workers. Plant B, the only significant tar producer, had mean exposure levels approximately equal to the levels measured in the delayed coker units and the FCCUs.

Caution must be exercised when comparing the gasification plants with the petroleum refinery environment. Two plants, A and C, were pilot test plants constructed to test various processes, operating conditions, and equipment. Only Plant B was a commercial facility designed to operate continuously with minimal modification and maintenance. Test plants by their nature are subject to short operational runs and frequent maintenance and process modifications. This is in contrast to the more or less continual operational status of refineries where maintenance is on an as needed basis. Since maintenance activities were shown to be the primary source of exposure to PNAs in all gasification plants, it may be expected that operational gasifiers not producing little tar would minimize this.

Contamination of process equipment, tools, and clothing with PNAs was detected through the collection and qualitative analysis of 41 wipe samples. Of these samples, 36 or 88% contained at least one PNA. With few exceptions these PNAs were found on all process tools and equipment. In addition, six or seven random samples taken from the control room, lunchroom, and locker-room of these plants were also positive for these compounds (Table 4-3).

Wipe samples taken from gloves, trousers, and coveralls detected PNA contamination of these items. Proper rubber glove selection and use will delay the penetration of PNAs from minutes to hours. Cotton gloves and coveralls are much less effective barriers, especially when the contaminated garment or glove material is rubbed against the skin.

The strongly suspected carcinogens phenanthrene and anthracene (coelutents) appeared to serve as a reliable indicator of the presense of PNAs and of high molecular weight PNAs in these wipe samples. They were present in 32 or 78% of all samples and 84% of the positive samples. More importantly,



phenanthrene/anthracene was present in all but two samples in which PNAs with greater than two rings were found. In these two exceptions, the equivocal carcinogen pyrene (4-rings) and pyrene plus naphthalene were present alone.

#### AROMATIC AMINES AND SIMPLE AROMATIC COMPOUNDS

Aromatic amine sampling was compromised by the use of silica gel sorbents under conditions of high humidity. Area samples were collected for analysis of up to eight aromatic amines (Table 4-4). In most cases no detectable levels ( $0.01 \text{ mg/M}^3$ ) of these compounds were found. Maximum concentration of aromatic amines measured in the area samples did not exceed  $0.1 \text{ ug/m}^3$  in any of the gasification plants (Table 4-4). The sampling method, however, used silica gel during high humidity conditions ( $> 75\%$ ); thus, these results may be in error.

The highest measured concentration of benzene in a personal sample was 0.1 ppm (Table 4-5), collected on a maintenance worker at Plant C. The highest concentration of benzene in an area sample (Table 4-6) was 8.2 ppm taken at the gas filter, also at Plant C. All measurements for toluene and xylene were well below 0.1 ppm in both area and personal samples.

#### HYDROGEN SULFIDE AND CARBON MONOXIDE

Hydrogen sulfide and carbon monoxide were detected sporadically at Plants B and C. Plant A, because of the negative pressure systems, appeared to be free of detectable emissions of the gases. However, maintenance operations occurring when the plant is down and when entry into the normally closed process system is required could create conditions where workers may be exposed to the gases. Plant B has experienced frequent incidents in which CO concentration in certain areas exceeded 50 ppm and activated the alarm system. Measurements made in this study (Table 4-7) showed basically the same pattern of intermittent emission of CO with the highest concentrations measured near the de-oilers and detarring units. Average overall plant levels did not exceed 5 ppm with the highest concentration, measured at Plant B, being 50 ppm. No significant levels of  $\text{H}_2\text{S}$  were found at Plant B.

Plant C has had on past occasions significant incidents of  $H_2S$  and CO exposures. Concentrations up to 1,745 ppm of CO were measured at the filter unit (Table 4-7) during changing of filters. The reported incidents of employees being overcome by CO during this operation show there is a CO hazard in this one particular area. The same area was also the source of the highest measured concentration of  $H_2S$  (120 ppm and 160 ppm) on two separate occasions. Procedures for entry have been instituted to reduce the probability of exposure in this area.

#### MEDICAL AND INDUSTRIAL HYGIENE PROGRAMS

The Industrial Hygiene/Occupational Medicine Programs of the coal gasification pilot plants in this study have been developed to minimize the risks of fire, accidents, explosions, and exposure to toxic chemicals. Programs to minimize the first three hazards are modeled after occupational programs in related industries and they comply with industrial standards and mandatory requirements. Unique programs to minimize exposure to toxic chemicals in the coal gasification environment are nonexistent in one plant and rudimentary in the other two; however, one plant is rapidly improving its program.

The personal hygiene measures discussed in the Results Chapter provide some degree of protection from pollutants; however, the following deficiencies have been identified:

- . failure to identify optimal materials for protective clothing manufacture
- . lack of guidelines for discarding nonlaunderable, contaminated clothing including shoes, boots, gloves, slickers
- . lack of provision for decontamination before meals
- . lack of a program for routinely determining the effectiveness of the personal hygiene program by checking for residual contamination of personnel after showers and of clothing after laundering, drycleaning, etc.
- . lack of effective dirty/clean separation in shower and locker room facilities.

Educational programs generally depend upon initial and continuing verbal instruction from plant supervisors supplemented by written and audiovisual aids. Such a format provides information and instruction to regular plant employees. However, an active program to include all plant maintenance workers employed by outside contractors needs to be developed in the coal gasification plants. Only in this way will this high-exposure group of workers be kept continuously aware of the potential hazards and special work practices associated with coal conversion.

Medical surveillance observed in coal gasification plants is patterned after routine screening programs in other industries. Most programs include a pre-employment physical, annual checkups, and a termination physical. Because many industrial exposures, including those in coal conversion plants, are to multiple chemicals whose toxic effects cannot always be predicted, a more complete screening program should include in part more specific heart and lung tests (EKG, and FVC and FEV<sub>1</sub> pulmonary function tests), as well as a standardized battery of serum chemistry tests which can detect a broad spectrum of organ dysfunctions, often before other signs and symptoms of disease become apparent.

For the coal conversion industry, this "routine" screening program may not be adequate to protect the health of the worker. Preliminary epidemiologic and toxicologic testing data have indicated an increased risk of cancer to multiple organs from chronic exposure to some coal-derived materials. Furthermore, these studies have pinpointed the skin, lungs, and urinary tract as organs at special risk from such exposure. For this reason, more extensive examination of these target organs should be included. Two plants provide special skin examinations for the detection of skin pathology.

No epidemiological programs are under way in any of the coal gasification plants.

Industrial hygiene monitoring programs have been developed to protect against hazardous gases such as  $H_2S$ , CO, and ammonia. The programs also monitor benzene solubles for compliance with coal tar pitch volatile guidelines. Little monitoring of specific polynuclear aromatic hydrocarbon compounds and none for polyaromatic amines suspected of causing cancer has been included in any of these programs.



## 6. CONCLUSIONS

Coal gasification plants were shown to be sources of worker exposure to PNAs. Although levels measured were relatively low when compared to other industries such as coal liquefaction plants and the fluid catalytic cracking units and delayed coking units in petroleum refineries, measurable levels of PNAs were found in all three of the plants studied. The major PNAs present were naphthalene and its methyl derivatives. Air sampling data showed almost no 4- and 5-ring PNAs present as particulate or vapor, hence inhalation exposure to PNAs presently known to be carcinogens does not appear to present a significant hazard in the plants, under the conditions monitored. Potential for dermal exposure to 4- and 5- ring PNAs was demonstrated.

Concentrations of PNAs found in area and personal samples varied with plant design and operating conditions. Fluidized- and entrained-bed high-temperature gasifiers had significantly lower PNA emissions than the fixed bed process. The negative-pressure systems in Plant A may have been a factor in the reduced PNA emissions. Enclosure of the entire process area for Plant B may have concentrated or inhibited diffusion of plant emissions.

PNA personal exposure levels varied with employee activities. Maintenance activities involving breaking into process equipment or handling tar-contaminated equipment resulted in higher exposures to airborne PNA concentrations. Routine plant operator activities did not result in PNA exposures comparable to maintenance operations. Mean operator levels of exposure were generally lower than the mean of area samples.

Dermal contact with process liquids is a significant source of potential PNA exposure in all three gasification plants. This exposure is not easily quantifiable but represents a significant hazard particularly at gasification plants which produce large volumes of coal-derived tars.

Aggressive equipment cleaning and decontamination programs combined with appropriate personal protective equipment and personal hygiene programs are necessary to reduce the dermal exposure risk. Since there is no standard method for assessing this risk, the effectiveness of programs is difficult to estimate. Visual inspection of equipment or clothing surfaces is not a reliable indicator of PNA contamination.

Employee exposure to simple non-substituted aromatic hydrocarbons resulting from plant emissions of benzene, toluene, and xylene does not appear to constitute a significant health hazard in the three coal gasification plants studied. Samples collected for these groups of chemicals rarely showed measureable concentrations. Sampling of phenolics and aromatic amines was compromised by the use of silica gel sampling media under environmental conditions of high humidity. No phenolic compounds (detection limit 0.2 mg/m<sup>3</sup>) were found, and only occasionally were any aromatic amines found at the three plants surveyed. These findings, however, are questionable, since the sampling medium is highly inefficient in high humidity environments, and humidity was high during all of the surveys. In fixed-bed gasification systems concentrations of these compounds in certain process streams may be as high as parts per thousand. Thus, one should use caution in suggesting that the data to date shows no exposure to these two classes of compounds.

Acute exposure to high levels of CO and H<sub>2</sub>S is an observed hazard in coal gasification plants. Emission of these gases and their subsequent concentration in confined areas require application of controls, alarm systems, and safe work procedures to eliminate their risk to employees engaged in maintenance and routine operational activities.

The medical surveillance programs established by the plants reflect their awareness of the occupational hazards associated with the facilities. Although no standard medical surveillance or battery of tests has been widely accepted for these types of facilities, each of the plants has based its program on those recommended in the NIOSH Criteria for Recommended Standard...Occupational Exposures in Coal Gasification Plant and its corporate medical officers' recommendations.

This report did not address exposures to other substituted PNAs (oxygenated, nitro, etc.), organo-cynates/nitriles and other chemical classes inherent to some gasification process streams. These chemicals are of toxicological concern, but were not included in this study.





## 7. RECOMMENDATIONS

Through the experience gained in these studies, several needs for improved data or for improved capabilities for the development of data have manifested themselves to contractor or NIOSH personnel. A partial listing follows:

- o Better data is needed on airborne phenolic and aromatic amine levels in coal gasification plants.
- o More detailed guidance should be provided for medical surveillance and industrial hygiene characterization efforts by plant management.
- o Additional toxicology studies should be conducted to assess the occupational health hazard of long-term inhalation exposure to low levels of 2-, 3-, and 4-ring PNAs.
- o Standardized sampling methods should be developed for assessing the workplace dermal and airborne exposure factor to PNAs; this should be related to health effects information when possible.
- o Methods should be developed for cleaning or decontaminating equipment and protective clothing of coal tar residues.
- o Additional studies should be conducted on the permeability and protection factor for PNAs afforded by various materials used in protective clothing, particularly gloves.
- o A PNA indexing system for selection of "proxy" PNAs for assessment of total PNA exposures needs to be developed. This method should be able to utilize analytical instrumentation other than mass spectrometry because of its high cost and inherent variability.

- o The feasibility of organic vapor sampling badges for light weight (2-, 3-ring) PNAs should be investigated.
- o Standarized medical protocols that will best identify early disease etiology and be of value to epidemiology studies need to be developed.
- o Clean and dirty change rooms and eating areas need to be provided at all coal gasification facilities.
- o Sampling and analytical methods need to be developed for several classes of compounds: substituted PNAs, aromatic/aliphatic amines, and other classes of chemicals of unique toxiological importance to coal gasification facilities.
- o Studies concerning the synergism effects of the multiple-chemical classes of exposures need to be implemented.

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**APPENDIX A**  
**PROCESS DESCRIPTIONS OF COAL GASIFICATION PLANTS**

# PROCESS DEVELOPMENT UNIT (PDU)

## PLANT A

### PDU GASIFICATION PROCESS

The Process Development Unit (PDU) Plant A is an entrained-bed gasifier which produces a low-Btu product gas. The process is shown schematically in Figure A-1, and Table A-1 identifies the major process areas of the PDU.

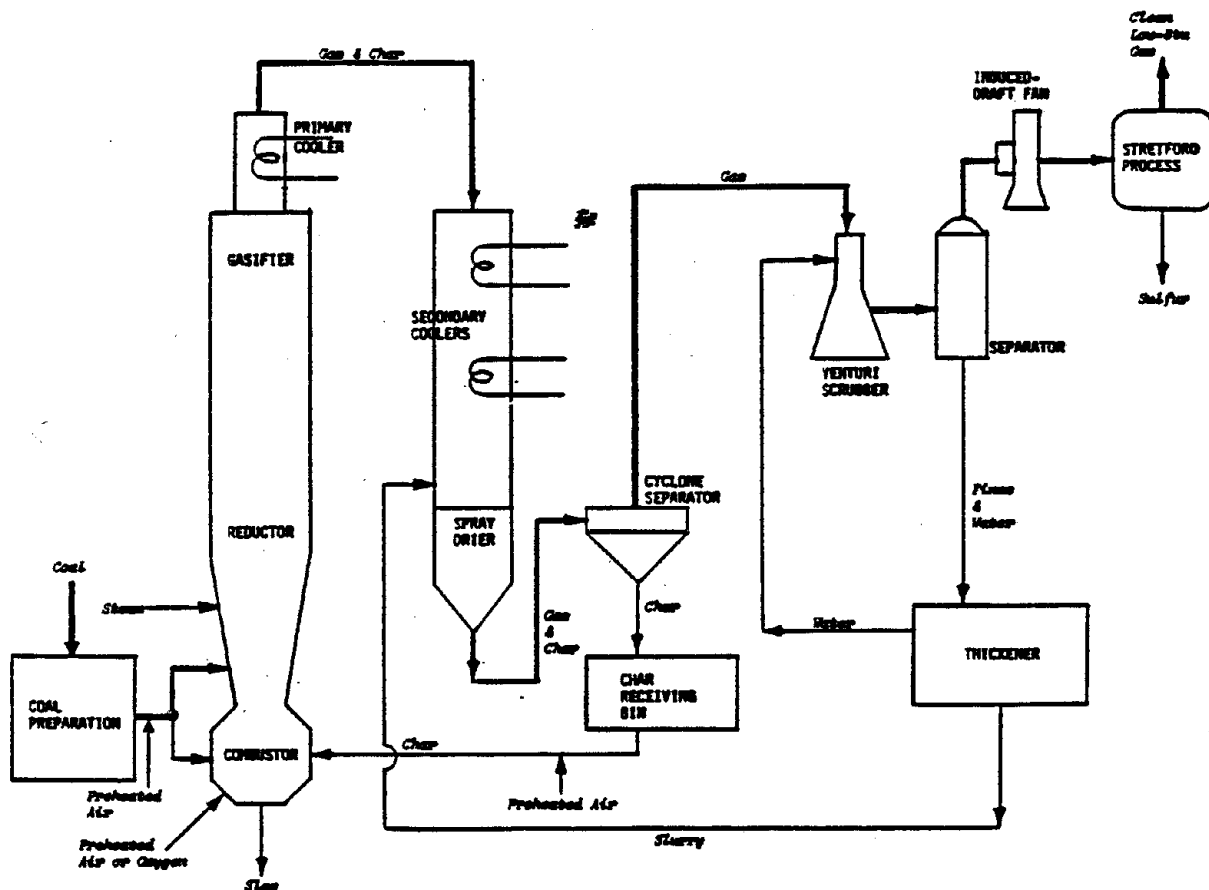


Figure A-1. Plant A Process Schematic (adapted from "Coal Gasification," Quarterly Report, January-March 1979, DOE/ET-0067, U.S. Department of Energy, Division of Coal Conversion)

Table A-1. Numerical Identification System for Unit Operations:  
Plant A

Identification Number	Process Area
100	Coal unloading and storage
200	Coal preparation — includes pulverizer and bag filters
300	Gasifier — includes induced heat removal
400	Ash handling — includes dewatering bin
500	Gas cleanup — includes spray dryer, cyclone, scrubber, sludge thickener
600	Char recycle — includes char receiving bin
700	Sulfur removal and disposal — includes Stretford units
800	Product gas incinerator
900	Plant utilities and general services

Coal is stored offsite in a 10,000-ton contract storage facility and trucked as needed to the PDU. Process Unit 100 of the PDU encompasses unloading and storage of coal. It consists of an unloading hopper, transfer belt, bucket elevator, screw conveyor at the top of the bucket elevator, and a 400-ton coal storage silo. A gravity feed system transfers the coal from the unloading hopper to a sublevel belt conveyor for transport to a bucket elevator, and subsequently to the elevated 400-ton storage silo located on the upper levels of the PDU structure. Water sprayers around the hopper are used to control dust in the unloading area, and the coal storage silo is provided with a small baghouse filter to minimize fugitive dust emissions.

Process Unit 200 is comprised of the coal pulverizing, drying, and feeding equipment. To provide experimental flexibility, the PDU gasifier is not direct-fired by the pulverizer as a commercial-size gasifier would be; the PDU uses an indirectly fired or bin-supplied firing system. This system consists of a small bowl mill under the coal storage silo; a 20-ton pulverized coal storage bin; a cyclone separator; recirculation and vent fans; a bag filter on the system vent; a hot flue gas supply duct from the



plant boiler; interconnecting duct work for the closed-loop pulverizing system; four pulverized coal feeders; two primary air fans; and the primary air and transport piping to the combustor wind boxes and reductor fuel nozzles.

Coal is gravity-fed from the storage silo to the bowl mill located on the ground level where it is pulverized and dried. A transport gas with less than 10 percent oxygen is used to convey the pulverized coal to a cyclone, where the coal is separated from the transport gas stream and gravity-fed to the 20-ton storage bin. The transport gas stream exiting the cyclone is partitioned, with one portion being recycled to the pulverizer and the other portion vented through baghouse filters to the atmosphere. Transport makeup gas is provided by flue gas from the PDU boiler. The flue gas with an oxygen level less than 10 percent by volume is used to control the explosion and fire hazards associated with the handling of coal fines.

The coal is transported from the storage bin to the gasifier using two separate feed systems: one feed system conveys one-third of the coal to the combustor where the coal is burned in the presence of either preheated air or oxygen; the other feed system transports the remaining two-thirds of the coal to the reductor. The system is arranged so that various combinations of burners and fuel nozzles in the gasifier can be fired.

Process Unit 300 is the gasifier itself. The PDU gasifier is approximately 90 feet tall and 11 feet in internal diameter. Temperatures inside the gasifier are high, ranging from a maximum of 1,724°C (3,200°F) in the combustion zone (combustor) to a minimum of 927°C (1,700°F) where the product gas exits the gasifier at the reductor outlet. Approximately one-third of the coal is fired in the gasifier combustor and the remaining two-thirds in the lower portion of the reductor called the diffuser. Construction of the gasifier walls is substantially the same as for commercial-size designs except that the inside of the gasifier is refractory lined.

A gastight, fusion-welded wall of 1-1/2-inch-thick steel, cased on the outside for thermal efficiency and personnel protection, comprises the main portion of the gasifier. The gasifier is airblown and operates slightly below atmospheric pressure (-1/2" water column at the reductor outlet).

The hot gases generated in the combustor provide the heat required for the endothermic reaction occurring in the reductor where coal is distilled and incompletely oxidized in the presence of steam to form the product gas. A product gas of higher Btu rating may be produced using oxygen instead of preheated air in the combustor.

The product gas exits at the top of the gasifier at a temperature of 927°C (1,700°F). The gas is cooled by a primary cooler to 450°C (842°F) and by secondary coolers to 150°C (302°F) before it enters the gas cleanup process.

The high combustor temperature produces a slagged ash which passes through a taphole located at the bottom of the combustor to collect and cool in a quench tank.

Process Unit 400 is the slagged ash handling system; it consists of conventional equipment of the same type supplied to commercial coal-fired utility power plants. The equipment consists of a refractory-lined slag tank located beneath the combustor taphole, a crusher, a slurry pump, an ash dewatering bin, and a cooling and low- and high-pressure circulating water pump and necessary interconnecting piping. The slagged ash from the combustor collects in an ash hopper, and is dumped when necessary into a dewatering bin. The dewatered slag is periodically disposed of by landfilling.

Process Unit 500 is the gas cleanup system which removes unburned carbon (char) and fly ash present in the product gas stream. The char is collected and refired into the combustor. Major equipment in this unit are a spray dryer, two cyclone collectors, a venturi scrubber and thickener, and necessary interconnecting piping and duct work.

The product gas is cleaned in the spray dryer using a slurry of organic sludge and water.

From the dryer, the product gas enters a cyclone separator where entrained particulates and char are removed. These particulates collect in the char receiving bin and are recycled to the combustor for burning.

Char passing through the cyclone separator is removed by a venturi scrubber and separator. The suspended particulates collect in the sludge thickener where they settle to the bottom. Water is removed at the top of the thickener and recycled to the venturi scrubber; the slurry at the bottom of the thickener is recycled to the spray dryer. The product gas exiting the separator enters the induced-draft fan at a pressure of minus 35 inches of water.

Process Unit 600 is the char storage and feeder system. It consists of a 20-ton storage bin, two auger-type gravimetric feeders, a char air fan, and the primary air and char transport piping to the combustor wind boxes. The normal mode of operation is that all char collected during operation of the gasifier is continuously recycled to and consumed in the combustor. The char bin and feed lines to the combustor are under a nitrogen blanket to control potential fire and explosion hazards even though the char is not considered reactive.

Process Unit 700 is the sulfur removal and disposal portion of the PDU. Included in this process unit are a combination  $H_2S$  absorber/reaction tank through which product gas flows countercurrent to the Stretford scrubbing solution; an oxidizer tank in which reacted Stretford solution is sparged with air to float elemental sulfur floc; a slurry tank; a rotary vacuum filter to wash and dewater the sulfur; and finally a sulfur storage hopper. Only the Stretford absorber vessel is part of the product gas duct work system, since the other equipment is "stand-alone, closed loop."

The clean product gas is burned in the PDU incinerator/boiler. The flue gas is recycled as makeup gas for the transport gas system which moves coal from the pulverizer to the cyclone.

Process Unit 800, the product gas incinerator, is the last process unit in the PDU. The incinerator/boiler is equipped to fire No. 2 fuel oil as an auxiliary fuel in order to start up and shut down the plant. It is also used to burn the product gas, produce steam for heat-tracing and inerting, and preheating secondary and primary air.

#### DESCRIPTION OF FACILITY

The gasification PDU is housed in an open, multi-story structure. The individual unit operations and associated equipment are identified in Figure A-2.

The unit operations are in close proximity to one another, making it difficult to delineate the boundaries of individual unit operations. The proximity of the unit operations probably caused some degree of cross-contamination during sampling, which creates uncertainties in evaluating and characterizing the contribution of each unit operation to the contaminant levels of the workplace environment. Under these circumstances, sampling was geared to specific equipment and plant areas expected to be associated with highest levels of emissions.

The ground level of the process structure is covered with gravel. Individual equipment located on this level is set on concrete blocks. Wet and caked coal dust and debris were evident at the ground and upper levels. Outside equipment and work surfaces in the PDU were coated with coal dust. This problem was most prominent on the ground level, east of the incinerator, where up to 4 inches of coal dust was on the ground. This dust leaked from the coal preparation area.

A combination of 18-gauge aluminized steel-ribbed and ribbed translucent panels are installed on the north, east, and west faces of the PDU structure. The installation of siding was designed to protect both equipment and operating personnel to a practical extent from adverse winter weather.

On each of the three faces, siding is installed only up to that elevation where rain and cold winds have inhibited work or presented problems with freezing. Above this level, isolated areas wherein freezing problems have occurred are being addressed individually. Except on the east side, siding does not begin at ground level but at the first elevation (approximately 12 feet above ground) to permit access by working personnel and equipment around the perimeter of the plant.

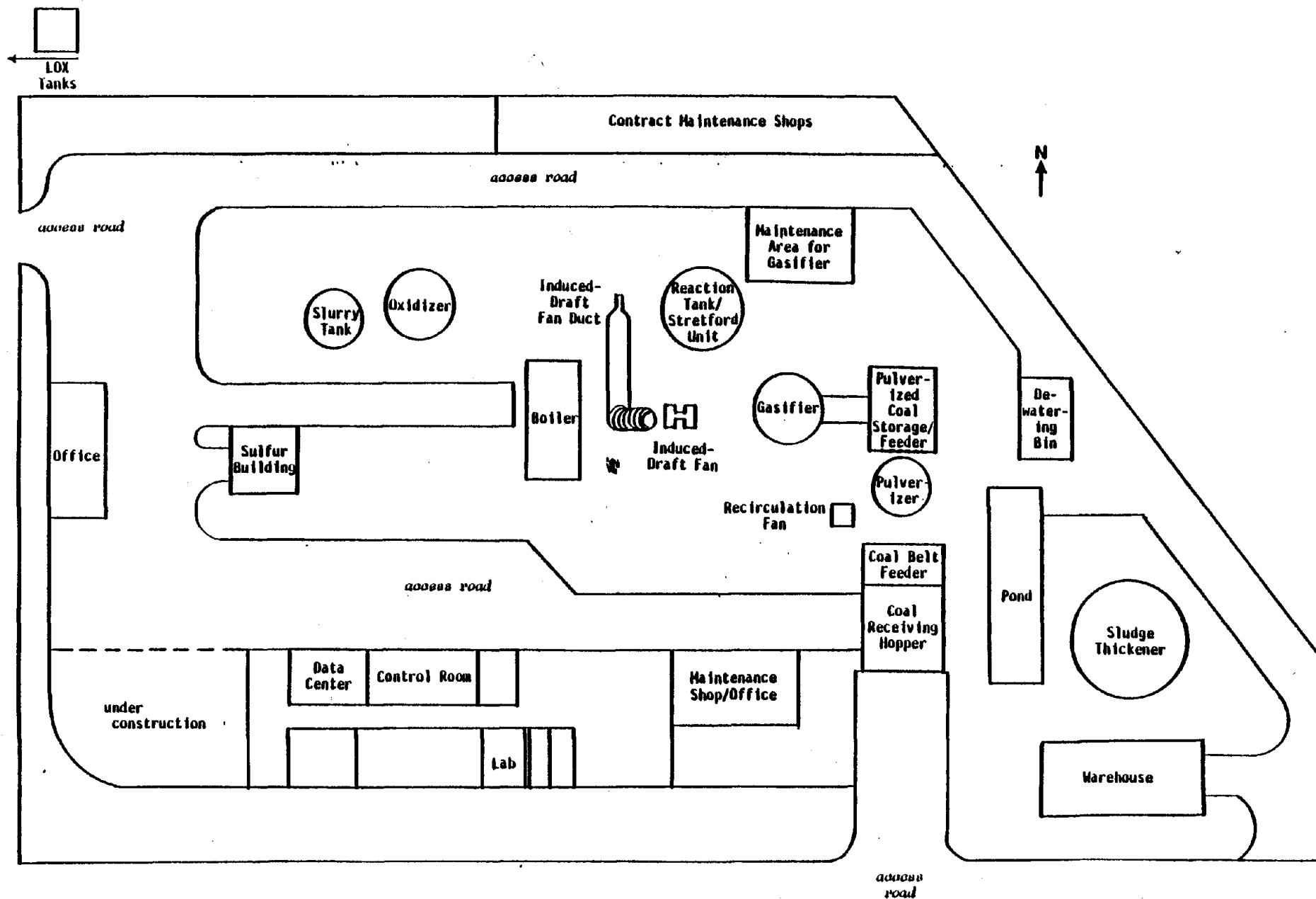


Figure A-2. Plant A Plant Layout (not to scale)

# COAL GASIFICATION PLANT DESCRIPTION

## PLANT B

### PROCESS DESCRIPTION

This two-stage, fixed-bed gasification plant utilizes two sets of gasifiers for production of low-Btu gas which is used in a manufacturing process. The gasifiers and product gas cleanup systems are shown schematically in Figure A-3. At the time of the survey, only one gasifier and cleanup system was in operation. This single unit produced the necessary synfuel gas for plant needs. Each gasifier has a designed coal feed capacity of 65 tons of coal per day.

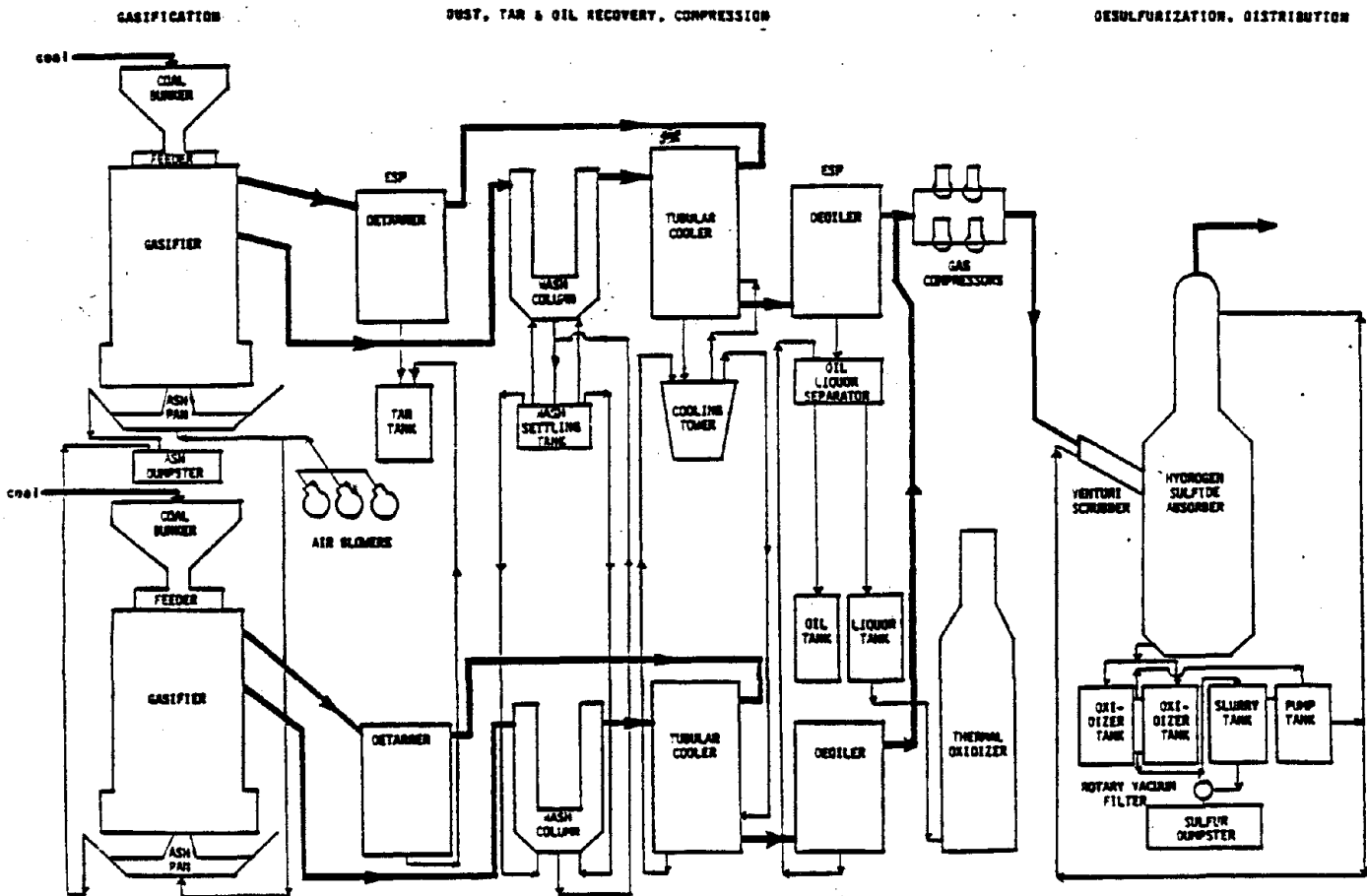


Figure A-3. Plant B Process Schematic  
A-10

Bituminous coal is stored onsite at ground level, screened, and gravity-fed to a vibrating feeder and belt conveyor located in the basement (410 level) of the facility. Noise exposure, therefore, is considered to be the principal problem for this area. From the feeder, sized coal is transported by bucket elevator to an enclosed vibrating screen on the 521 level and then by screw conveyor to the coal bunker. Undersized coal from the 521 screening operation is sent to the plant boilers. From the bunker, coal is then gravity-fed to the gasifier. During charging of coal, off-gas (displaced gas from the gasifier exiting through the coal bunker) from the feeding operation is passed through a baghouse before being vented to the atmosphere. Ash from the gasification process is deposited into a water-filled ash pan at the bottom of the gasifier. The cooled wet ash is then transported by belt conveyor to the ash dumpster for disposal.

The gasifier has a normal operating temperature of 982-1,119°C (1,800-2,100°F) at the bottom fire-bed depth. Two product gas fractions are taken off of the gasifier: a bottom gas with an exit temperature of 427-538°C (800-1,000°F), and a top gas with an exit temperature of 93-149°C (200-300°F). Normal operating pressure for the gasifier is 0.25-0.50 psig.

The top gas which contains tars and oil is passed through an electrostatic precipitator (detarrer) before entering the tubular cooler. The collected tars have a viscosity equivalent to that of No. 6 bunker fuel and contain high molecular weight polynuclear aromatics (PNAs) formed by the process. Tars are stored in the day tar tank prior to being pumped to the tar tank. The tars are retained in the tar tank for disposal to a commercial buyer.

The bottom gas and entrained dust is passed through a wash column before entering the tubular cooler. The two gas fractions are recombined in the cooler and exit the cooler at a temperature of 52°C (125°F). Water for the wash column is recycled, being passed through a settling tank to remove particulates. The wash column water is recycled with a minimal addition of makeup water. The wash water is used to remove particulates from the product gas in the wash column; however, this step also results in the removal of water-soluble contaminants such as hydrogen sulfide and ammonia.



Suspended particulates are separated from the wash water in a wash settling tank which is enclosed. Removal of nonsettleable solids and dissolved contaminants is done by a charcoal filter ("coke basket") in the wash tank.

The recombined product gas from the cooler then passes through an electrostatic precipitator (deoiler) for removal of oil and liquor. The oil is stored in an oil tank either for pickup by a commercial buyer or for use in the heating plant boiler. The liquor contains phenols and is burned in a thermal oxidizer. The gas is further treated in a Stretford unit for hydrogen sulfide removal. The cleaned product gas is distributed for in-plant use.

The gasifier startup procedures take 24 to 36 hours; they differ from the normal operating procedures described above in that anthracite coal instead of bituminous coal is used to initially fire the gasifier. The transport and introduction of anthracite into the gasifier, however, is the same as that described above for bituminous coal.

The gas produced during startup is not divided into a top and bottom fraction; instead, the takeoff line for the bottom gas is closed, with all product gas exiting the gasifier at the top. Upon leaving the gasifier, the product gas is diverted from the detarrer/deoiler cleanup system into a condenser/cyclone system for removal of liquids and particulates; the gas is then flared. The detarrer/deoiler system is not used because prolonged runs with anthracite coal will clog the electrostatic precipitators.

#### DESCRIPTION OF FACILITY

The two-stage gasifiers are housed in an enclosed, three-tiered structure. The elevation schematic is shown in Figure A-4. The gasifiers are located in the highest tier; the tar, dust, and oil recovery units in the middle tier; and the Stretford unit in the lowest tier. The wash settling tank, cooling tower, thermal oxidizer, and the main tar and oil storage tanks are located outside the structure.

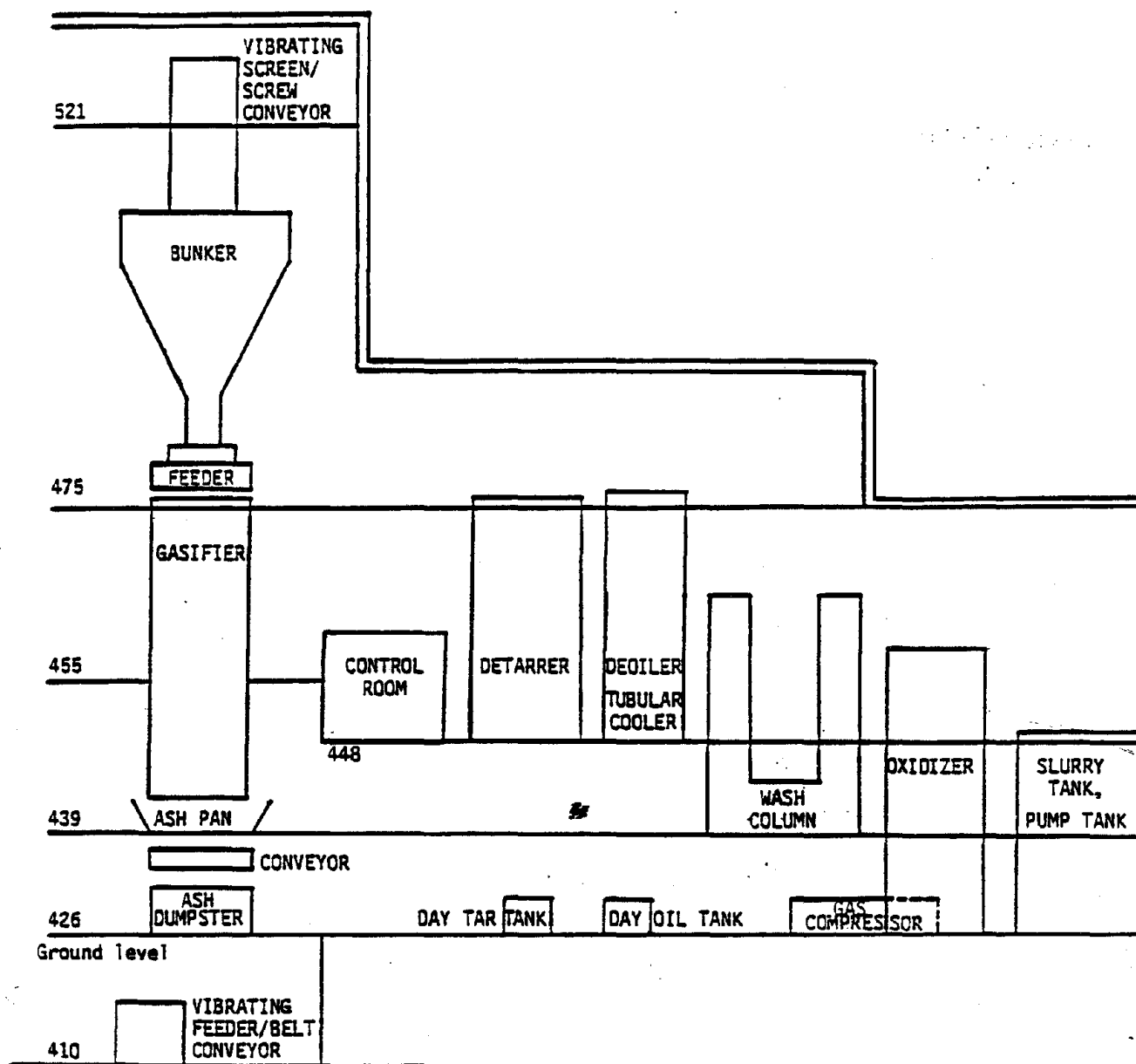


Figure A-4. Plant B Schematic Elevation of Major Process Equipment (not to scale)

The facility has open-grating flooring except for specific areas including the control room, the rectifier room, the ash pan section, and the 521 level of the gasifier tier all of which have poured-concrete flooring. All levels are identified by their elevation above sea level; Table A-2 shows the major levels, their elevation, and descriptions. Figure A-5 is the plant layout which shows the relative locations of major process equipment.

Table A-2. Description of Major Plant Levels at Plant B

Level	Elevation	Description
Basement	410	Vibrating feeder, belt conveyor
Ground	426	Ash conveyor system, gas compressors, vibrating screen (in yard)
First	439	Ash pan for gasifier
Second	448	Control room floor
Third	455	Gasifier poke holes
Fourth	473	Top of gasifier, coal bunker, coal feeder, rectifier room, baghouse
Fifth	521	Screw conveyor, coal chute, vibrating screen
Roof	534	Flare

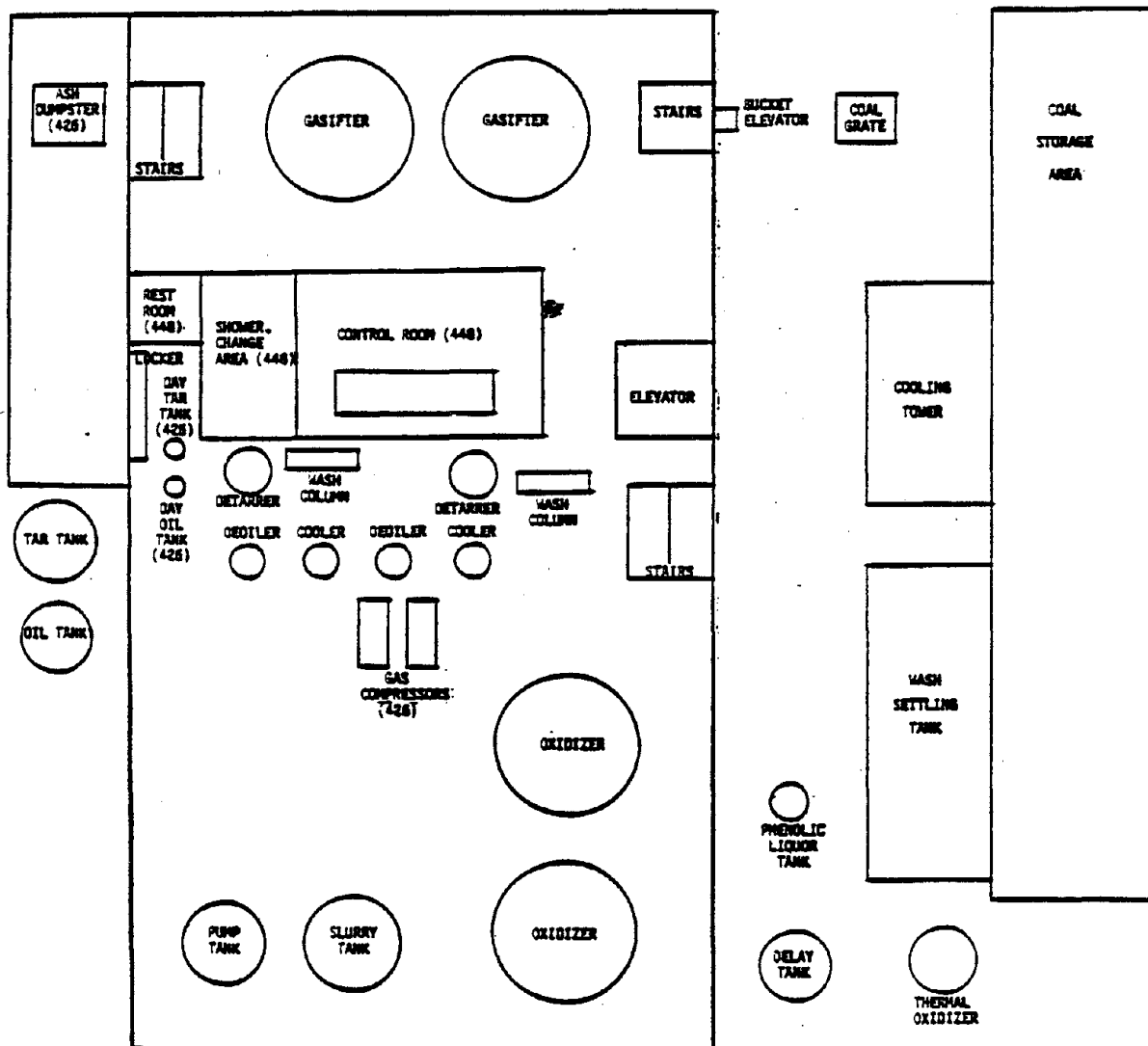


Figure A-5. Plant B Plant Layout (not to scale)

Several modifications to the plant have been made since the walk-through survey of August 18-20, 1980. All outside equipment and vessels except for coal storage have been enclosed with a chain-link fence to limit access. Openings in the Stretford oxidizer and slurry tanks, and the wash settling tank have been enclosed and vented to reduce fugitive emissions into the work environment.

## GOAL GASIFICATION PILOT PLANT C

### PROCESS DESCRIPTION

The Plant C coal gasification process is a fluidized-bed, ash agglomerating system which can utilize various types of coal. The system can be either oxygen- or air-fired and produce either a medium- or low-Btu gas. A process schematic is shown in Figure A-6.

Indiana No. 7 (May 13 through 16) and Wyoming subbituminous (June 22, 23) coals were used during the survey. Front-end loaders transport and feed coal into the coal preparation system, where it is crushed to 1/4" and dried to 10% moisture levels. Oversized pieces are recycled, and all fines are used. The prepared coal is stored in three bins having a combined capacity of 60 tons. Industrial-grade carbon dioxide is used to inert the air in these areas.

Coal is moved by a starwheel feed to a screw conveyor and deposited by bucket elevator into a pressurizing double-lockhopper system. Coal is pressurized in the first lockhopper (C103A) and fed to the gasifier at operating pressure from the second lockhopper (C103B). Pneumatic conveyance using recycled product gas carries the coal into the gasifier via a central feed pipe, through which either oxygen or air is also introduced.

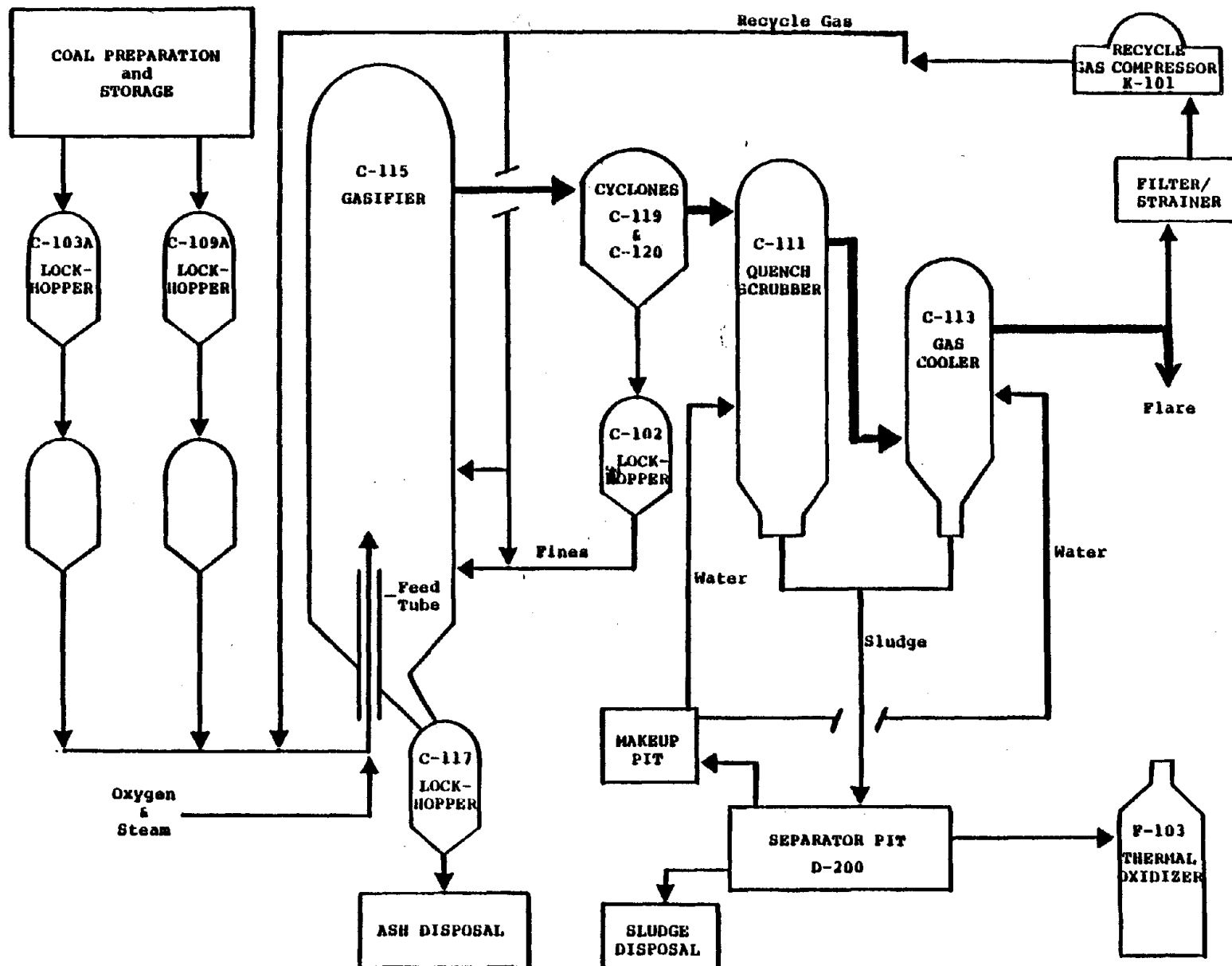


Figure A-6. Plant C Process Schematic

The operating parameters for the Fluid Bed gasifier are as follows:

- . Coal Feed Rate: 15-30 tons/day
- . Oxygen Feed Rate: 1,400 pounds/hour
- . Gasifier Temperature: 870°C (1,600°F) for Western coal 1,050°C (1,950°F) for Eastern coal
- . Gasifier Pressure: 215 psig
- . System Pressure Range: 130-230 psig

Feed rates and temperatures are dependent on coal type. Bed fluidization in the gasifier is maintained by radially introduced recycle gas. Temperatures in the fluidized bed effectively eliminate tar production, and detarring equipment is not included in the system. Approximately 30 percent of the coal feed is carried over as fines. About two-thirds of the fines are collected and recycled to the gasifier bed. The remaining one-third is removed at the quench scrubber, gas coolers, and recycle gas compressor filter and strainer.

Ash residue agglomerates in the fluidized bed and settles to the bottom of the gasifier. This agglomerated ash is withdrawn through rotary valves into lockhoppers (C-117A and C-117B), depressurized, and dumped into bins. Forklifts move the ash to storage before removal to landfill sites by an outside contractor. Dust does not appear to be a problem in this process.

The product stream, with entrained fines, exits the top of the gasifier at an approximate temperature of 700-950°C (1,300-1,750°F). Cyclones are used to recover fines and feed them to lockhoppers (C-108 and C-102) for recycle to the gasifier. During the first portion of the survey, only the primary cyclone (C-119) was operational and about two-thirds of the entrained fines were recovered. During the second portion of the survey, the secondary cyclone was also on line, and fines carryover was reduced to about 1 percent.

Gas cleanup and cooling are accomplished in a two-stage recirculating water system. The product stream enters the quench scrubber (C-111) at approximately 600°C (1,100°F) and flows through a bubbler and water spray. It then enters the packed-bed gas cooler (C-113) and exits at about 50°C (120°F). Particulates removed in these units are discharged to a covered separator pit (D-200). Sludge is flocculated in the pit and removed for treatment and landfill. Water is routed to the make-up pit and recirculated. Accumulation of hydrogen sulfide, ammonia, and other gases is controlled by fan venting to the thermal oxidizer (F-103).

Recycled product gas is used as a transport media for coal fines. Excess gas is burned in the thermal oxidizer (F-103).

Recycle gas requires further cooling and cleaning. Cooling is carried out in a second packed-bed gas cooler connected to the recirculating water system. The recycle gas stream is then cleaned with in-line stainless steel strainers and Cuno filtration (K-103). These strainers and the Cuno filters require regular maintenance, and are potential sources of exposure to process stream emissions.

Pressure of the recycle gas stream at this stage is about 185 psig. Recycle gas is recompressed to approximately 265 psig before being used for coal fines transport. It is supplemented with industrial-grade carbon dioxide when necessary.

#### FACILITY DESCRIPTION

The Fluid Bed PDU, located at the base of a hill, is surrounded on three sides by an earth bank whose highest point is level with the second story of the PDU. This high spot is on the east side of the PDU; the west side is free of embankment. Since the wind comes generally from the south, the grade level is potentially shielded from the wind, leading to the possible development of a calm air zone where process gas constituents could accumulate.



The PDU itself is an open, multistoried structure divisible into three distinct sections. The tallest section of the structure, with nine levels, comprises the southern end of the structure. This section houses the two coal and fines lockhopper systems, char cooler conveyor, and the devolatilization equipment which is not in use. The regular gas compressor and its filter and strainer system are also located in this section, at grade level.

The middle section has six levels and contains most onstream equipment including the gasifier, cyclone, quench scrubber, and gas coolers. At grade level are the water circulation pumps and makeup pumps, and the makeup pit. The third northern section also has six levels and contains the second cyclone. This section, the newest part of the PDU structure, is intended to house the Stretford unit and accessory equipment. The separator pit is located in this section at grade level.

The coal preparation section is housed in a semienclosed building (the coal shed) located at the southeast corner of the structure. The pulverized coal is stored in three bins attached to the south side of the PDU. These bins also serve as a windbreaker for the PDU, and feed coal to the lockhoppers in the southern section of the structure.

Figure A-7 gives the plant layout with the relative location of these major facilities and equipment. The control room and facilities north of the PDU are elevated relative to the PDU.

Grade level is gravel floored with concrete blocks for equipment. This area has poor drainage, and standing water was present throughout the survey. Because of the poor drainage, there is a tendency for the separator pit to overflow during heavy rains. Heavy deposits of coal dust were observed at this level below the coal storage bins and in the area of the recycle gas compressor which is adjacent to the storage bins. The dust is manually removed on a periodic basis scheduled to coincide with plant downtime.

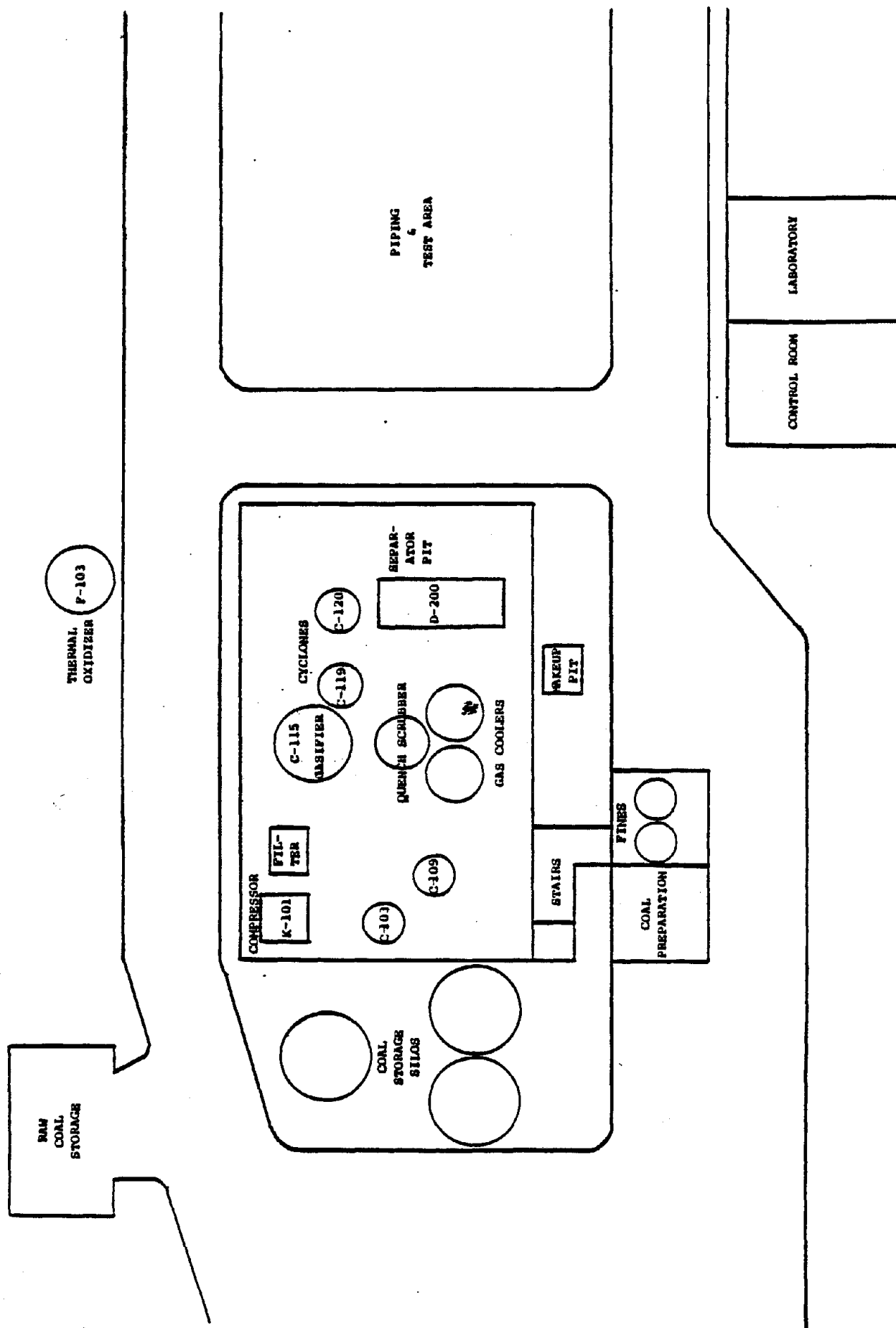


Figure A-7. Plant C Plant Layout



Appendix B

RESULTS OF SAMPLING PROGRAMS  
AT THREE COAL GASIFICATION PLANTS

PLANT A  
ENTRAINED BED GASIFICATION

Table B-1.	Plant A Area Sampling Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for PNAs (January 26-27, 1979).....	B-3
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Table B-1. Plant A Area Sampling Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for PNAs (January 26-27, 1979)

Compound	Sample Site:		Cyclone Scrubber	Thickener	Gasifier	Induced-Draft Fan	Blank <sup>a</sup>	
	Sample Number:		001	015	026	027	016	036
	Sample Volume (l):		3.450	3.538	4.508	4.462		
	Sampling Time:		1330-1945	1321-1945	0941-1841 <sup>b</sup>	0945-2050 <sup>b</sup>		
Naphthalene	(0.01)	<sup>c</sup>	0.02	-- <sup>d</sup>	--	0.03	0.01	0.03
1-Methylnaphthalene	(0.01)		--	--	--	--	--	--
2-Methylnaphthalene	(0.01)		0.05	--	--	0.04	0.01	0.02
Quinoline	(0.01)		--	--	--	--	--	--
Acenaphthalene	(0.01)		--	--	--	--	--	--
Acenaphthene	(0.01)		--	--	--	--	--	--
Fluorene	(0.01)		0.1	--	--	--	0.02	0.03
Phenanthrene/Anthracene	(0.01)		0.08	--	--	--	0.02	--
Acridine	(0.01)		--	--	--	--	--	--
Carbazole	(0.01)		--	--	--	--	--	--
Fluoranthene	(0.01)		--	--	--	--	--	--
Pyrene	(0.01)		--	--	--	--	0.02	0.02
Benzo(a)fluorene/ Benzo(b)fluorene	(0.01)		--	--	--	--	--	--
Benzo(a)anthracene/ Chrysene/Triphenylene	(0.01)		--	--	--	--	--	--
Benzo(j)fluoranthene/ Benzo(b)fluoranthene/ Benzo(k)fluoranthene	(0.01)		--	--	--	--	--	--
Benzo(e)pyrene/ Benzo(a)pyrene	(0.01)		--	--	--	--	--	--
Perylene	(0.01)		--	--	--	--	--	--
Dibenz(a,j)acridine	(0.01)		--	--	--	--	--	--
Dibenz(a,i)carbazole	(0.01)		--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene	(0.01)		--	--	--	--	--	--
Dibenz(a,h)anthracene	(0.01)		--	--	--	--	--	--
Benzo(g,h,i)perylene	(0.01)		--	--	--	--	--	--
Coronene	(0.02)		--	--	--	--	--	--
Dibenz(a,i)pyrene	(0.02)		--	--	--	--	--	--
Dimethylbenz(a)anthracene	(0.02)		--	--	--	--	--	--
3-Methylcholanthrene	(0.02)		--	--	--	--	--	--
6,13-Dimethyldibenz(a,h)- anthracene	(0.02)		--	--	--	--	--	--
TOTAL			0.2	--	--	0.07	0.08	0.1

<sup>a</sup> Blank values in  $\mu\text{g}/\text{sample}$ .

<sup>b</sup> Compressed air pumps turned off for 30 minutes for sample 026 and for 3 hours for sample 027 because of drop in air pressure.

<sup>c</sup> Detection limits in  $\mu\text{g}/\text{m}^3$ .

<sup>d</sup> "--" indicates compound not detected.

Table B-2. Plant A Area Sampling Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for PNAs (April 16-21, 1981)

Location Sampled:	Gasifier Combustor			Gasifier Reductor	Gas Duct (Top of Gasifier)		Induced-Draft Fan	Control Room		Upwind Perimeter		Blank (pg/sample)	
Sample Number:	020	016	089	056	054	008	053	055	007	015	105	021	050
Sample Volume (l):	1,993	1,856	752	1,947	1,929	701	1,915	1,978	746	1,716	494		
Sample Volume (l):	0011-	1625-	0844-	0740-	0732-	0900-	0721-	0711-	0827-	1426-	0832-		
Sampling Time:	2400	0709	1426	2315	2313	1419	2255	2253	1406	0326	1646		
Date Collected:	4/16/81	4/16/81	4/21/81	4/20/81	4/20/81	4/21/81	4/20/81	4/20/81	4/21/81	4/16/81	4/21/81	4/16	4/17
Compound (detection limit, $\mu\text{g}/\text{m}^3$ ) <sup>a</sup>													
Naphthalene (0.1)	0.3	1.2	-- <sup>b</sup>	--	--	--	0.2	0.1	--	0.5	--	0.5	0.3
1-Methylnaphthalene (0.1)	0.1	0.4	--	--	--	--	0.1	0.1	--	0.1	--	0.1	--
2-Methylnaphthalene (0.1)	0.3	1.0	--	0.4	--	--	0.6	0.4	--	0.3	--	0.4	0.02
Quinoline (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Acenaphthalene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Acenaphthene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Fluorene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Phenanthrene/Anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--	0.05	--
Acridine (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Carbazole (0.1)	--	--	--	--	--	--	--	--	--	--	--	0.1	0.03
Fluoranthene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Pyrene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(a)fluorene/ Benzo(b)fluorene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(a)anthracene/Chrysene/ Triphenylene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(j)fluoranthene/ Benzo(b)fluoranthene/ Benzo(k)fluoranthene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(e)pyrene/ Benzo(a)pyrene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Perylene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,j)acridine (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,i)carbazole (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,h)anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(g,h,i)perylene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
Coronene (0.6)	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,i)pyrene (0.6)	--	--	--	--	--	--	--	--	--	--	--	--	--
Dimethylbenz(a)anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
3-Methylcholanthrene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
6,11-Dimethylbenz(a,h)- anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--	--
TOTAL	0.7	2.6	0	0.4	0	0	0.9	0.6	0	0.9	0	1.2	0.4

<sup>a</sup> Assuming a sample volume of greater than 1,500 liters.<sup>b</sup> "--" indicates not detected.

Table B-3. Plant A Personal Sampling Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for PNAs<sup>1</sup> (April 15-21, 1981)

Personnel Sampled:	Equipment Operator								Maintenance								Chemical Technician		Instr. Tech.	Blanks ( $\mu\text{g}/\text{Sample}$ )	
Sample Number:	008	009	010	034	047	083	084	094	011	019	033	037	071	085	101	102	032	093	070	024	051
Sample Volume (L):	683	592	672	500	147	728	721	501	631	673	644	546	644	650	721	606	532	521	525		
Sampling Time:	1455-2303	0700-1435	0702-1430	1500-2110	1534-1641	1512-2252	1518-2253	0740-1435	0735-1545	0749-1550	1600-2340	1204-1904	0804-1545	1555-2245	0815-1550	0815-1525	1507-2220	0754-1415	0822-1417		
Date Collected (1981):	4/15	4/16	4/16	4/16	4/17	4/20	4/20	4/21	4/16	4/16	4/16	4/16	4/20	4/20	4/21	4/21	4/16	4/21	4/20	4/16	4/17
Compound (detection limit, $\mu\text{g}/\text{m}^3$ ) <sup>a</sup>																					
Naphthalene (0.4)	1.0	1.2	1.0	4.1	1.3	4.9	-- <sup>b</sup>	0.4	4.6	0.9	2.6	7.0	1.0	3.6	1.1	--	1.0	--	1.4	--	--
1-Methylnaphthalene (0.4)	--	0.6	0.6	1.1	0.8	3.6	--	--	1.7	0.6	1.5	2.5	--	1.5	0.6	--	--	--	--	--	--
2-Methylnaphthalene (0.4)	0.4	1.3	1.3	3.6	0.9	6.0	0.8	--	3.9	1.1	3.6	6.4	0.8	4.1	1.0	--	0.7	--	0.5	--	--
Quinoline (0.4)	--	--	--	--	--	7.1	--	--	--	--	--	--	--	1.3	--	--	--	--	--	--	--
Acenaphthalene (0.4)	--	--	--	--	--	0.5	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Acenaphthene (0.4)	--	--	--	--	--	0.6	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Fluorene (0.4)	--	--	--	--	--	0.4	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Phenanthrene/Anthracene (0.4)	--	--	--	--	--	1.3	--	--	--	--	--	0.6	--	--	--	--	--	--	--	--	--
Acridine (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Carbazole (0.4)	--	--	--	--	--	0.6	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Fluoranthene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Pyrene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(a)fluorene/ Benzo(b)fluorene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(a)anthracene/Chrysene/ Triphenylene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(j)fluoranthene/ Benzo(h)fluoranthene/ Benzo(k)fluoranthene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(e)pyrene/ Benzo(a)pyrene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Perylene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,j)acridine (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,i)carbazole (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,h)anthracene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(g,h,i)perylene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Coronene (1.6)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,i)pyrene (1.6)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dimethylbenz(a)anthracene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
1-Methylcholanthrene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
6,13-Dimethyldibenz(a,h)- anthracene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
TOTAL	1.4	3.1	2.9	8.7	3.0	24.6	0.8	0.4	10.2	2.6	7.7	16.5	1.8	10.5	2.6	--	1.7	--	1.9	--	--

<sup>a</sup> Assuming a sample volume of approximately 600 liters.<sup>b</sup> "--" indicates not detected.



Table B-4. Plant A wipe sampling Analytical Results for PNAs (April 15-21, 1981)

Compound	Sample Location:	Sludge Thickener	Maintenance Tools	Rail to Cyclone Scrubber	Gasifier	Induced-Draft Fan	Lockers (shower area)	Lunchroom	Control Room	Gloves of Welder	Hands of Welder
	Sample Number:	039	044	045	046	040	041	042	041	106	107
Naphthalene		•	•	•	•	•	•	•	•	•	•
1-Methylnaphthalene		-	-	•	-	•	-	-	-	-	-
2-Methylnaphthalene		-	-	•	-	•	-	-	-	-	-
Quinoline		-	-	-	-	-	-	-	-	-	-
Acenaphthalene		-	•	-	-	-	-	-	-	-	-
Acenaphthene		-	•	-	-	-	-	-	-	-	-
Fluorene		-	•	•	-	•	-	-	-	-	-
Phenanthrene/Anthracene		•	•	•	•	•	•	•	•	•	•
Acridine		-	-	-	-	-	-	-	-	-	-
Carbazole		-	-	-	-	-	-	-	-	-	-
Fluoranthene		•	•	•	-	•	-	-	-	•	-
Pyrene		•	•	•	-	•	-	-	-	•	-
Benzo(a)fluorene/ Benzo(b)fluorene		-	-	-	-	-	-	-	-	-	-
Benz(a)anthracene/ Chrysene/Triphenylene		-	-	-	-	-	-	-	-	-	-
Benzo(j)fluoranthene/ Benzo(b)fluoranthene/ Benzo(k)fluoranthene		-	-	-	-	-	-	-	-	-	-
Benzo(e)pyrene/ Benzo(a)pyrene		-	-	-	-	-	-	-	-	-	-
Perylene		-	-	-	-	-	-	-	-	-	-
Dibenz(a,j)acridine		-	-	-	-	-	-	-	-	-	-
Dibenz(a,l)carbazole		-	-	-	-	-	-	-	-	-	-
Indeno(1,2,3-cd)pyrene		-	-	-	-	-	-	-	-	-	-
Dibenz(a,h)anthracene		-	-	-	-	-	-	-	-	-	-
Benzo(g,h,i)perylene		-	-	-	-	-	-	-	-	-	-
Coronene		-	-	-	-	-	-	-	-	-	-
Dibenz(a,i)pyrene		-	-	-	-	-	-	-	-	-	-
Dimethylbenz(a)anthracene		-	-	-	-	-	-	-	-	-	-
1-Methylcholanthrene		-	-	-	-	-	-	-	-	-	-
6,11-Dimethyldibenz(a,h)- anthracene		-	-	-	-	-	-	-	-	-	-

KEY: • indicates compound detected; - indicates compound not detected.

Table B-5. Plant A Area Sampling Analytical Results (mg/m<sup>3</sup>)  
for Aromatic Amines (January 26-27, 1979)<sup>d</sup>

Location Sampled	Sample Number	Sample Volume (L)	Sampling Time	Date Collected	Aromatic Amines <sup>a</sup> (detection limit, ppm) <sup>b</sup>			
					A (0.13)	B (0.05)	C (0.05)	D (0.05)
Cyclone/Scrubber	003	47	1239-2030	1/26/79	-- <sup>c</sup>	--	--	--
Gasifier	006	49	1231-2037	1/26/79	--	--	--	--
Induced-Draft Fan	033	52	1032-1908	1/27/79	--	--	--	--
Blanks (mg/sample)	041			1/27/79	--	--	--	--
	042			1/27/79	--	--	--	--

<sup>a</sup>Aromatic amines: A = Aniline; B = N,N-Dimethylaniline; C = o-Anisidine;  
D = p-Anisidine.

<sup>b</sup>Assuming a sample volume of 50 liters.

<sup>c</sup>-- indicates not detected.

<sup>d</sup>sampling system compromised by humidity

Table B-6. Plant A Area Sampling Analytical Results (ppm) for  
Benzene, Toluene, and Xylene (January 26-27, 1979)

Location Sampled	Sample Number	Sample Volume (L)	Sampling Time	Date Collected	Compound (detection limit, ppm) <sup>a</sup>		
					Benzene (0.01)	Toluene (0.01)	Xylene (0.01)
Cyclone/Scrubber	002	47	1235-2027	1/26/79	0.02	-- <sup>b</sup>	--
Gasifier	008	49	1232-2039	1/26/79	0.02	--	--
Induced-Draft Fan	028	52	1021-1903	1/27/79	0.02	--	--
Sludge Thickener	031	48	1036-1856	1/27/79	0.02	--	--
Blanks (mg/sample)	081			1/26/79	--	--	--
	039			1/27/79	--	--	--

<sup>a</sup>Assuming a sample volume of 50 liters.

<sup>b</sup>-- indicates not detected.

Table B-7. Plant A Area Sampling Analytical Results (ppm) for Benzene, Toluene, and Xylene (April 15-21, 1981)

Sample Location	Sample Number	Sample Volume (L)	Sampling Time	Date Collected	Compound (detection limit, ppm)		
					Benzene (0.01)	Toluene (0.02)	Xylene (0.02)
Control Room	003	79	1500-2302	4/15/81	-- <sup>a</sup>	--	--
	057	103	0711-1519	4/20/81	--	--	--
	086	74	0827-1406	4/21/81	--	--	--
Cyclone/Scrubber	004	93	1446-2247	4/15/81	--	--	--
	077	98	1527-2313	4/20/81	0.01	--	--
Gasifier	002	96	1514-2255	4/15/81	--	--	--
	021	106	0813-1600	4/15/81	--	--	--
	022	97	0815-1600	4/16/81	--	--	--
	029	87	1625-2400	4/16/81	--	--	--
	060	65	0748-1601	4/20/81	--	--	--
	079	92	1522-2316	4/20/81	--	--	--
	090	47	0844-1425	4/21/81	--	--	--
Gas Duct	006	105	1439-2216	4/15/81	--	--	--
	059	101	0733-1549	4/20/81	--	--	--
Induced-Draft Fan	007	73	1519-2258	4/15/82	--	--	--
	080	86	1520-2255	4/20/81	--	--	--
Sludge Thickener	061	93	0724-1534	4/20/81	--	--	--
	091	74	0845-1428	4/21/81	--	--	--
Stretford	005	85	1508-2250	4/15/81	0.01	--	--
	058	104	0737-1552	4/20/81	--	--	--
	078	95	1525-2315	4/20/81	--	--	--
	092	62	0858-1421	4/21/81	--	--	--
Upwind	027	102	1427-2230	4/16/81	--	--	--
	081	100	1535-2331	4/20/81	--	--	--
	104	78	0822-1646	4/21/81	--	--	--
Blanks	025				--	--	--
	026				--	--	--
	052				--	--	--
	053				--	--	--

<sup>a</sup>-- indicates not detected.

Table B-8. Plant A Personal Sampling Analytical Results (ppm) for Benzene, Toluene, and Xylene (April 15-21, 1981)

Personnel Sampled	Sample Number	Sample Volume (L)	Sampling Time	Date Collected	Compound (detection limit, ppm)		
					Benzene (0.01)	Toluene (0.02)	Xylene (0.02)
Equipment Operators	001	91	1504-2237	4/15/81	-- <sup>a</sup>	--	--
	011	66	0709-1215	4/16/81	--	--	--
	012	89	0740-1430	4/16/81	--	--	--
	028	59	1500-2110	4/16/81	0.01	0.05	--
	031	53	1533-2237	4/16/81	0.07	--	--
	048	14	1535-1642	4/17/81	0.01	--	--
	049	15	1537-1642	4/17/81	--	--	--
	063	91	0734-1435	4/20/81	--	0.03	--
	066	83	0740-1435	4/20/81	0.01	--	--
	067	73	0804-1435	4/20/81	0.01	--	--
	096	76	0740-1430	4/21/81	--	--	--
	098	66	0740-1435	4/21/81	--	--	--
Maintenance Workers	014	74	0743-1545	4/16/81	0.01	--	--
	017	100	0745-1545	4/16/81	0.2	0.08	--
	030	87	1601-2340	4/16/81	--	--	--
	038	92	2150-0706	4/16/81	0.1	--	--
	068	93	0805-1550	4/20/81	--	0.03	--
	082	77	0355-1145	4/20/81	0.06	--	--
	099	93	0815-1535	4/21/81	--	--	--
	100	76	0815-1530	4/21/81	--	0.03	--
Instrument Technicians	069	56	0820-1434	4/20/81	0.02	0.04	--
	097	81	0735-1430	4/21/81	--	--	--
Chemical Technicians	062	70	0720-1430	4/20/81	0.02	--	--
	065	72	0800-1445	4/20/81	0.01	--	--
	076	98	1514-2250	4/20/81	--	--	--
	095	40	1120-1435	4/21/81	--	--	--
Blanks	025				--	--	--
	026				--	--	--
	052				--	--	--
	053				--	--	--

<sup>a</sup>-- indicates not detected.

Table B-9. Plant A Area Sampling Analytical Results (ppm) for Phenolic Compounds (January 26-27, 1979)<sup>c</sup>

Location Sampled	Sample Number	Sample Volume (l)	Sampling Time	Date Collected	Phenolic Compound (detection limit, ppm) <sup>a</sup>	
					Phenol (0.1)	Cresol (0.1)
Gasifier (Bottom)	007	48	1239-2039	1/26/79	-- <sup>b</sup>	--
Char Receiving Bin	010	48	1231-2037	1/26/79	--	--
Blanks (mg/sample)	017			1/26/79	--	--
	040			1/27/79	--	--

<sup>a</sup>Assuming a sample volume of 50 liters.

<sup>b</sup>-- indicates not detected.

<sup>c</sup>sampling system compromised by humidity

Table B-10. Plant A Area Sampling Analytical Results (ug/m<sup>3</sup>) for Trace Metals (January 26-27, 1979)

Location Sampled:	Cyclone/ Scrubber	Gasifier	Char Receiving Bin	Pulver- izer	Induced- Draft Fan	Blanks (ug/sample)	
Sample Number:	004	005	009	011	032	019	037
Sample Volume (l):	946	972	956	1,014	1,040		
Sampling Time:	1237-2030	1232-2038	1243-2041	1226-2053	1027-1907		
Date Collected:	1/26/79	1/26/79	1/26/79	1/26/79	1/27/79	1/26/79	1/27/79
Compound (detection limit, ug/m <sup>3</sup> ) <sup>a</sup>							
Arsenic (0.13)	-- <sup>b</sup>	--	--	--	--	--	--
Beryllium (0.26)	--	--	--	--	--	--	--
Cadmium (0.13)	--	--	--	--	--	--	--
Copper (2.6)	--	--	--	--	--	--	--
Mercury (0.25)	--	--	--	--	--	--	--
Magnesium (2.6)	--	--	--	--	--	--	--
Manganese (0.26)	--	--	1	--	--	--	--
Nickel (2.6)	20	--	--	--	--	--	--
Strontium (2.6)	--	--	--	--	--	--	--
Tellurium (0.26)	--	--	--	--	--	--	--

<sup>a</sup>Assuming a sample volume of 1,000 liters.

<sup>b</sup>-- indicates not detected.

PLANT B  
FIXED-BED GASIFICATION

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Table B-11. Plant B Area Sampling Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for PNAs (August 18-19, 1980; April 28-May 1, 1981)

Sample Site:	Deoiler/Deaerator				Top of Gasifier			Poke Hole			Oil/Liquor Separator	Ash Pan
Sample Number:	020	021	1-011	1-022	005	1-012	3-053	009	1-013	3-055	1-063	1-023
Sample Volume (L):	4,020	4,020	1,476.2	1,600.2	4,416	1,467.4	1,508.4	4,480	1,450.6	1,504	1,053.0	1,504
Sampling Time:	2118-0435	2118-0435	0801-1950	0818-2029	2205-0605	0804-1911	1252-2454	2203-0610	0807-1910	0219-1419	0705-1504	0825-2026
Date Collected:	8/19/80	8/19/80	4/28/81	4/29/81	8/18/80	4/28/81	4/30/81	8/18/80	4/28/81	4/30/81	5/1/81	4/29/81
Compound (detection limit, $\mu\text{g}/\text{m}^3$ ) <sup>a</sup>												
Naphthalene (0.1)	4.2	5.1	16.5	15.7	12.4	6.4	14.0	3.2	17.8	11.5	32.7	16.3
1-Methylnaphthalene (0.1)	1.1	1.1	5.8	5.0	3.2	3.1	5.9	0.6	4.2	3.9	9.2	6.7
2-Methylnaphthalene (0.1)	2.7	2.5	16.5	10.7	-- <sup>b</sup>	5.2	12.8	--	9.6	9.6	26.8	16.0
Quinoline (0.1)	--	--	1.3	0.3	4.1	0.5	0.6	1.4	1.0	0.2	1.8	--
Acenaphthalene (0.1)	--	--	0.3	0.1	--	--	0.1	--	0.2	--	0.3	0.1
Acenaphthene (0.1)	0.1	0.1	0.4	0.4	0.1	0.2	0.5	0.1	0.4	0.2	0.6	0.7
Fluorene (0.1)	0.1	--	0.7	0.5	0.1	0.4	0.5	0.1	0.8	0.3	0.9	0.8
Phenanthrene/Anthracene (0.1)	0.2	0.1	1.0	0.9	0.1	0.6	0.6	0.1	1.3	0.3	0.7	1.4
Acridine (0.1)	--	--	--	0.2	--	--	0.6	--	0.2	0.6	0.9	--
Carbazole (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Fluoranthene (0.1)	--	--	--	--	--	--	--	--	0.1	--	--	0.1
Pyrene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(a)fluorene/ Benzo(b)fluorene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(a)anthracene/Chrysene/ Triphenylene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(j)fluoranthene/ Benzo(b)fluoranthene/ Benzo(k)fluoranthene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(e)pyrene/ Benzo(a)pyrene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Perylene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,j)acridine (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,l)carbazole (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,h)anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(g,h,i)perylene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
Coronene (0.6)	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,l)pyrene (0.6)	--	--	--	--	--	--	--	--	--	--	--	--
Dimethylbenz(a)anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	0.3	--
3-Methylcholanthrene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
6,12-Dimethyldibenz(a,h)-anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--	--
TOTAL	8.4	8.9	42.5	33.0	20.0	16.4	35.6	5.5	35.6	26.6	74.2	42.1

<sup>a</sup> Assuming a sample volume of greater than 1,500 liters.

<sup>b</sup> -- indicates not detected.

(continued)

Table B-11 (concluded)

Sample Site: Sample Number: Sample Volume (l): Sampling Time: Date Collected:	Day Tar/Oil Tank	Gas Compressor	Tank T-101		Control Room		Upwind		Blanks	
			1-026	1-016	1-014	3-054	1-015	3-057	0-046	0-047
	017	1-025	1-026	1-016	1-014	3-054	1-015	3-057	0-046	0-047
	4,618	1,566.4	444	450	1,460.8	1,592.8	1,445.4	1,584		
	2208-	0833-	1002-	1014-	0810-	0103-	0817-	0232-		
	0630	2025	1458	1515	1914	1307	1914	1432		
	8/18/80	4/29/81	4/29/81	4/28/81	4/28/81	4/30/81	4/28/81	4/30/81		
Compound (detection limit, µg/m <sup>3</sup> ) <sup>a</sup>										
Naphthalene (0.1)	5.4	12.7	23.7	22.3	16.7	5.2	1.9	0.1	b	--
1-Methylnaphthalene (0.1)	1.7	6.4	14.4	12.5	2.8	1.8	0.5	--	--	--
2-Methylnaphthalene (0.1)	3.1	14.3	34.3	26.9	7.2	4.1	1.1	0.1	--	--
Quinoline (0.1)	--	0.4	1.4	1.0	0.7	0.2	0.2	--	--	--
Acenaphthalene (0.1)	0.3	--	--	--	0.3	--	--	--	--	--
Acenaphthene (0.1)	0.2	0.5	1.4	1.1	0.7	0.6	0.2	--	--	--
Fluorene (0.1)	0.6	0.6	0.8	1.3	0.7	0.4	0.3	--	--	--
Phenanthrene/Anthracene (0.1)	0.6	0.6	0.4	2.2	1.6	0.8	0.7	--	--	--
Acridine (0.1)	--	0.2	--	1.4	0.3	0.3	0.5	0.3	--	--
Carbazole (0.1)	--	--	--	--	--	--	--	--	--	--
Fluoranthene (0.1)	--	--	--	--	0.2	--	--	--	--	--
Pyrene (0.1)	--	--	--	--	--	--	--	--	--	--
Benzo(a)fluorene/ Benzo(b)fluorene (0.1)	--	--	--	--	--	--	--	--	--	--
Benzo(a)anthracene/Chrysene/ Triphenylene (0.1)	--	--	--	--	0.1	--	--	--	--	--
Benzo(j)fluoranthene/ Benzo(b)fluoranthene/ Benzo(k)fluoranthene (0.1)	--	--	--	--	--	--	--	--	--	--
Benzo(a)pyrene/ Benzo(a)pyrene (0.1)	--	--	--	--	--	--	--	--	--	--
Perylene (0.1)	--	--	--	--	--	--	--	--	--	--
Dibenz(a,j)acridine (0.1)	--	--	--	--	--	--	--	--	--	--
Dibenz(a,l)carbazole (0.1)	--	--	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene (0.1)	--	--	--	--	--	--	--	--	--	--
Dibenz(a,h)anthracene (0.1)	--	--	--	--	--	--	--	--	--	--
Benzo(g,h,i)perylene (0.1)	--	--	--	--	--	--	--	--	--	--
Crotonene (0.6)	--	--	--	--	--	--	--	--	--	--
Dibenz(a,l)pyrene (0.6)	--	--	--	--	--	--	--	--	--	--
Dimethylbenz(a)anthracene (0.1)	--	0.3	--	--	--	--	--	0.1	--	--
3-Methylcholanthrene (0.1)	--	--	--	--	--	--	--	--	--	--
6,11-dimethyldibenz(a,h)- anthracene (0.1)	--	--	--	--	--	--	--	--	--	--
TOTAL	11.9	35.7	76.4	60.7	31.3	13.4	5.4	0.6	--	--

<sup>a</sup> Assuming a sample volume of greater than 1,500 liters.<sup>b</sup> --- indicates not detected.



Table B-12. Plant B Personal Sampling Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for PNAs (April 27-May 1, 1981)

Personnel Sampled:	Is				Maintenance Personnel								Blanks (µg/sample)					
	Sample Number:	1-008	1-041	2-034	2-006	Millwright	1-010	1-020	Utility Helper	3-037	1-059	Maintenance	1-061	2-013	Elec- trician	3-039	3-040	0-076
Sample Volume (l):	667.5	625.5	598.5	709.5	646.5	561	435	616.5	511.5	618	529.5	474						
Sampling Time:	0737-	0749-	1554-	1543-	0753-	0805-	2345-	0753-	0800-	1555-	1207-	2350-						
	1502	1446	2233	2240	1504	1105	0700	1444	1455	2247	0554	0419						
Date Collected:	4/28/81	4/30/81	4/29/81	4/27/81	4/28/81	4/29/81	4/30/81	5/1/81	5/1/81	4/28/81	4/30/81	4/30/81						
Compound (detection limit, µg/m <sup>3</sup> ) <sup>a</sup>																		
Naphthalene (0.4)	11.8	1.9	11.6	5.4	16.4	62.9	7.0	7.7	69.9	55.0	146.0	12.7	-- <sup>b</sup>	--				
1-Methylnaphthalene (0.4)	3.4	5.1	3.2	1.1	3.0	10.2	1.7	2.2	10.8	4.0	53.5	6.0	--	--				
2-Methylnaphthalene (0.4)	9.3	11.4	8.8	3.5	8.4	20.0	6.1	4.7	22.1	11.6	150.7	12.1	--	--				
Quinoline (0.4)	--	--	--	--	0.8	2.0	--	--	0.5	0.6	5.4	--	--	--				
Acenaphthalene (0.4)	--	--	--	--	--	--	--	--	--	--	9.0	--	--	--				
Acenaphthene (0.4)	--	0.5	0.5	--	0.6	3.0	--	0.4	1.9	0.6	5.6	0.8	--	--				
Fluorene (0.4)	0.4	0.4	0.6	--	0.5	2.0	--	--	1.1	0.5	11.3	1.0	--	--				
Phenanthrene/Anthracene (0.4)	0.6	0.6	1.5	0.4	0.8	2.2	--	0.4	1.2	0.6	7.2	2.0	--	--				
Acridine (0.4)	--	--	--	--	--	--	--	--	--	--	--	0.5	0.059	0.216				
Carbazole (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Fluoranthene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Pyrene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Benzo(a)fluorene/ Benzo(b)fluorene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Benzo(a)anthracene/Chrysene/ Triphenylene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Benzo(j)fluoranthene/ Benzo(h)fluoranthene/ Benzo(k)fluoranthene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Benzo(e)pyrene/ Benzo(a)pyrene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Perylene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Dibenz(a,j)acridine (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Dibenz(a,i)carbazole (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Indene(1,2,3-cd)pyrene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Dibenz(a,h)anthracene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Benzo(g,h,i)perylene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Coronene (1.6)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Dibenz(a,i)pyrene (1.6)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
Dimethylbenz(a)anthracene (0.4)	--	--	--	--	--	--	--	0.5	--	--	--	--	--	--				
3-Methylcholanthrene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
6,13-Dimethylbenz(a,h)- anthracene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--				
TOTAL	25.5	19.9	26.2	10.4	30.5	110.3	14.8	15.9	107.5	72.8	389.4	35.1	0.059	0.216				

<sup>a</sup> Assuming a sample volume of 600 liters.<sup>b</sup> "--" indicates not detected.

Table B-13. Plant B Wipe and Bulk Sampling Analytical Results for PNAs (August 20, 1980; April 28-May 1, 1981)

Compound	Sample Site:	Wipe Samples																		Bulk Samples	
		Equipment					Tools			Clothing						Control Room				S	T
		A	D	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R		
		Sample Number:	2-036	2-019	2-018	2-017	046	1-017	1-018	1-073	040	041	042	043	1-027	1-028	1-075	1-019	045		
Date Collected:	4/29*	4/28*	4/28*	4/28*	8/20†	4/28*	4/28*	5/1*	8/20†	8/20†	8/20†	8/20†	4/29*	4/29*	5/1*	4/28*	8/20†	8/20†	5/1*	5/1*	
Naphthalene	●	●	●	●	-	●	●	●	-	-	-	-	●	●	●	●	-	-	●	●	
1-Methylnaphthalene	-	●	●	-	-	●	-	●	-	-	-	-	●	-	-	●	-	-	●	●	
2-Methylnaphthalene	-	●	●	-	-	●	-	●	-	-	-	-	●	-	-	●	-	-	●	●	
Quinoline	-	-	-	-	-	-	-	-	-	-	-	-	●	-	-	-	-	-	-	-	
Acenaphthalene	-	-	-	-	-	●	-	-	-	-	-	-	●	-	-	-	-	-	●	●	
Acenaphthene	-	-	●	-	-	●	●	●	-	-	-	-	●	●	-	-	-	-	●	●	
Fluorene	-	●	-	-	-	●	-	-	-	-	-	-	●	●	-	●	-	-	●	●	
Phenanthrene/Anthracene	●	●	●	●	●	●	●	●	●	●	-	-	●	●	●	●	●	-	●	●	
Acridine	-	-	-	-	-	-	-	-	-	-	-	-	●	-	-	-	-	-	●	●	
Carbazole	-	-	-	-	-	-	-	-	-	-	-	-	●	-	-	-	-	-	●	●	
Fluoranthene	●	●	●	●	-	●	●	●	●	-	-	-	●	●	●	●	-	-	●	●	
Pyrene	●	●	●	●	-	●	●	●	●	●	-	-	●	●	●	●	-	-	●	●	
Benzo (a) fluorene/ Benzo (b) fluorene	-	●	-	-	-	●	-	●	-	-	-	-	●	●	-	-	-	-	●	●	
Benzo (a) anthracene/ Chrysene/Triphenylene	●	●	●	●	-	●	●	●	●	-	-	-	●	●	●	●	-	-	●	●	
Benzo (j) fluoranthene/ Benzo (b) fluoranthene/ Benzo (k) fluoranthene	-	-	-	-	■	●	-	-	■	■	■	■	●	-	-	-	■	■	●	●	
Benzo (c) pyrene/ Benzo (a) pyrene	-	-	-	-	-	●	-	-	-	-	-	-	●	●	-	-	-	-	●	●	
Perylene	-	-	-	-	-	●	-	-	-	-	-	-	●	-	-	-	-	-	-	-	
Dibenz (a, j) acridine	-	-	-	-	-	●	-	-	-	-	-	-	-	-	-	-	-	-	●	●	
Dibenz (a, i) carbazole	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Indeno (1, 2, 3-cd) pyrene	-	-	-	-	-	●	-	-	-	-	-	-	●	-	-	-	-	-	●	●	
Dibenz (a, h) anthracene	-	-	-	-	-	-	-	-	-	-	-	-	●	-	-	-	-	-	-	●	
Benzo (g, h, i) perylene	-	-	-	-	-	●	-	●	-	-	-	-	●	●	-	-	-	-	●	●	
Coronene	-	-	-	-	-	-	-	-	-	-	-	-	●	-	-	-	-	-	●	-	
Dibenz (a, i) pyrene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	●	-	
Dimethylbenz (a) anthracene	-	-	-	-	■	-	-	-	■	■	■	■	■	-	-	-	■	■	●	-	
3-Methylcholanthrene	-	-	-	-	■	-	-	-	■	■	■	■	-	-	-	-	■	■	●	-	
6, 11-Dimethyldibenz (a, j) - anthracene	-	-	-	-	■	-	-	-	■	■	■	■	-	-	-	-	■	■	●	-	

Key: \*1981. †1980. • = compound detected. - = compound not detected. • = samples not analyzed for these compounds.

#### Equipment

A = oil/liquor separator, weir handle  
B = handrail above compressor  
C = handrail below Stretford unit  
D = handrail on top of gasifier  
E = side of gasifier

#### Tools

F = used on tar pump  
G = stored in control room  
H = used on gas compressor

#### Clothing

I = rubber glove, outside surface  
J = rubber glove, outside surface  
K = rubber glove, inside surface  
L = rubber glove, inside surface  
M = gloves of millwright at tar pump  
N = trousers (under coveralls) of tar pump worker

#### Control Room

O = bathroom handles  
P = desk top  
Q = desk top  
R = stair rail

#### Bulk Samples

S = tar from day tar tank  
T = oil from day oil tank

Table B-14. Plant B Area Sampling Analytical Results (mg/m<sup>3</sup>) for Aromatic Amines (August 18-19, 1980) (sampling method compromised by humidity)

Location Sampled	Sample Number	Sample Volume (L)	Sampling Time	Date Collected	Aromatic Amine <sup>a</sup> (detection limit, mg/m <sup>3</sup> )								
					A (0.5)	B (0.2)	C (0.3)	D (0.2)	E (0.3)	F (0.3)	G (0.5)	H (0.1)	I (0.1)
Top of Gasifier (475 level)	006	433	2133-0534	8/18/80	" <sup>b</sup>	"	"	"	"	"	"	-- <sup>c</sup>	--
Top of Gasifier	008	96	2157-0558	8/18/80	--	--	--	--	--	--	--	--	--
Poke Hole (455 level)	010	432	2136-0536	8/18/80	"	"	"	"	"	"	"	--	--
Poke Hole	012	97	2207-0614	8/18/80	--	--	--	--	--	--	--	--	--
Between Detarrer and Deoiler (448 level)	022	350	2118-0435	8/19/80	"	"	"	"	"	"	"	--	--
Washer (448 level)	025	434	2121-0435	8/19/80	"	"	"	"	"	"	"	--	--
Blanks (mg/sample)	030			8/19/80	--	--	--	--	--	--	--	--	--
	031			8/19/80	"	"	"	"	"	"	"	--	--
	033			8/19/80	--	--	--	--	--	--	--	--	--
	039			8/19/80	"	"	"	"	"	"	"	--	--

<sup>a</sup> Aromatic amines: A = Aniline; B = N,N-Dimethylaniline; C = o-Toluidine; D = 2,4-Dimethylaniline; E = o-Anisidine; F = p-Anisidine; G = p-Nitroaniline; H = 1-Naphthylamine; I = 2-Naphthylamine.

<sup>b</sup> "n" indicates sample not analyzed for this compound. <sup>c</sup> "--" indicates not detected.

Table B-15. Plant B Area Sampling Analytical Results (ppm) for Benzene, Toluene, and Xylene (August 18-19, 1980; April 27-30, 1981)

Sample Location	Sample Number	Sample Volume (L)	Sampling Time	Date Collected	Compound (detection limit, ppm) <sup>a</sup>		
					Benzene (0.01)	Toluene (0.02)	Xylene (0.02)
Deoiler/Detarrer	023	87	2119-0435	8/19/80	-- <sup>b</sup>	--	--
	024	87	2120-0435	8/19/80	--	--	--
	2-002	103	1447-2248	4/27/81	--	--	--
	2-009	100	1530-2248	4/28/81	--	--	--
	3-058	13	0512-0608	4/30/81	--	--	--
Top of Gasifier	007	96	2156-0557	8/18/80	--	--	--
	2-001	81	1444-2250	4/27/81	--	--	--
	2-008	94	1529-2247	4/28/81	--	--	--
Poke Hole	011	98	2205-0613	8/18/80	--	--	--
	2-030	65	1705-2240	4/29/81	--	--	--
	3-042	84	0012-0720	4/30/81	--	--	--
Oil/Liquor Separator	2-031	90	1518-2241	4/29/81	--	--	--
Day Tar/Oil Tank	2-004	97	1455-2254	4/27/81	--	--	--
Compressor	2-003	92	1453-2253	4/27/81	--	--	--
	2-010	85	1532-2245	4/28/81	--	--	--
Sump Blowdown	2-005	105	1259-2254	4/27/81	--	--	--
	2-029	96	1525-2244	4/29/81	--	--	--
Stretford Unit	2-032	100	1521-2242	4/29/81	--	--	--
	3-044	81	0018-0720	4/30/81	--	--	--
Control Room	2-033	85	1527-2237	4/29/81	--	--	--
	3-043	85	0010-0722	4/30/81	--	--	--
Blanks (ug/sample)	030			8/19/80	2.2	--	--
	032			8/19/80	1.4	0.2	--

<sup>a</sup> Assuming a sample volume of 90 liters.

<sup>b</sup> "--" indicates not detected.

Table B-16. Plant B Personal Sampling Analytical Results (ppm) for Benzene, Toluene, and Xylene (April 27-May 1, 1981)

Personnel Sampled	Sample Number	Sample Volume (l)	Sampling Time	Date Collected	Compound (detection limit, ppm) <sup>a</sup>		
					Benzene (0.01)	Toluene (0.02)	Xylene (0.02)
Operator	2-011	81.7	1553-2247	4/28/81	-- <sup>b</sup>	--	--
Operator	1-021	96.3	0742-1503	4/29/81	--	--	--
Operator	3-038	83.6	1135-1855	4/30/81	--	--	--
Operator	1-062	82.3	0750-1457	5/1/81	--	--	--
Millwright	1-009	76.6	0753-1334	4/28/81	--	--	--
Utility Helper	2-007	79.7	1546-2240	4/27/81	--	--	--
Utility Helper	2-035	85.5	1559-2233	4/29/81	--	--	--
Utility Helper	3-045	85.9	0032-0706	4/30/81	--	--	--
Utility Helper	1-040	82.3	0746-1445	4/30/81	--	--	--
Maintenance	2-012	74.2	1554-2247	4/28/81	--	0.3	--
Maintenance	1-060	75.8	0800-1345	5/1/81	--	--	--
Blanks	0-049				--	--	--
	0-050				--	--	--
	0-051				--	--	--

<sup>a</sup> Assuming a sample volume of 80 liters.

<sup>b</sup> "--" indicates not detected.

Table B-17. Plant B Area Sampling Analytical Results (mg/m<sup>3</sup>) for Mercaptans (August 20, 1980; April 28, 1981)

Sample Site	Sample Number or Type	Sample Volume (l)	Sampling Time	Date Collected	Compound (detection limit)			
					Total mercaptan (2 ppm)	n-Propyl mercaptan (0.4 mg/m <sup>3</sup> )	n-Butyl mercaptan (0.4 mg/m <sup>3</sup> )	n-Amyl mercaptan (0.4 mg/m <sup>3</sup> )
Stretford Oxidizer	Detector tube			8/20/80	-- <sup>a</sup>			
Wash Settling Tank	Detector tube			8/20/80	16 <sup>b</sup>			
	Detector tube			8/20/80	16			
	2-041	2.8	1702-1802	4/28/81		--	--	--
	2-015	3.1	1845-1945	4/28/81		--	--	--
	2-016	3.8	2100-2205	4/28/81		--	--	--
Top of Gasifier	Detector tube			8/20/80	--			
Poke Hole	Detector tube			8/20/80	--			
Deciler/Detarrer	Detector tube			8/20/80	--			
	Detector tube			8/20/80	--			
Ash Pan	Detector tube			8/20/80	--			

<sup>a</sup> "--" indicates compound not detected.

<sup>b</sup> In ppm.

Table B-18. Plant B Area Sampling Analytical Results (ppm) for  
Toxic Gases (August 18-22, 1980; April 27-May 1, 1981)

Sample Site	Compound (detection limit, ppm)		
	Hydrogen cyanide (0.01)	Hydrogen sulfide (1)	Carbon monoxide (3)
Stretford Unit Adsorber		-- <sup>a</sup>	--
Stretford Unit Oxidizer	--	--	--
	2	--	--
	0.12		
	--		
	--		
Wash Settling Tank	--	2	--
Wash Column	--	--	--
Top of Gasifier	--	--	--
			10
Poke Hole	--	--	8
			--
			10
Deoiler/Detarrer	--	--	--
		--	--
Ash Pan	--	--	--

<sup>a</sup>-- indicates not detected.

Table B-19. Plant B Area Sampling Analytical Results (mg/m<sup>3</sup>) for Trace Metals (August 18-19, 1980)

Location Sampled:	Front End of Conveyor Belt (521 level)	Ash Pan (439 level)	Middle of Conveyor Belt (521 level)	Ash Pan (439 level)	Blanks (mg/sample)	
Sample Number:	001	014	018	028	027	036
Sample Volume (l):	964	925	966	912		
Sampling Time:	2150-0552	2214-0621	2130-0533	2132-0532		
Date Collected:	8/18/80	8/18/80	8/19/80	8/19/80	8/19	8/19
Compound (detection limit, mg/m <sup>3</sup> )						
Beryllium (0.001)	-- <sup>a</sup>	--	--	--	--	--
Cadmium (0.005)	--	--	--	--	--	--
Tellurium (0.001)	--	--	--	--	--	--
Copper (0.005)	--	--	--	--	--	--
Manganese (0.001)	--	--	--	--	--	--
Nickel (0.001)	--	--	--	--	--	--
Arsenic (0.001)	--	--	--	--	--	--
Strontium (0.1)	--	--	--	--	--	--
Magnesium (0.05)	--	--	--	--	--	--
Mercury (0.005)	--	--	--	--	--	--

<sup>a</sup>-- indicates not detected.

Table B-20. Plant B Bulk Sampling Analytical Results (% by weight) for Trace Metals (August 19, 1980)

Bulk Sample:	Coal	Ash
Sample Number:	037	038
Date Collected:	8/19/80	8/19/80
Compound		
Beryllium	0.001	-- <sup>a</sup>
Cadmium	0.00006	0.0004
Tellurium	--	0.00007
Copper	0.0014	0.0024
Manganese	0.0008	0.0004
Nickel	0.0015	0.0032
Arsenic	0.0008	0.0010
Strontium	0.0026	0.0124
Magnesium	0.0423	0.0374
Mercury	0.00008	0.00004

<sup>a</sup>-- indicates not detected.

Table B-21. Plant B Area Sampling Analytical Results for Ionizing Radiation (August 18-19, 1980)

Sample Location or Type	Sample Number	Sample Volume (L)	Sampling Time	Date Collected	Ionizing Radiation (detection limit, pCi/filter)	
					Gross alpha (0.1)	Gross beta/gamma (0.5)
Front End of Conveyor Chute (521 level)	004	819	2153-0555	8/18/80	background <sup>a</sup>	-- <sup>b</sup>
Ash Pan (439 level)	016	980	2211-0621	8/18/80	--	--
Blanks	029			8/19/80	background	--
	034			8/19/80	background	--
Bulk Coal <sup>c</sup>	037			8/19/80	--	--
Bulk Ash <sup>c</sup>	038			8/19/80	--	--

<sup>a</sup>Background is 5 to 10 counts per 100 minutes.

<sup>c</sup>Values are in pCi/gram.

<sup>b</sup>--" indicates radiation type not detected.



PLANT C  
FLUIDIZED BED GASIFICATION

Table B-22.	Plant C Area Sampling Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for PNAs (May 15-17, 1981; June 22-23, 1981).....	B-23
Table B-23.	Plant C Personal Sampling Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for PNAs (May 14-16, 1981; June 22, 1981).....	B-25
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Table B-22. Plant C Area Sampling Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for PNAs (May 15-17, 1981; June 22-23, 1981)

Location Sampled:	Control Room				Gas Compressor				5th Level - Sample Port		
Sample Number:	3-026	3-112	3-113	3-154	3-033	3-117	3-150	3-149	3-103	3-104	3-115
Sample Volume (l):	1,758	1,463	1,476	1,476	1,602	1,469	959	1,411	1,442	1,442	1,464
Sampling Time:	0810-2051	1215-2245	1230-2245	1150-2205	0815-2136	1245-2257	0013-0710	0013-1010	0755-1756	0755-1756	1240-2250
Date Collected:	5/15/81	6/22/81	6/22/81	6/22/81	5/15/81	6/22/81	6/23/81	6/23/81	6/22/81	6/22/81	6/22/81
Compound (detection limit, $\mu\text{g}/\text{m}^3$ ) <sup>a</sup>											
Naphthalene (0.1)	0.1	2.1	2.6	2.6	-- <sup>b</sup>	0.3	1.3	2.9	0.2	0.7	0.3
1-Methylnaphthalene (0.1)	0.1	0.7	0.8	0.7	--	--	--	0.6	--	--	--
2-Methylnaphthalene (0.1)	0.2	2.2	2.5	1.2	0.1	0.2	0.5	1.1	--	0.1	0.3
Quinoline (0.1)	--	--	--	--	--	--	--	--	--	--	--
Acenaphthalene (0.1)	--	--	--	--	--	--	--	0.2	--	--	--
Acenaphthene (0.1)	--	0.1	0.2	0.1	--	--	--	--	--	--	--
Fluorene (0.1)	--	0.1	0.1	0.1	--	--	--	--	--	--	0.1
Phenanthrene/Anthracene (0.1)	--	--	--	0.4	0.4	0.3	0.6	0.3	--	--	0.4
Acridine (0.1)	--	--	0.2	--	0.1	--	--	--	--	0.2	--
Carbazole (0.1)	--	--	--	--	--	--	--	--	--	--	--
Fluoranthene (0.1)	--	--	--	--	--	--	0.3	0.2	--	--	--
Pyrene (0.1)	--	--	--	--	--	--	0.4	0.3	--	--	--
Benzo(a)fluorene/ Benzo(b)fluorene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Benzo(a)anthracene/Chrysene/ Triphenylene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Benzo(j)fluoranthene/ Benzo(b)fluoranthene/ Benzo(k)fluoranthene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Benzo(a)pyrene/ Benzo(a)pyrene (0.1)	--	--	--	--	--	--	--	0.1	--	--	--
Perylene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,j)acridine (0.1)	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,l)carbazole (0.1)	--	--	--	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,h)anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Benzo(g,h,i)perylene (0.1)	--	--	--	--	--	--	--	0.1	--	--	--
Coronene (0.6)	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,l)pyrene (0.6)	--	--	--	--	--	--	--	--	--	--	--
Dimethylbenz(a)anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--
1-Methylcholanthrene (0.1)	--	--	--	--	--	--	--	--	--	--	--
6,12-Dimethyldibenz(a,h)- anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--
TOTAL	0.4	5.2	6.4	5.1	0.6	0.8	3.1	5.0	0.2	1.0	1.1

<sup>a</sup> Assuming a sample volume of 1,500 liters.

<sup>b</sup> "--" indicates not detected.

(continued)

Table B-22 (concluded)

Location Sampled:	Asifler - 6th Level				Filter/Strainer		Upwind			Blanks (µg/sample)	
Sample Number:	3-030	3-114	3-083†	3-085†	3-116	3-148	3-062	3-091	3-150	3-037	3-119
Sample Volume (l):	1,767	1,398	294	425	1,469	1,435	1,550	1,620	1,404		
Sampling Time:	0800-	1240-	2020-	2024-	1245-	0012-	0755-	0927-	0015-		
	2123	2248	2350	0312	2057	1010	1015	2015	1000		
Date Collected:	5/15/81	6/22/81	5/16/81	5/16/81	6/22/81	6/23/81	5/16/81	5/17/81	6/23/81	5/15/81	6/22/81
Compound (detection limit, µg/m <sup>3</sup> ) <sup>a</sup>											
Naphthalene (0.1)	0.4	0.7	74.4	6.8	0.3	1.0	0.6	1.8	0.4	2.8	0.4
1-Methylnaphthalene (0.1)	-- <sup>b</sup>	0.2	--	--	--	0.2	0.1	0.2	--	0.6	--
2-Methylnaphthalene (0.1)	0.2	0.9	1.0	--	--	0.6	0.2	0.2	--	2.0	--
Quinoline (0.1)	--	--	--	--	--	--	--	--	--	--	--
Acenaphthalene (0.1)	--	--	0.9	--	--	--	--	--	--	--	--
Acenaphthene (0.1)	--	--	--	--	--	--	--	--	--	0.2	--
Fluorene (0.1)	--	0.2	--	--	--	--	--	0.1	--	0.6	--
Phenanthrene/Anthracene (0.1)	--	0.7	--	--	0.1	--	0.2	0.5	--	2.6	0.2
Acridine (0.1)	--	--	--	--	--	--	--	--	--	--	--
Carbazole (0.1)	--	--	--	--	--	--	--	--	--	--	--
Fluoranthene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Pyrene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Benzo(a)fluorene/ Benzo(b)fluorene (0.1)	--	--	--	--	0.1	--	--	--	--	--	--
Benz(a)anthracene/Chrysene/ Triphenylene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Benzo(j)fluoranthene/ Benzo(b)fluoranthene/ Benzo(k)fluoranthene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Benzo(e)pyrene/ Benzo(a)pyrene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Perylene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,j)acridine (0.1)	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,i)carbazole (0.1)	--	--	--	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,h)anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Benzo(g,h,i)perylene (0.1)	--	--	--	--	--	--	--	--	--	--	--
Coronene (0.6)	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,i)pyrene (0.6)	--	--	--	--	--	--	--	--	--	--	--
Dimethylbenz(a)anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--
3-Methylcholanthrene (0.1)	--	--	--	--	--	--	--	--	--	--	--
6,11-Dimethyldibenz(a,h)- anthracene (0.1)	--	--	--	--	--	--	--	--	--	--	--
TOTAL	0.6	2.7	76.3	6.8	0.5	1.0	1.1	2.8	0.4	8.8	0.6

<sup>a</sup> Assuming a sample volume of 1,500 liters.<sup>b</sup> "--" indicates not detected.

†Area samples taken with two-stage personal cassettes.

Table B-23. Plant C Personal Sampling Analytical Results ( $\mu\text{g}/\text{m}^3$ ) for PNAs (May 14-16, 1981; June 22, 1981)

Personnel Sampled:	Lower Level Technicians						Upper Level Technicians						Maintenance	Blanks ( $\mu\text{g}/\text{sample}$ )	
Sample Number:	3-002	3-018	3-059	3-138	3-141	3-095	3-004	3-016	3-056	3-094	3-137	3-119	3-007	3-016	3-120
Sample Volume (l):	664	668	597	656	692	602	650	657	412	690	669	645	462		
Sampling Time:	1525-	0730-	0737-	1540-	2329-	0740-	1536-	0737-	0740-	0735-	1540-	2335-	2014-		
Date (1981) Collected:	5/14	5/15	5/16	6/22	6/22	6/22	5/14	5/16	5/16	6/22	6/22	6/22	5/16	5/15	6/22
Compound (detection limit, $\mu\text{g}/\text{m}^3$ ) <sup>b</sup>															
Naphthalene (0.4)	4.2	-- <sup>a</sup>	18.6	2.0	2.8	1.4	1.3	1.0	7.0	0.9	0.6	94.3	49.3	0.1	--
1-Methylnaphthalene (0.4)	0.8	--	2.7	0.4	--	0.6	--	--	1.0	--	--	12.1	2.3	--	--
2-Methylnaphthalene (0.4)	1.4	--	3.4	0.8	0.5	0.7	0.4	0.5	2.0	--	--	17.3	3.7	1.7	--
Quinoline (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Acenaphthalene (0.4)	--	--	1.2	--	--	--	--	--	--	--	--	20.1	0.6	--	--
Acenaphthene (0.4)	--	--	0.6	--	--	--	--	--	--	--	--	2.6	0.6	--	--
Fluorene (0.4)	0.5	--	0.7	--	--	--	--	--	--	--	--	7.1	0.7	--	--
Phenanthrene/Anthracene (0.4)	2.4	0.6	4.4	0.6	0.5	--	0.9	1.0	1.9	--	--	27.0	3.2	--	--
Acridine (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Carbazole (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Fluoranthene (0.4)	--	--	1.7	--	--	--	--	--	--	--	--	12.9	--	--	--
Pyrene (0.4)	--	--	2.2	--	--	--	--	--	--	--	--	14.9	--	--	--
Benzo(a)fluorene/ Benzo(b)fluorene (0.4)	--	--	0.9	--	--	--	--	--	--	--	--	2.4	--	--	--
Benzo(a)anthracene/Chrysene/ Triphenylene (0.4)	--	--	3.9	--	--	--	--	--	1.7	--	--	2.2	--	--	--
Benzo(j)fluoranthene/ Benzo(b)fluoranthene/ Benzo(k)fluoranthene (0.4)	--	--	1.0	--	--	--	--	--	--	--	--	3.0	--	--	--
Benzo(e)pyrene/ Benzo(a)pyrene (0.4)	--	--	0.7	--	--	--	--	--	--	--	--	5.2	--	--	--
Perylene (0.4)	--	--	--	--	--	--	--	--	--	--	--	2.0	--	--	--
Dibenz(a,j)acridine (0.4)	--	--	--	--	--	--	--	--	--	--	--	1.1	--	--	--
Dibenz(a,i)carbazole (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene (0.4)	--	--	0.4	--	--	--	--	--	--	--	--	1.3	--	--	--
Dibenz(a,h)anthracene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzo(g,h,i)perylene (0.4)	--	--	0.7	--	--	--	--	--	--	--	--	2.5	--	--	--
Coronene (1.6)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,i)pyrene (1.6)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Dimethylbenz(a)anthracene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
3-Methylcholanthrene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
6,13-Dimethyldibenz(a,h)- anthracene (0.4)	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
TOTAL	9.3	0.6	43.1	3.8	3.8	2.7	2.6	2.5	13.6	0.9	0.6	228.0	60.4	1.8	--

<sup>a</sup> Pump taken off employee early since he claimed pump was interfering with ability to do job.

<sup>b</sup> Assuming a sample volume of 700 liters.

-- indicates not detected.

Table B-24. Plant C Air Sampling Analytical Results for PNAs (May 15-18, 1981)

Sample Site:	Equipment <sup>a</sup>							Tools <sup>b</sup>			Clothing <sup>c</sup>		
	A	B	C	D	E	F	G	H	I	J	K	L	M
	3-051	3-072	3-073	3-074	3-075	3-076	3-090	3-052	3-051	3-000	3-015	3-092	3-091
Date Collected:	5/15/81	5/16/81	5/16/81	5/16/81	5/16/81	5/16/81	5/17/81	5/15/81	5/15/81	5/16/81	5/15/81	5/16/81	5/16/81
Compound													
Naphthalene	-- <sup>d</sup>	• <sup>e</sup>	•	•	•	--	•	--	•	--	•	•	•
1-Methylnaphthalene	--	--	--	--	--	--	--	--	--	--	--	--	•
2-Methylnaphthalene	--	--	--	--	--	--	--	--	--	--	--	--	•
Quinoline	--	--	--	--	--	--	--	--	--	--	--	--	--
Acenaphthalene	--	--	•	--	--	--	--	--	--	--	--	--	•
Acenaphthene	--	--	•	--	--	--	--	--	--	--	--	--	•
Fluorene	--	--	•	--	--	--	--	--	--	--	--	--	•
Phenanthrene/Anthracene	--	--	•	•	--	--	•	--	--	•	•	•	•
Acridine	--	--	--	--	--	--	--	--	--	--	--	--	--
Carbazole	--	--	--	--	--	--	--	--	--	--	--	--	•
Fluoranthene	--	--	•	•	--	--	•	--	--	•	•	•	•
Pyrene	--	•	•	•	--	•	•	--	•	•	•	•	•
Benzo(a)fluorene/ Benzo(b)fluorene	--	--	--	--	--	--	--	--	--	--	--	--	•
Benzo(a)anthracene/ Chrysene/Triphenylene	--	--	--	•	--	--	--	--	--	--	•	--	•
Benzo(j)fluoranthene/ Benzo(b)fluoranthene/ Benzo(k)fluoranthene	--	--	•	--	--	--	--	--	--	--	•	--	•
Benzo(e)pyrene/ Benzo(a)pyrene	--	--	•	--	--	--	--	--	--	--	•	--	•
Perylene	--	--	--	--	--	--	--	--	--	--	•	--	•
Dibenz(a,j)acridine	--	--	--	--	--	--	--	--	--	--	--	--	--
Dibenz(a,i)carbazole	--	--	--	--	--	--	--	--	--	--	--	--	--
Indeno(1,2,3-cd)pyrene	--	--	--	--	--	--	--	--	--	--	--	--	•
Dibenz(a,h)anthracene	--	--	--	--	--	--	--	--	--	--	--	--	•
Benzo(g,h,i)perylene	--	--	--	--	--	--	--	--	--	--	--	--	•
Coronene	--	--	--	--	--	--	--	--	--	--	--	--	•
Dibenz(a,i)pyrene	--	--	--	--	--	--	--	--	--	--	--	--	--
Dimethylbenz(a)anthracene	--	--	--	--	--	--	--	--	--	--	--	--	--
3-Methylcholanthrene	--	--	--	--	--	--	--	--	--	--	--	--	--
6,11-Dimethyldibenz(a,j)- anthracene	--	--	--	--	--	--	--	--	--	--	--	--	--

<sup>a</sup> Equipment key: A = lift truck steering wheel; B = sample port, 5th level; C = separator pit; D = filter housing; E = pipe duct (between gasifier and cyclone); F = control room desk top; G = work platform gasifier.

<sup>b</sup> Tools key: H = wrench at ground level sample port; I = wrench at filter; J = wrench at top of gasifier.

<sup>c</sup> Clothing key: K = gloves of lower level technician; L = coveralls of upper level technician; M = coveralls of lower level technician.

<sup>d</sup> "--" indicates compound not detected.

<sup>e</sup> "•" indicates compound detected.

Table B-25. Plant C Area Sampling Analytical Results (mg/m<sup>3</sup>) for Aromatic Amines (May 14-16, 1981; June 22-23, 1981) (sampling method compromised by humidity)

Location Sampled	Sample Number	Sample Volume (L)	Sampling Time	Date Collected	Aromatic Amine <sup>2</sup> (detection limit, mg/m <sup>3</sup> ) <sup>3</sup>					
					A (0.01)	B (0.01)	C (0.01)	D (0.01)	E (0.01)	F (0.01)
Make-up Pumps	3-006	71	1618-2231	5/14/81	-- <sup>c</sup>	--	--	--	--	--
	3-045	89	1546-2312	5/15/81	--	--	--	--	--	--
	3-060*	18	0810-1200	5/16/81	--	--	--	--	--	--
	3-107	88	0804-1545	6/22/81	--	--	--	--	--	--
Separator Pit	3-046	88	1532-2310	5/15/81	--	--	--	0.01	0.04	--
	3-061*	94	0810-1612	5/16/81	--	--	--	--	--	--
	3-132	115	1546-0154	6/22/81	--	--	--	--	--	--
Sample Port	3-010	58	1555-2100	5/14/81	--	--	--	--	--	--
	3-042	84	1526-2257	5/15/81	--	--	--	--	--	--
	3-066*	66	0810-1600	6/23/81	--	--	--	--	--	--
5th Level/ Cyclone	3-011	76	1630-2235	5/14/81	--	--	--	--	--	--
	3-067*	73	0810-1614	5/16/81	--	0.01	--	0.01	0.03	--
	3-144	65	0003-0802	6/23/81	--	--	--	--	--	--
6th Level/ Gasifier	3-041	10	1511-2250	5/15/81	--	--	--	--	--	--
	3-068*	73	0810-1418	5/16/81	0.01	0.01	--	0.01	--	--
	3-143	96	0002-0800	6/23/81	--	--	--	0.01	--	--
Compressor Pump/Filters	3-009	78	1620-2201	5/14/81	--	--	--	--	--	0.09
	3-044	95	1523-2258	5/15/81	--	--	--	--	--	--
	3-049	2.2	1731-1742	5/15/81	--	--	--	--	--	--
	3-065*	73	0810-1415	5/16/81	--	--	--	--	--	--
	3-109	80	0825-1505	6/22/81	--	--	--	--	--	--
	3-110	80	0825-1505	6/22/81	--	--	--	--	--	--
Control Room	3-001	90	1500-2255	5/14/81	--	--	--	--	--	--
	3-043	82	1552-2313	5/15/81	--	--	--	--	--	--
	3-063*	74	0755-1415	5/16/81	--	--	--	--	--	--
	3-111	81	0830-1505	6/22/81	--	0.01	--	--	--	--
	3-101	100	0745-1550	6/22/81	--	--	--	--	--	--
	3-100	93	0745-1550	6/22/81	--	0.1	--	--	--	--
Blanks (mg/sample)	3-040			5/15/81	--	--	--	--	--	--
	3-078			5/16/81	--	--	--	--	--	--
	3-123			6/22/81	--	--	--	--	--	--

<sup>2</sup> Aromatic amines: A = Aniline; B = N,N-Dimethylaniline; C = o-Toluidine; D = 2,4-Dimethylaniline; E = o-Anisidine; F = p-Anisidine.

<sup>3</sup> Assuming a sample volume of 100 liters.

<sup>c</sup> -- indicates not detected.

\*Plant down.

Table B-26. Plant C Area Sampling Analytical Results (ppm) for Benzene, Toluene, and Xylene (May 15-16, 1981; June 22-23, 1981)

Location Sampled	Sample Number	Sample Volume (l)	Sampling Time	Date Collected	Compound (detection limit, ppm) <sup>a</sup>		
					Benzene (0.01)	Toluene (0.01)	Xylene (0.01)
Char Sample Port	3-027	87	0810-1519	5/15/81	0.01	-- <sup>b</sup>	--
5th Level	3-031	83	0805-1517	5/15/81	0.02	--	--
	3-130	125	1540-0200	6/22/81	--	--	--
6th Level	3-029	89	0800-1513	5/15/81	--	--	--
	3-082	84	2023-0312	5/16/81	--	--	--
	3-084	52	1031-1510	5/16/81	--	--	--
	3-129	124	1536-0158	6/22/81	--	--	--
Gas Compressor	3-032	88	0815-1518	5/15/81	--	--	--
	3-126	131	1508-0205	6/22/81	--	--	--
	3-151	95	0013-0810	6/23/81	0.05	--	--
	3-152	95	0014-0810	6/23/81	0.04	--	--
Filters	3-050	2.2	1830-1842	5/15/81	8.2	--	--
	3-125	129	1507-0210	6/22/81	0.04	--	--
	3-147	84	0012-0810	6/23/81	0.1	--	--
Control Room	3-023	64	0830-1600	5/15/81	0.2	--	--
	3-134	120	1548-0148	6/22/81	0.4	--	--
	3-156	96	2350-0750	6/22/81	0.4	--	--
	3-157	96	2350-0750	6/22/81	0.5	--	0.1
Blanks (ppm/sample)	3-038			5/15/81	--	--	--
	3-077			5/16/81	--	--	--
	3-121			6/22/81	--	--	--

<sup>a</sup> Assuming a sample volume of 100 liters.

<sup>b</sup> "--" indicates not detected.

Table B-28. Plant C Area Sampling Analytical Results (mg/m<sup>3</sup>) for Phenolic Compounds (May 14-16, 1981; June 22-23, 1981)  
(sampling system complicated by humidity)

Location Sampled	Sample Number	Sample Volume (l)	Sampling Time	Date Collected	Phenolic Compound <sup>2</sup> (detection limit, µg/m <sup>3</sup> ) <sup>3</sup>							
					A (0.02)	B (0.02)	C (0.02)	D (0.02)	E (0.02)	F (4.0)	G (0.02)	H (4.0)
Make-up Pumps	3-007	74	1614-2230	5/14/81	-- <sup>a</sup>	--	--	--	--	--	--	--
	3-047	86	1540-2312	5/15/81	--	--	--	--	--	--	--	--
	3-106	87	0804-1545	6/22/81	--	--	--	--	--	--	--	--
Separator Pit	3-008	69	1612-2229	5/14/81	--	--	--	--	--	--	--	--
	3-048	87	1535-2310	5/15/81	--	--	--	--	--	--	--	--
	3-146	84	0008-0710	6/23/81	--	--	--	--	--	--	--	--
5th Level	3-124	93	0755-1540	6/22/81	--	--	--	--	--	--	--	--
	3-131	125	1540-1400	6/22/81	--	--	--	--	--	--	--	--
6th Level	3-102	95	0752-1545	6/22/81	--	--	--	--	--	--	--	--
	3-128	124	1536-0158	6/22/81	--	--	--	--	--	--	--	--
Gas Compressor	3-108	80	0825-1505	6/22/81	--	--	--	--	--	--	--	--
	3-127	128	1508-0205	6/22/81	--	--	--	--	--	--	--	--
Control Room	3-098	95	0745-1550	6/22/81	--	--	--	--	--	--	--	--
	3-099	58	0745-1550	6/22/81	--	--	--	--	--	--	--	--
	3-133	119	1548-0148	6/22/81	--	--	--	--	--	--	--	--
	3-155	96	2350-0750	6/22/81	--	--	--	--	--	--	--	--
Blanks (mg/sample)	3-039			5/15/81	--	--	--	--	--	--	--	--
	3-079			5/16/81	--	--	--	--	--	--	--	--
	3-122			6/22/81	--	--	--	--	--	--	--	--

<sup>a</sup> Phenolic compounds: A = Phenol; B = o-Cresol; C = m-Cresol; D = p-Cresol; E = o-Ethylphenol; F = p-Ethylphenol; G = 2,3-Xylenol; H = 3,5-Xylenol.

<sup>3</sup> Assuming a sample volume of 100 liters.

<sup>c</sup> "--" indicates not detected.



Table B-29. Plant C Area Sampling Analytical Results (ppm) for Toxic Gases (May 14-15, 1981)

Location Sampled	Sample Number	Sampling Time	Date Collected	Compound (ppm)	
				Carbon Monoxide <sup>a</sup>	Hydrogen Sulfide <sup>b</sup>
5th Level - on deck near cyclone, south of flare	3-012	1811-1816	5/14/81	16	-- <sup>c</sup>
Separator Pit - near mixer	3-013	1736-1741	5/14/81	2-5	--
Recycle Gas Compressor/ Filters	3-014	1742-1747	5/14/81	13-14	--
Recycle Gas Compressor, during process stream sampling	3-015	1011-1016	5/14/81	>50	--
Filter Unit, during replacement of filters	3-054	1830-1835	5/15/81	= <sup>d</sup>	120
Filter Unit, during replacement of filters	3-055	1830-1835	5/15/81	5-1,745 <sup>e</sup>	160
Separator Pit	3-056	1043-1048	5/15/81	=	--
6th Level	3-057	1049-1054	5/15/81	=	--
6th Level - top of gasifier (lid off)	3-089	1036-1044	5/15/81	27	--

<sup>a</sup>Direct-reading instrument.

<sup>d</sup>"=" indicates not sampled.

<sup>b</sup>Detector tube. <sup>c</sup>"--" indicates not detected.

<sup>e</sup>Range of CO concentrations at filter unit during replacement.



**APPENDIX C**  
**HEALTH EFFECTS OF COAL-DERIVED MATERIALS**



## EPIDEMIOLOGICAL STUDIES

Epidemiological studies of workers throughout the world have long established an association between exposure to the combustion or distillation products of coal and an increased incidence of cancer at many sites throughout the body.

One epidemiologic study of workers in a coal conversion plant can be found in the literature (Sexton, 1960). This study is based on 5 years of medical surveillance of 359 workers employed in a direct coal hydrogenation plant in Institute, WV. Fifty workers were described as having skin abnormalities, and 10 of these lesions were originally diagnosed as skin cancer. The conclusion by the author stated that "an increased incidence of skin cancer was found in workers exposed nine months or more to contact with coal hydrogenation chemicals."

In a subsequent review of the data, a consulting pathologist confirmed only 5 of the 10 cases of skin cancer, and statistical analysis of this new incidence does not support the initial conclusion (Palmer, 1979). Follow-up studies on these 50 workers have not as yet revealed an increase in systemic cancers or in cancer mortalities in that work force. However, the age of the workers, the long latency period of systemic tumors, and the small number of workers studied (the group of 309 workers without skin lesions were not followed) preclude conclusions concerning long-term health effects. The follow-up studies were limited primarily to maintenance personnel expected to have high contact but low inhalational exposure to coal process liquids.

In addition, the relevance of these studies to today's coal conversion processes is questionable. Process and control technology, as well as work procedures and hygiene practices, result in significantly reduced worker exposure levels in present-day plants.

Epidemiological studies of other workers exposed to soot and carbon black, as well as to coal tar and pitch, over a long period of time have established an association between exposure to these related materials and an increased incidence of cancer.

Soot was first noted as a cause of skin cancer by Pott (1775) and later by Butlin (1892a) in chimney sweeps. Supporting evidence was provided by Schamberg (1910) who noted the reduction of scrotal cancer after the institution of control measures. Positive correlations between increased systemic cancer and exposure to carbon black and oil in the rubber industry were reported by Henry (1946). Polynuclear aromatic compounds (PNAs) which are carcinogenic to mice have subsequently been identified in carbon black and processed rubber tire extracts (Falk and Steiner, 1952).

Skin cancer among coal tar and pitch workers was first described by Butlin (1892b). Since that time, studies by Henry (1946, 1947) and by Bogovski (1960) have enumerated over 3,000 cases of occupational skin cancer attributed to tar and pitch. Subsequent chemical analysis of coal tar has identified numerous PNAs including benz(a)anthracene, benz(a)pyrene, dibenz(a,h)pyrene, dibenz(a,i)pyrene, benzo(b)fluoranthene, and dibenz(a,h)-anthracene (IARC, 1973).

Exposure to coal tar products as they are produced in the coking industry and in the coal gas industry provides the closest industrial analogy to coal conversion. The common use of coal, similar temperatures and the reducing atmosphere used in its processing provide the basis for this comparison. The latter factor of temperature is of significance because the production of carcinogenic materials and the incidence of lung cancer in occupational workers appear to increase with coal processing temperatures up to about 815°C (1,500°F) (U.S. DOE, 1980).

While the chemical content of these materials can be argued to be similar, the potential exposures are not. Coking is carried out in batches with poor containment of materials. Fugitive emissions are much higher than those expected from the continuous, enclosed coal conversion processes. In addition, concurrent exposures to other chemicals will be different in the two industries. For example, coking involves significant exposure to sulfur dioxide which is reported to have synergistic effects on carcinogenicity.

Nonetheless, a knowledge of the health hazards of these related industries can be expected to provide a base for chemical and medical monitoring and future risk assessment of coal conversion technologies.

Doll et al. (1972) reported the results of a 12-year prospective mortality study of over 11,000 gas industry workers in Great Britain having exposure to coal tar products. Significantly higher rates of death from lung cancer were found for the high-exposure coal-carbonizing workers than for men in general; this was not true for other workers in the plant. Subsequent longer term cumulative studies indicated an increased risk of death from bladder cancer as well as possible scrotal cancer in these high-exposure workers.

Similarly, Kuroda and Kawahata (1936) reported excesses of lung cancer among Japanese coal gas workers, and Kennaway and Kennaway (1947) found a threefold increase in lung cancer mortalities in coke oven-charger workers.

Redmond et al. (1976) reported on an epidemiologic study of cancer in steelworkers including coke plant workers. They found that coke oven workers with 5 or more years of exposure had a higher risk of cancer of the lung and kidney than did the workers in the plant who were not coke oven workers.

Reid and Buck (1956) conducted an epidemiologic study to determine the cancer mortality of coke plant workers in Great Britain. Their results also showed higher-than-expected numbers of deaths from respiratory and other cancer in coke oven workers but not for other workers in the plant.

The NIOSH (1977a) criteria document on coal tar products contains a recommendation for a permissible exposure limit (PEL) of  $0.1 \text{ mg/m}^3$  of coal tar measured as the cyclohexane-extractable fraction of total particulate matter. This recommendation takes into consideration both the carcinogenicity of this material and the lowest concentration that can be reliably detected by environmental monitoring. The federal OSHA standard is  $0.2 \text{ mg/m}^3$  of coal tar pitch volatiles defined as "the fused polycyclic hydrocarbons which volatilize from the distillation residues of coal, petroleum, wood, and other organic matter" (OSHA, 1978).

## TOXICOLOGICAL TESTING OF COAL CONVERSION MATERIALS

Coal conversion materials have been estimated to contain over 10,000 different chemical substances, often of unknown biological activity. The first toxicological testing of these materials was undertaken by Hueper (1956a, 1956b) on oils produced in Bruceton, PA, by the original German Bergius process and in Louisiana, MO, by the old Fischer-Tropsch process. Carcinogenicity of the higher boiling fractions when applied to animals (skin painting and injection) was thus established. In addition, greater carcinogenic potential was seen for materials produced by the Bergius process than by the Fischer-Tropsch process.

Low-Btu gasifier effluents have undergone mutagenicity testing (ITRI, 1980). Condensed materials ("dirty gas") have been found to be highly mutagenic in the Ames assay. This mutagenicity was attributed to alkane polymers, neutral and polar PNA derivatives, and polar nonaromatic components. Inhalation studies of these materials in rats are ongoing. Preliminary results from all of these toxicological programs are discussed below and summarized in Table C-1. However, the materials tested are generic and do not necessarily represent current or future process streams. Therefore, results of testing of these materials are only suggestive of the toxicity of currently produced or projected coal conversion materials.

High-boiling point (over 230°C or 450°F) coal-derived liquids and tars have displayed significant mutagenic activity in the Ames microbial system. In general, higher boiling point materials exhibit greater mutagenicity. This activity exceeds that of petroleum crudes, and resides primarily in the basic fractions as contrasted with petroleum crudes where the major mutagenic activity is found in the neutral fractions and is attributed to nonsubstituted PNA's.

Battelle's Pacific-Northwest Laboratory (PNL), under the aegis of the Department of Energy (DOE), has performed biological testing programs of Solvent Refined Coal I and -II (SRC-I and SRC-II) liquefaction materials. Dupont has published limited and preliminary toxicological data on SRC-II



and EDS materials. Oak Ridge National Laboratory (ORNL) is evaluating H-Coal materials. Some results from these programs are discussed below and summarized in Table C-1.

#### Acute and Subchronic Toxicity

Acute toxicities of the three SRC-II coal liquefaction products (light, middle, and heavy distillate), SRC-I process solvent, and SRC-I light oil have been determined from oral feeding studies in female rats. SRC-II materials were found to have toxicities which were similar to those of many compounds in commercial use (benzoic acid, phosphoric acid, and sodium tartrate) but which exceeded that of crude petroleum. SRC-I wash solvent was at least five times more toxic than any of the other process streams in this study. All materials or their effects were shown to be cumulative (Mahlum, 1981).

In cultures of Vero (African green monkey kidney) cells, SRC-II heavy distillate and SRC-I process solvent were significantly more toxic than either middle or light distillate or than Prudhoe Bay or Wilmington petroleum crudes (Battelle PNL, 1979).

Table C-1. Toxicological Testing Results for Coal Conversion Materials

Tests	SRC-II (Fort Lewis)							SRC-I (Fort Lewis)		SRC-I (Wilsonville)		H-Coal (PDU)		EDS (Baytown)	Low-Btu Gasifier "Dirty Gas"	Crude Petroleum	
	Raw Naphtha (Light Distillate)	Middle Distillate	Heavy Distillate	Recycle Process H <sub>2</sub> O	Waste-water Plant In-fluent	Waste-water Plant Effluent	Vacuum Bottoms	Light Oil	Process Solvent	Solid Product	Process Solvent	Blended Distillate*	Severely Hydro-Treated Blended Distillate*	Heavy Gas/Oil Product		Prudhoe Bay	Wilmington
<u>Acute Toxicity</u>																	
In vivo LD <sub>50</sub> (g/kg)	2.3	3	3.8					3.0				2.8					
In vitro VERO <sup>a</sup>	-	-	+						+								
CHO <sup>b</sup>				+	+	-										-	-
RAM <sup>a</sup>							+										
<u>Subchronic Toxicity</u>																	
5-day (g/kg)	1	1.2	1.5					2.4				1.0					
14- or 28-day(g/kg)																	
<u>Mutagenicity/ Carcinogenicity</u>																	
Point Mutation Ames	-	-	+	+	-	-	+	-	+	+	+	+	-	+	+	+	+
Chromosomal SHE <sup>d</sup>			+						+					+			
Skin Painting	-		+											+			
<u>Reproduction</u>																	
Decreased Fertility	-	-	+														
Reproductive Success	+	+	+														
Perinatal and Post-natal Survival	+	+	+														
Fetal Abnormalities	-	-	+														

<sup>a</sup> Monkey Kidney Cell Cytotoxicity.<sup>b</sup> Chinese Hamster Ovary Cytotoxicity.<sup>c</sup> Rabbit Alveolar Macrophage Cytotoxicity.<sup>d</sup> Syrian Hamster Embryo Transformation.

\*A blend of 2.9 medium distillate and 1 part heavy distillate.

High-boiling point materials (over 230°C; over 450°F) from all four of the major coal liquefaction processes having potential for commercialization (SRC-I, SRC-II, H-Coal, and EDS ) have displayed significant mutagenic activity in the Ames microbial system. In general, higher boiling point materials exhibit greater mutagenicity. This activity exceeds that of petroleum crudes, and resides primarily in the basic fractions as contrasted with petroleum crudes where the major mutagenic activity is found in the neutral fractions and is attributed to PNAs.

In the cases of SRC-I, SRC-II, and H-Coal materials, this mutagenicity has been found to be associated mostly with primary aromatic amines. Further, in the cases of SRC-I and SRC-II materials, these primary aromatic amines were found to be mostly 2- to 4-ring compounds including aminonaphthalenes, aminoanthracenes, aminophenanthrenes, aminopyrenes, and aminochrysenes (Battelle PNL, 1979). The mutagenic/carcinogenic role of PNAs in coal liquids (found in the neutral fractions and in both greater quantities and variety than in petroleum fractions) is unclear. Elucidation awaits further advances in subfractionation and characterization techniques.

In the case of SRC-II materials specifically, the light-oil fraction was found to be negative in the Ames assay, while the heavy-distillate product was positive and the heavier vacuum bottoms even more strongly positive. Inconsistent results for middle-distillate oil [found inactive by Pelroy (1981) but active by Calkins et al. (1979)] can possibly be attributed to the variability of the chemical composition of different test samples. No temperature ranges for definition of these distillate fractions were included.

Skin painting studies in mice have been carried out using SRC-II heavy and light distillates (Mahlum, 1981). Heavy distillate was found to cause malignant skin tumors following dermal application. Increasing concentrations of this material both increased the incidence of these tumors and decreased the latency period for tumor development. Light distillate did not exhibit tumorigenic properties in mice similarly treated.

Hydrotreatment of SRC-II distillate materials has been shown to alter both the chemical composition and the mutagenicity of these materials. A distillate blend of SRC-II product containing 3 parts middle distillate and 1 part heavy distillate was found to contain primarily 2- and 3-ringed aromatic and heteroatomic species together with high concentrations of phenolic and polynuclear aromatic components. Hydrotreatment resulted in predominately hydroaromatic species of lower overall molecular weight, along with reduced concentrations of heteroatomic species. Most nitrogen- and sulfur-containing compounds underwent transformation. Oxygen content was reduced, resulting in lowered phenolic concentrations and the elimination of the furans (Battelle PNL, 1980).

The mutagenic response, as measured by the Ames assay, was considerably reduced for this hydrotreated material. Hydrotreatment severe enough to remove 67 percent of the nitrogen and 82 percent of the oxygen produced mutagenic rates comparable to those of the controls (Battelle PNL, 1980).

A second, less expensive approach to reducing the genotoxic potential of high-boiling coal liquids, that of fractional distillation of the liquid products, correlated with positive results in the Ames mutagenicity assay, is currently being investigated by Battelle Laboratories (Pelroy and Wilson, 1981). Uncertainties concerning analytical methods and masking of genetic effects of individual fractions require further study.

Of SRC-I materials, SRC solid product and SRC process solvent have both been found to be mutagenic in the Ames assay. Unlike SRC-II materials, however, part of this activity was found to be located in fractions identified with phenolic compounds (Pelroy, 1981).

SRC-I materials exhibiting a positive effect in the microbial test also caused mammalian cell transformation. For most materials, the presence of S9 was necessary to effect the transformation; however, a small amount of activity was observed with SRC-I process solvent without the S9 fraction of Aroclor 1254 treated rat livers., indicating the presence of direct-acting agents (Mahlum, 1981).

Toxicity testing of H-Coal materials has shown that the neutral and basic fractions of blended H-Coal distillates from the Trenton, NJ, process development unit (PDU) exhibit significant mutagenic activity eliminated by high-severity hydrotreatment (Cowser, 1980). Mammalian toxicity and skin carcinogenesis assays with these materials are under way. Process materials from the H-Coal pilot plant are being added as they become available. However, no test results for specific streams produced under standard operating conditions are yet available.

An Exxon Donor Solvent (EDS) product sample (heavy gas oil) was tested for mutagenic and tumorigenic activity by Calkins et al. (1979). The heavy gas oil was found to be strongly mutagenic in the Ames assay and a potent tumorigenic agent in a mouse skin painting assay. In the latter study, 18 of 30 mice developed skin tumors.

#### Reproductive Effects/Teratogenicity

Reproductive effects/teratogenicity studies in rats using SRC-II light, middle, and heavy distillate (by gavage) showed some increased prenatal mortality by all three materials, and an increase in the incidence of malformations by heavy distillate when administered on the 12th through 16th day of gestation (Battelle PNL, 1979). The increased frequency of prenatal mortality occurred occasionally in the absence of signs of maternal toxicity, but the increase in malformations nearly always was accompanied by a decrease in maternal weight gain during pregnancy.

Likewise, SRC-I light oil and wash solvent were not significantly fetotoxic or teratogenic at doses below those causing maternal toxicity; thus, the fetus may be no more sensitive to these exposures than are adult females. However SRC-I process solvent consistently induced fetal mortality and major malformations at levels below those producing signs of maternal toxicity (Battelle PNL, 1979).

Polynuclear aromatic compounds (PNAs) are produced when organic materials are subjected to high temperatures. Hundreds of different compounds result which can be absorbed following skin contact, inhalation, and ingestion. Polynuclear aromatic compounds (PNA's) are produced when organic materials are subjected to high temperatures. Hundreds of different compounds result which can be absorbed following skin contact, inhalation, and ingestion. Several new books are now available that describe the health effects and chemistry of polyaromatic compounds.

The content of PNAs in coal-derived crude oil has been estimated to be 5 to 20 percent compared to 1 percent in petroleum crudes (Zedeck, 1980). Analysis of coal conversion process streams and the industrial hygiene air and bulk sampling carried out in the present study have confirmed the presence of vapor and particulate PNAs at coal conversion plants. Emissions from plants have not been completely characterized, many processes and resulting material streams are being changed as the technology matures and improved control technologies are implemented.

The most important concern regarding the effects of this exposure (dermal, oral, and/or inhalation) is the potential risk of cancer and/or inheritable chromosomal damage in persons chronically exposed to low levels of these chemicals over long periods of time.

The chemical family of PNAs has been found to contain many potent mutagens and carcinogens that act in minute amounts almost universally at the site of application. That is to say, tumors appear in the tissue directly exposed to the carcinogen, usually in the skin or lung. The property of carcinogenicity appears to depend on metabolic activation of these chemicals by the

microsomal mixed-function oxidase system to biologically active diepoxide derivatives. It also appears to be stereospecific. Slight changes in molecular structure can result in significant changes in carcinogenic activity. Only PNAs with three or more rings have been found to be strong mutagens and carcinogens, and alkylation often produces an increase in this mutagenicity. Nonetheless, despite recent advances in the understanding of some structure-activity relationships of these chemicals, it is not possible to predict mutagenic activity based on molecular structure.

Interactions among carcinogens, cocarcinogens, and promoters must also be considered when exposure to complex mixtures of chemicals occurs. Co-carcinogens increase the overall carcinogenic process caused by a carcinogen when exposure to the cocarcinogen occurs simultaneously with exposure to the carcinogen. Kuschner (1981) demonstrated that cancer incidence in rats exposed to benz(a)pyrene (a carcinogen) increased directly with simultaneous exposure to sulfur dioxide (a cocarcinogen). The aliphatic hydrocarbon dodecane was found by Smith et al. (1951) to have cocarcinogenic properties. Bingham and Falk (1969) demonstrated a 1,000-fold increase in the potency of low concentrations of benz(a)pyrene by the simultaneous application of dodecane. The authors suggest that certain long-chain hydrocarbons may play the decisive role in determining the carcinogenic potency of a mixture; the importance of the concentration of the initiator (carcinogen) may be minimal. Finally, certain sulfur compounds, aldehydes, and phenolics have all been shown to stimulate the effects of PNAs and other carcinogens in mouse skin (Slaga et al., 1978).

Equally complex and imperfectly understood is the role of promoters in cancer production. These chemicals increase the tumorigenic response to a chemical carcinogen when they are applied after the carcinogen, but do not have carcinogenic properties when applied alone. For example, Van Duuren et al. (1978) have shown that the application of a PNA can be followed by months and, in fact, 1 year later by a promoting stimulus such as the application of phorbol esters from croton oil and still result in the production of skin tumors.

To further complicate the picture, other interactions occur between chemicals as they undergo transformation by chemical and physical processes in the environment, and alteration during uptake and transport by the human body. This often leads to health effects totally unpredictable on the basis of a simple knowledge of effects of exposure to individual PNA compounds in animals. Thus, while information concerning effects of individual chemicals fills many gaps in the understanding of general PNA toxicity, it has severe limitations when applied to analysis of the risk involved from exposure to complex mixtures.

### Toxicity

Very limited acute or chronic toxicity information, other than that concerning carcinogenicity, is available for PNAs. In general, these chemicals are primary irritants which on repeated or prolonged contact with the skin cause photosensitization and dermatitis, and upon contact with lung tissue cause pulmonary edema, pneumonitis, and hemorrhage (Boulos, 1978).

A review by Philips et al. (1973) pinpoints the hematopoietic system, gonads, and intestinal epithelium as being especially susceptible to PNA injury. The cells of all these tissues are rapidly dividing, and it is easy to speculate that injury to the DNA replicative phase of the cell accounts for this toxicity, as well as for the carcinogenic potential associated with many of these chemicals.

Naphthalene is the most abundant constituent of coal tar. Inhalation of naphthalene causes headache, confusion, nausea, and perspiration. Severe exposure has been reported to cause severe hemolysis, vomiting, hematuria, and optic neuritis (Boulos, 1978). The OSHA standard for exposure to naphthalene of 10 ppm is intended to minimize the risk of adverse ocular effects.

### Carcinogenicity

The Environmental Protection Agency has compiled a list of 124 PNAs identified in the environment which summarizes the toxicity/carcinogenicity data available for them. Those PNAs ranked by EPA and also included in the



present industrial hygiene study as well as several related compounds are listed in Table C-2 (adapted from Kingsbury and White, 1979). Also shown in the table are information summaries of the experimental animal testing data for each compound.

Thirty-one PNAs, including many of those measured in this industrial hygiene study, have been rated by the National Academy of Science (NAS). This information based on an evaluation by the International Agency for Research on Cancer (IARC) is presented in Table C-3. Other carcinogenicity rankings for PNAs are available as well. However, quantification and ordering in the field of carcinogenicity is difficult due to the necessity of weighing diverse factors such as percentage and species of animals at risk with tumor, multiplicity of developing tumors, time of tumor occurrence, and routes of exposure utilized by the investigators.

No federal health standards exist for individual PNAs, although 13 of these compounds\* are listed in the EPA Consent Degree List and are considered as a group to be potential carcinogens. A threshold limit value (TLV)/time-weighted average (TWA) of  $0.2 \text{ mg/m}^3$  for total particulate PNAs determined as cyclohexane-solubles has been recommended by the American Conference of Governmental Industrial Hygienists (ACGIH, 1981). This TLV recognizes the carcinogenic potential of PNAs collectively and is an attempt to minimize concentrations of the higher weight PNAs that are suspected carcinogens.

Individual species of PNAs that were measured in the present industrial hygiene study are pictured in Table C-4; molecular weights, boiling points, and the number of aromatic rings are included when available. Tumorigenic citations of either "CAR" or "NEO" are listed in the Registry of Toxic Effects of Chemical Substances (NIOSH, 1980) for 17 of these chemicals (footnoted in Table C-4), and several others including the prevalent naphthalene are rated as equivocal tumorigenic agents on the basis of at least one experimental study in the literature. A special occupational hazard review for chrysene has been published by NIOSH (1978b).

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\*Benz(a)anthracene, benzo(a)pyrene, 3,4-benzofluoranthene, benzo(k)fluoranthene, chrysene, acenaphthalene, anthracene, benzo(g,h,i)perylene, fluorene, phenanthrene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, and pyrene.

Table C-2. Carcinogenicity Data for Selected PNAS

Compound	Information Summary	Compound	Information Summary
Anthracene	Lowest effective dose for tumor- genic response in mice is 3300 mg/kg.	Fluoranthene	ID50 (oral, rat): 2000 mg/kg.
Phenanthrene	Lowest dose for tumorigenic response in mice is 71 mg/kg.	Benzo (k) Fluoranthene	Lowest effective dose for tumor- genic response in mice is 72 mg/kg.
Benzo (a) anthracene	Lowest effective dose for tumor- genic response in mice is 2 mg/kg.	Benzo (i) Fluoranthene	Lowest effective dose for tumor- genic response in mice is 288 mg/kg.
7,12-Dimethylbenzo (a) - anthracene	Tumors in 7 species reported. Lowest effective dose is 21 ug/kg.	1,2,3,6-Dibenzo- fluoranthene	Lowest effective dose for tumor- genic response in mice is 590 mg/kg.
3-Methylcholanthrene	Tumors in 8 species reported. Lowest effective dose is 0.312 mg/kg.	Benzo (b) Fluoranthene	Lowest effective dose for tumor- genic response in mice is 40 mg/kg.
Benzo (c) phenanthrene and allyl derivatives	Lowest effective dose for tumor- genic response in mice is 10 mg/kg.	Dibenzo (1,2,3-cd) - pyrene	Lowest effective dose for tumor- genic response in mice is 72 mg/kg.
Chrysene	Lowest effective dose for tumor- genic response in mice is 99 mg/kg.	Phenanthridine	Based on acridine. ID50 (oral, rat): 2000 mg/kg.
Triphenylene	...	Benzo (g) quinoline	Based on acridine. ID50 (oral, rat): 2000 mg/kg.
Pyrene	Lowest effective dose reported for tumorigenic response in mice is 10 g/kg.	Benzo (h) quinoline	Based on acridine. ID50 (oral, rat): 2000 mg/kg.
Benzo (g) chrysene	Lowest effective dose reported for tumorigenic response in mice is 720 mg/kg.	Benzo (a) acridine	...
Dibenz (a,c) anthracene	Lowest effective dose reported for tumorigenic response in mice is 440 mg/kg.	Benzo (c) acridine	Lowest effective dose for tumor- genic response in mice is 468 mg/kg.
Dibenz (a,h) anthracene	Tumors in 5 species are reported.	Dibenz (a,i) acridine	Lowest effective dose for tumor- genic response in mice is 11 mg/kg.
Benzo (a) pyrene	Tumors in 6 species are reported.	Dibenz (a,h) acridine	Lowest effective dose for tumor- genic response in mice is 10 mg/kg.
Benzo (e) pyrene	Lowest effective dose is 2 ug/kg.	Dibenz (a,c,h) acridine	Lowest effective dose for tumor- genic response in mice is 1020 mg/kg.
Benzo (a) pyrene	Tumors in 2 species are reported.	Carbazole	Lowest lethal dose (oral, rat): 500 mg/kg.
Perylene	Lowest effective dose is 140 mg/kg.	Benzo (c) carbazole	Lowest effective dose for tumor- genic response in mice is 840 mg/kg.
Picene	...	Dibenz (a,i) carbazole	Lowest effective dose for tumor- genic response in mice is 510 mg/kg.
Dibenz (a,h) pyrene	Lowest effective dose for tumor- genic response in mice is 111 mg/kg.	Dibenz (c,g) carbazole	Tumors in 4 species reported. Lowest effective dose is 8 mg/kg.
Dibenz (a,i) pyrene	Lowest effective dose for tumor- genic response in mice is 165 mg/kg.	Dibenz (a,g) carbazole	Lowest effective dose for tumor- genic response in mice is 270 mg/kg.
Dibenz (a,i) pyrene	Tumors in 2 species reported. Lowest effective dose is 2 mg/kg.	Benzo (b) thiophene	Lowest lethal dose (intraperitoneal, mouse): 512 mg/kg
Dibenz (a,i) pyrene	Lowest effective dose for tumor- genic response in mice is 48 mg/kg.		
Benzo (ghi) perylene	...		
Carbazene	...		
2,3-Benzofluorene	...		

Adapted from: Knappdury and White (1979)

Table C-3. IARC Evaluation of 31 PNAs

Compound	Indications of Carcinogenicity <sup>2</sup>	
	Rating Suggested by NAS <sup>1</sup>	Comments
Benzo (a) pyrene	+++	Produced tumors in all 9 animal species reported tested. Latent periods shorter than for other polycyclics with possible exception of dibenz(a,h)anthracene.
Dibenz (a,h) anthracene	+++	Tumors produced in 6 animal species. Both local and systemic carcinogenic effects observed. Effective at low doses. Single dose effective in newborn mice.
7,12-dimethylbenz (a) - anthracene	+++	Not addressed
3-methylcholanthrene	+++	Not addressed
Dibenz (a,i) pyrene	+++	Rapid appearance of local sarcoma observed from subcutaneous injection in mice and hamsters. Skin painting on mice was also effective but less active than benzo(a)pyrene.
Benzo (a) anthracene	+	Carcinogenic in mice by several routes. Effective oral dose similar to methylcholanthrene but without gastrointestinal tract tumors.
Dibenz (c,g) carbazole	+++	Carcinogenic in rat, mouse, hamster, and possibly dog. Both local and systemic effects observed. Appears to be stronger respiratory tract carcinogen than benzo(a)pyrene in hamster.
Benzo (c) phenanthrene (and -C8g derivatives)	+++	Not addressed
Dibenz (a,h) acridine	++	Skin tumors and lung tumors in mice observed following skin painting or subcutaneous administration. Not tested adequately by other routes or in other species.
Dibenz (a,j) acridine	++	Skin tumors in mice followed topical application. Subcutaneous administrations at highest dosage produced local sarcomas and lung tumors. Not tested in other species.
Benzo (b) fluoranthene	++	Produced skin tumors in mice following repeated skin painting but only at levels 10 times higher than effective benzo(a)pyrene levels. Not tested by other routes.
Dibenz (a,l) pyrene	+	Subcutaneous administration in mice resulted in sarcomas in all animals. Not treated by other routes or in other species.
Phenanthrene	-	Not addressed
Benzo (k) fluoranthene	-	Not addressed
Indeno (1,2,3-cd) pyrene	+	A complete carcinogen and initiation of skin carcinogenesis in mice, but of lower potency than benzo(a)pyrene. Local sarcomas followed subcutaneous injection in mice. Not treated by other routes as in other species.
Methylchrysenes	Not listed	Not addressed
Chrysene	±	Skin tumors in mice followed repeated painting at high concentrations only. High dose, subcutaneous injections produced low incidence of tumors after long induction time.
Picene	Not listed	Not addressed
Benzo (e) pyrene	-	Data from skin painting experiments in mice evoked weaker response than benzo(a)pyrene or dibenz(a,h)anthracene. Not tested by other routes.
Dibenz (a,h) pyrene	+++	Carcinogenic effects demonstrated following repeated skin painting in mice and injections in mice and rats. Not tested by other routes or in other species.

(continued)

Table C-3 (concluded)

Compound	Indications of Carcinogenicity <sup>a</sup>	
	Ratings Suggested by NAS <sup>b</sup>	Comments
Dibenzo(a,g)carbazole	±	Not addressed
Benzo(j)fluoranthene	++	A high incidence of skin carcinomas results from repeated skin painting in mice. Not tested in other species or by other routes.
Cholanthrene	++	Not addressed
Dibenz(a,c)anthracene	+	Not addressed
Benzo(c)acridine	Not listed	Skin tumors in mice followed topical application. Bladder tumors in rats followed paraffin wax pellet implantation. Not tested by other routes or in other species.
Benzo(a)carbazole	±	Not addressed
Dibenz(a,i)carbazole	±	Not addressed
Dibenz(c,h)acridine	±	Not addressed
Dibenz(a,g)fluorene	+	Not addressed
Dibenz(a,j)anthracene	+	Not addressed
Dibenz(a,c)fluorene	±	Not addressed

<sup>a</sup> Indications of Carcinogenicity, refer to the Public Health Service Survey.

<sup>b</sup> Carcinogenicity code given by NAS:

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







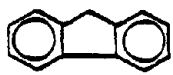

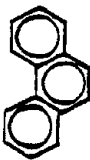


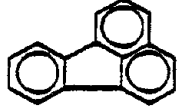
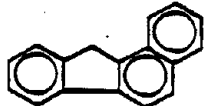

++, +++, ++++ strongly carcinogenic

Adapted from: Kingsbury and White (1979)

The PNAs contain some species which are also highly teratogenic. Not all of these PNAs are alike in their teratogenic properties, and the teratogenic effects are even less well understood than the carcinogenic effects. For example, benzo(a)pyrene is not an effective teratogen, whereas 7,12-dimethylbenzanthracene produces a high incidence of defects in exposed animals (Weisburger and Williams, 1980). The evidence for inheritable chromosomal damage is limited and inconclusive.


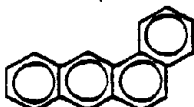
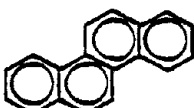
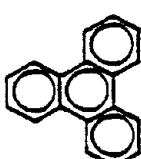
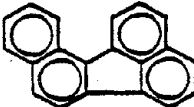
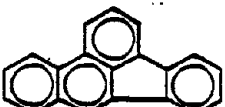
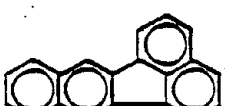
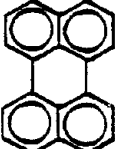
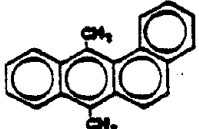
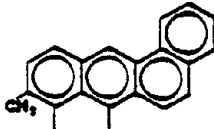
Virtually no toxicological data are available for the oxygen or sulfur heterocyclic PNAs. On the other hand, nine nitrogen heterocyclic PNAs have demonstrated carcinogenic activity, whereas data are lacking on many others (Kingsbury and White, 1979). Five nitrogen heterocyclics were measured in the present industrial hygiene study. Three of them (quinoline, dibenz(a,j)acridine, and dibenz(a,i)carbazole) are suspected of having carcinogenic properties; information on the other two (acridine and carbazole) has not demonstrated this carcinogenicity.

Table C-4. Polynuclear Aromatic Hydrocarbons

Compound	Structure	Molecular Weight	Boiling Point (°C)	Number of Aromatic Rings
Naphthalene		128.19	218	2
Quinoline*		129.16	238.05	2
1-Methylnaphthalene		142.2	244.64	2
2-Methylnaphthalene		142.2	241.05	2
Acenaphthalene		152.21	265-275	2
Acenaphthene		154.21	279	2
Fluorene		166.23	293-295	2
Carbazole		167.21	355	3
Phenanthrene*		178.22	340	3
Anthracene*				
Acridine		179.22	345-346	3
Fluoranthene		202.24	375	3
Benzo(a)fluorene		216.29	413	3
Benzo(b)fluorene				

\* Associated with tumorigenic citations of either "NEO" or "CAR" in the 1979 Registry of Toxic Effects of Chemical Substances (NIOSH, 1980).

Table C-4 (continued)

Compound	Structure	Molecular Weight	Boiling Point (°C)	Number of Aromatic Rings
Pyrene		202.24	393	4
Benz(a)anthracene*		228.28	435	4
Chrysene*				
Triphenylene				
Benzo(j)fluoranthene*		252.32	480	4
Benzo(b)fluoranthene*				
Benzo(k)fluoranthene				
Perylene		252.32	350-400	4
Dimethylbenz(a)anthracene* (7,12- is pictured)		256.35	—	4
3-Methylcholanthrene*		268.34	—	4

\*Associated with tumorigenic citations of either "NEO" or "CAR" in the 1979 Registry of Toxic Effects of Chemical Substances (NIOSH, 1980).

Table C-4 (concluded)

Compound	Structure	Molecular Weight	Boiling Point (°C)	Number of Aromatic Rings
Benzo(e)pyrene		252.32	310-312	5
Benzo(a)pyrene*				
Dibenz(a,i)carbazole*		267	—	5
Indeno(1,2,3-cd)pyrene*		276.22	—	5
Benzo(g,h,i)perylene*		276.22	273	5
Dibenz(a,h)anthracene*		278.33	262	5
Dibenz(a,j)acridine*		280.32	—	5
6,13-Dimethyldibenz(a,h)-anthracene*		306.35	—	5
Dibenzo(a,i)pyrene*		302.28	—	6
Coronene*		300.34	525	7

\*Associated with tumorigenic citations of either "NEO" or "CAR" in the 1979 Registry of Toxic Effects of Chemical Substances (NIOSH, 1980).



Aromatic amines have been detected in high-boiling point (over 370°C; over 700°F) coal liquids. They have been shown by chemical fractionation and analytical methods to be largely responsible for the high level of mutagenicity associated with these materials in the Ames test. The most mutagenically active boiling-point cuts appear to contain the highest concentration of 4- and 5-ring polynuclear aromatic amines as well as the highest concentration of total polynuclear aromatic amines (Pelroy and Wilson, 1981). Sources for further reading may include reports from ORNL, BPNW, and ITRI.

The major health concern regarding occupational exposure to aromatic amines is the potential risk of cancer, especially of the urinary tract. Absorption of these chemicals occurs readily through both the lungs and the skin, and can result in the appearance of tumors following a latency period of from 4 to 40 years. In addition, exposure to many of the aromatic amines results in methemoglobinemia which, in very large, acute exposures, can be fatal.

Many aromatic amines, derivatives, and analogs have been found positive in the Ames Salmonella bioassay for mutagenicity and/or to be carcinogenic for animals undergoing toxicity testing. Unlike the carcinogenic PNAs, these compounds do not usually cause cancer at the point of application, but rather at distant locations in the body. An exception is 2-anthramine which, in addition to causing a variety of tumors in areas distant from the site of exposure, causes skin cancer in rats subjected to dermal applications. The specific target site seems to depend on the animal species tested and on the specific structure of the aryl group. In man, the urinary bladder appears to be the most common target (Weisburger and Williams, 1980).

The property of carcinogenicity appears to require metabolic activation. Studies have established that, with few exceptions, a key activation reaction, N-hydroxylation (a liver mixed-function oxidase-dependent metabolic reaction) is a prerequisite for tumor production. Animals lacking this metabolic pathway often exhibit negative aromatic amine carcinogenic assays. Further, the sensitivity of a particular tissue to carcinogenicity induced by aromatic amines appears to depend at least partially on the ability of the target organ to convert the carcinogen or an intermediate metabolite to

its active form. Thus, it is generally believed that aromatic amine-induced cancer of the urinary bladder is most likely due to the release of active carcinogens such as arylhydroxylamine derivatives from their transport conjugates at this site (Clayson and Gardner, 1976).

Certain structure-activity relationships have been elucidated for the aromatic amines. For example, the monocyclic arylamines (including aniline) show weak or no carcinogenic potential in animal tests, whereas a number of substituted anilines are positive. In general, arylamines, when substituted by an electron donating methyl or halogen in the ortho position, appear to be more powerful carcinogens than the unsubstituted compound. Although these relationships are important in the selection of suspected chemicals for testing and/or monitoring, it is not yet possible to predict carcinogenic activity on the basis of molecular structure.

OSHA (1978) recognizes 17 chemicals as causing cancer in humans; nine of these are aromatic nitro and amino compounds.\* Of the nine aromatic amines measured in this industrial hygiene study of coal conversion facilities, two (1-naphthylamine and 2-naphthylamine) are on this OSHA list. Two others (o-toluidine and o-anisidine) are suspected carcinogens, having induced cancers in animals but only at high doses and without the establishment of dose-dependent relationships. On the other hand, aniline (long thought to be the agent responsible for human bladder cancer in the dye industry) has been found to have only very weak carcinogenic properties in animals (Beard and Noe, 1981).

\*2-Acetylaminofluorene, 4-aminodiphenyl, benzidine (and salts), 3,3-dichlorobenzidine (and salts), 4-dimethylaminoazobenzene, 1-naphthylamine, 2-naphthylamine, 4-nitrobiphenyl, and 4,4-methylenebis-(chloroaniline).

The monocyclic arylamines (aniline, o-toluidine, o-anisidine) have all been found to be carcinogenic in animals, but only after continuous intake of high doses. Aniline studies failed to produce the characteristic bladder tumors, but unexpectedly resulted in subcutaneous carcinoma (NCI, 1978). These chemicals, when substituted in the ortho position by an electron donating methyl or halogen, appear to be more powerful carcinogens than the unsubstituted compounds (Weisburger and Williams, 1980). In addition, hemorrhagic cystitis has been observed in workers handling toluidines and chlortoluidines in other industries; however, a relationship to urinary tract cancer has not been established (Hamilton and Hardy, 1974).

2-Naphthylamine is one of the most potent industrial carcinogens ever encountered (Clayson and Gardner, 1976). Occupational exposure to commercial-grade 2-naphthylamine has shown a strong association with bladder cancer. In a report by Case et al. (1954), 26 deaths occurred among exposed workers where 0.3 were expected. Other studies found incidences of bladder tumors in exposed workers of up to 94 percent.

In addition, 2-naphthylamine was the first aromatic amine conclusively established as an experimental carcinogen. Subsequent testing has shown positive tumorigenic results from exposure in dogs, monkeys, mice, and hamsters (the latter response occurring only after high doses); results in rats and rabbits have been negative. Good correlation between tumor production and the appearance of N-oxidative products in the urine lends support to the belief that an active metabolite is the carcinogenic agent (Clayson and Gardner, 1976).

1-Naphthylamine remains unproven as a carcinogenic agent. Occupational exposure to it in a number of industries has been correlated with bladder cancer (Parkes, 1976); however, the possibility of simultaneous exposure to 2-naphthylamine cannot be ruled out. In animals, no carcinogenic effect has been found after testing in dogs or hamsters. However, its metabolite N-(1-naphthyl)-hydroxylamine causes cancer in animals when administered intraperitoneally.

Federal standards for exposure to seven of the aromatic amines measured in the industrial hygiene of coal conversion facilities are as follows:


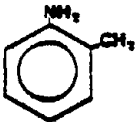
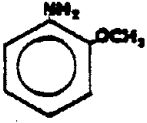


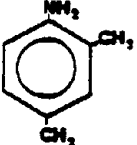

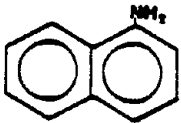
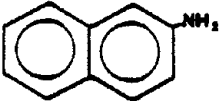
. aniline	5 ppm	19 mg/m <sup>3</sup>
. N,N-dimethylaniline	5 ppm	25 mg/m <sup>3</sup>
. o-toluidine	5 ppm	22 mg/m <sup>3</sup>
. 2,4-dimethylaniline	5 ppm	25 mg/m <sup>3</sup>
. o-anisidine		0.5 mg/m <sup>3</sup>
. p-anisidine		0.5 mg/m <sup>3</sup>
. p-nitroaniline	1 ppm	6 mg/m <sup>3</sup>

Because there is no known threshold dose below which a carcinogen will not induce cancer, 1-naphthylamine and 2-naphthylamine have no exposure limits; all contact is to be avoided.

The most important toxic effect following exposure to many aromatic amines including aniline, N,N-dimethylaniline, p-nitroaniline, and the toluidines, other than the development of cancer, is the development of methemoglobinemia. Methemoglobin, a chemical oxidative product of hemoglobin, cannot combine reversibly with oxygen, and at blood levels approaching 60 percent produces symptoms of hypoxia (Beard and Noe, 1981).

Table C-5 shows the molecular structure, molecular weight, and when available, the vapor pressure of the nine aromatic amines measured in this study.

Table C-5. Aromatic Amines

Aromatic Amine	Structure	Molecular Weight	Boiling Point (°C)	Vapor Pressure (mm Hg)
Aniline		93.13	184.13	0.6
o-Toluidine		107.16	200.23	<1
o-Anisidine		123.16	224	<0.1
p-Anisidine		123.16	243	<0.1
p-Nitroaniline		138.13	284	<<1
2,4-Dimethylaniline		119.18	—	—
N,N-Dimethylaniline		121.18	194.15	<1
1-Naphthylamine		143.19	300.8	—
2-Naphthylamine		143.19	306.1	—

## THE SIMPLE AROMATICS (BENZENE, TOLUENE, XYLENE)

Due to high volatility and low skin absorption, the major exposure to these hydrocarbons is from vapor inhalation. The major acute toxic effect is narcosis. In addition, chronic exposure to benzene produces damage to the blood and the blood-forming organs. However, this myelotoxicity has not been demonstrated for either toluene or xylene.

Light and middle coal liquefaction distillates have been found to contain concentrations of the monocyclic (simple) aromatics ranging from 0.1 to 1.0 percent by volume (Pittsburg and Midway Coal Mining Co., 1980).

### Benzene

The major effect of acute inhalation of benzene is central nervous system (CNS) depression with death resulting from respiratory failure and circulatory collapse. For man, an exposure of 20,000 ppm is usually fatal within 5 to 10 minutes, and 7,500 ppm inhaled for 30 to 60 minutes produces toxic effects (Flury, 1928). The NIOSH (1978c) IDLH (immediately dangerous to life or health) level is 2,000 ppm.

Other toxic effects from severe, acute exposure to benzene include CNS symptoms of convulsions, paralysis, and unconsciousness. Milder exposure produces reversible euphoria, giddiness, headache, nausea, and unsteadiness (NIOSH, 1974). Postmortem findings in fatal cases include petechial hemorrhages of the brain, pleura, pericardium, urinary tract, mucous membranes, and skin (Gerarde, 1960). Breathlessness, nervous irritability, and unsteady gait have been found to persist for up to 3 weeks following an acute exposure (Gerarde, 1960).

Strong evidence linking chronic benzene exposure with damage to the blood-forming tissue and to chromosomal aberrations has long been recognized. Depression of such blood parameters as erythrocyte count, hemoglobin, hematocrit, mean corpuscular red cell volume, platelet counts, and leukocyte counts in persons exposed to benzene was the basis for the former NIOSH recommendation of 10 ppm TWA exposure limit (NIOSH, 1974).

In addition, more recent clinical and epidemiological evidence has implicated benzene in the causation of leukemia. Presumptive case histories of benzene-induced leukemia reported by NIOSH (1974) include those of: Mallory et al. (1939), 2 such cases; Vigliani and Saita (1964), 6 cases; Forni and Moreo (1967), 1 case; Forni and Moreo (1969), 1 case; and Tareeff et al. (1963), 16 cases in the U.S.S.R. Vigliani and Saita (1964), comparing the incidence of acute leukemia in Milan in 1959-1961 with that in 1962-1963, found a 20-fold increase in leukemia in the latter period which coincided with a sharp increase in benzene poisonings. Cavignaux (1962) demonstrated a high incidence of leukemia among cases of benzene poisoning in France.

These reports are substantiated by a Japanese case-control study (Ishimaru et al., 1971) in which leukemia patients were paired with controls. The authors concluded that occupations involving exposure to benzene occurred more than twice as frequently among leukemia victims than among controls. On the other hand, Thorpe (1974), studying 28,000 petroleum workers exposed to low levels of benzene, found the incidence of leukemia to be no higher for these petroleum workers than for the general population.

In 1979 NIOSH issued a revised recommendation for an occupational exposure standard for benzene. The NIOSH recommendation stated "...because it [benzene] causes progressive malignant diseases of the blood forming organs...benzene shall be considered a carcinogen in man." and suggested a permissible exposure level of 1 ppm and avoidance of dermal contact (NIOSH 1979).

The early symptoms of chronic benzene poisoning are vague, consisting of headache, fatigue, and anorexia; and early blood examination usually shows only slight abnormalities in hematological parameters. As the disease progresses, however, bone marrow changes including aplasia or hyperplasia, and peripheral blood changes including anemia, leukopenia, and thrombocytopenia develop.

Acute dermal contact with liquid benzene may cause local erythema and blistering of the skin. Repeated or prolonged contact may result in drying, scaling, or dermatitis. However, no evidence exists for systemic injury following dermal contact.

## Toluene and Xylene

The primary health effect associated with occupational exposure to both toluene and xylene is CNS depression following acute inhalation of vapors. Reports comparing the relative acute toxicities of benzene, toluene, and xylene are conflicting, possibly because of the different toxicities associated with various isomers. However, these toxicities all appear to be of the same order of magnitude (NIOSH, 1975).

Distinct symptoms from an exposure to toluene appear at about 200 ppm; they include headache, lassitude, anorexia, fatigue, and skin paresthesias. As concentration and/or length of exposure is increased, more severe symptoms appear, including muscular weakness, incoordination, mental confusion, and loss of consciousness (NIOSH, 1973).

Exposure to both toluene and xylene vapors produces local effects as well; they are irritating to the eyes, nose, and throat. In a subjective study by Nelson et al. (1943), reported in NIOSH (1975), a majority of test subjects felt that they could work in an atmosphere of 200 ppm for toluene, but only of 100 ppm for xylene.

Current scientific evidence indicates that, unlike benzene, neither toluene nor xylene cause injury to the blood-forming tissues of the body (NIOSH, 1973). In addition, other effects from chronic exposure to low concentrations of toluene and xylene have not been documented.

The OSHA (1978) standard for toluene is 200 ppm as an 8-hour TWA, with an acceptable ceiling concentration of 300 ppm; maximum peaks of 500 ppm are allowed for 10 minutes. However, NIOSH (1973) recommends a TWA of 100 ppm and a ceiling of 200 ppm. The OSHA standard for xylene is 100 ppm, which is in agreement with the NIOSH recommendation.

## PHENOLIC COMPOUNDS

Phenolic compounds are formed from coal during conditions of high temperature and high pressure. Production of phenolic compounds is highly variable



depending upon process conditions and quench system operations. In the liquefaction process, phenolics can comprise up to 25 percent of the light-oil fractions and are present in concentrations of up to 10,000 mg/L in untreated wastewater (Herbes et al., 1976). During gasification, phenolic compounds exit the gasifier with the raw product gas.

Industrial exposure to phenolic compounds is chiefly from dermal contact resulting in both local injury and systemic toxicity following absorption. However, at high process temperature, inhalation of vapors and particulate phenolics with rapid absorption is also possible.

In general, these compounds are highly irritating to the skin, mucous membranes, and eyes. Systemic effects usually involve the central nervous or cardiovascular systems, or both; this may be accompanied by renal and hepatic damage. Of the phenolics measured\* in this liquefaction study, phenol is by far the most prevalent and the one that has been studied most. Therefore, the health effects from exposure to phenol are discussed in the most detail here; information concerning the cresols and the xylenols is also discussed when their toxicological manifestations differ from those of phenol.

## Phenol

Phenol is a general cell toxin that coagulates protein and produces tissue necrosis (Liao and Oehme, 1980). Its potent corrosive properties cause local damage to exposed tissue. Dermal contact initially produces painless whitening of the exposed area; continuing exposure results in severe burns and necrosis. Skin contact by humans with solutions, emulsions, or pure preparations containing from 80 to 100 percent phenol for a little as 5 to 20 minutes has resulted in death. Eye contact may cause severe damage and blindness (NIOSH, 1976).

The systemic action of a large, acute exposure following absorption appears to be on the CNS resulting in collapse and unconsciousness. Death may occur

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\*Phenol, o-cresol, m-cresol, p-cresol, o-ethylphenol, p-ethylphenol, 2,3-xyleneol, and 2,4-xyleneol.

from respiratory arrest or from direct cardiac paralysis (Sollmann, 1957; Deichmann and Keplinger, 1981). The "immediately dangerous to life or health" (IDLH) concentration has been set by NIOSH (1978c) at 100 ppm. Absorption from the lungs following smaller acute or chronic inhalation exposure and from the skin following acute or chronic contact with solid, liquid, or vaporized phenol is rapid and results in systemic damage to the nervous system, heart, respiratory system, liver, and kidneys (Whitthaus, 1911; Piotrowski, 1971). In some exposures, hemolysis leading to hemoglobinuria and jaundice have been reported. NIOSH (1976) further states that "phenol in excess of normal physiologic capacities adversely affects nearly all organs."

The significant health hazard from chronic exposure to low levels of phenol, especially in industrial environments, may be its tumor-promoting activity which has been demonstrated in several strains of mice. However, no information is available concerning chronic human exposure to phenol from inhalation or skin contact; nor are epidemiological studies of occupational exposure to phenol by inhalation found in the literature.

However, animals clinically exposed to phenol vapor have exhibited myocardial, pulmonary, vascular, hepatic, and renal damage (Deichmann et al., 1944). In addition, phenol appears to have tumor-promoting activity in many strains of mice when repeatedly applied to the shaved skin after initiation with known carcinogens (Boutwell and Bosch, 1959; Van Duuren et al., 1971; Van Duuren and Goldschmidt, 1976). It was not found to be carcinogenic when applied alone to the skin of standard strains of mice.

A threshold limit value of  $20 \text{ mg/m}^3$  (5 ppm) determined as a TWA, or of  $60 \text{ mg/m}^3$  as a ceiling concentration for 15 minutes has been recommended by NIOSH (1976) and is in agreement with the OSHA standard.

### Cresol

Cresol presents an occupational hazard from both dermal contact and vapor/aerosol inhalation. Due to the similarities between the reported health effects of exposure to cresol and phenol, these two chemicals have usually been considered analogous with regard to toxicological manifestations. Both

chemicals are readily absorbed, cause skin and eye burns, and produce systemic damage to the nervous system, heart, liver, and kidneys.

However, NIOSH (1978a) cites a French study of 34 resin workers exposed to cresol, formaldehyde, and ammonia (Corcos, 1939) and a Russian animal study (Uzhdavini et al., 1974) as evidence for setting a more stringent limit on exposure levels of cresol. They conclude that, while dermal exposure to phenol and cresol produces similar effects, inhalation of cresol results in more severe upper airway irritation. In addition, NIOSH reports that repeated or prolonged skin exposure to low concentrations of cresol may cause skin rash and discoloration -- a sensitization reaction not seen in phenol exposure.

A threshold limit value of 2.3 ppm determined as a time-weighted average is recommended by NIOSH (1978a). The OSHA standard is 5 ppm (22 mg/m<sup>3</sup>).

### Xylenol

Inhalation and dermal contact with xylene result in absorption, rapid metabolism, and excretion in the urine (NIOSH, 1978a). Much of the information on the toxic effects of exposure to xylene comes from Russian studies in animals.

Acute exposures to xylene cause moderate toxic effects, but less than exposure to phenol or to the monomethylphenols (cresols) (Uzhdavini et al., 1974). Signs of acute toxicity include irritation of the skin and mucous membranes, blood vessel dilation, and neuropathy, all of which vary with dose and route of exposure.

In chronic toxicity studies using mice, xylene inhalation produced slight growth retardation (Uzhdavini et al., 1979). A study with rats given oral doses of xylene resulted in decreased liver, kidney, and heart weights, and dystrophy of liver cells (Maazik, 1968).

Xylene dissolved in benzene promoted papillomas and carcinomas when skin-painted on mice after one subcarcinogenic dose of the initiator DMBA

(Boutwell and Bosch, 1959). Some of the results indicated that xyleneol might also be a carcinogen; however, the mice used (Sutter) are highly susceptible to carcinomas. No information was found on xyleneol's possible carcinogenicity for humans, but contact is generally avoided at levels far below those used in the animal studies.

No exposure guidelines are available for xyleneol.

#### TOXIC GASES AND VAPORS

Coal conversion processes which involve the reaction of coal constituents under high temperatures and high pressures present a potential for leakage of toxic gases and vapors into the industrial environment. Although these gases and vapors are normally confined in vessels and pipelines, release can occur from leaking valves, seals, flanges, and vents, as well as during a process upset or vessel rupture.

The toxic gas that is expected to be present in all coal conversion processes at concentrations that can be dangerous is hydrogen sulfide. In addition, lower levels of other toxic gases and vapors including hydrogen cyanide (HCN), carbon disulfide (CS<sub>2</sub>), carbonyl sulfide (COS), and various metal carbonyls may be present. Carbon monoxide is present in coal gasification processes as a major constituent of the product gas, in some processes exceeding 20%.

#### Hydrogen Sulfide

A large, acute exposure to hydrogen sulfide can cause respiratory failure and death within a few minutes. Other CNS symptoms of an acute, sublethal dose include weakness, dizziness, headaches, nervousness, and convulsions. Recovery is usually complete, although residual polyneuritis from resulting CNS damage has been reported (Hamilton and Hardy, 1974). The mechanism of actions appears to be inhibition of the cytochrome oxidase system necessary for cellular respiration (Doull et al., 1980), and toxic action on the carotid body (Hamilton and Hardy, 1974) leading to central respiratory paralysis. Hypoxia resulting from the inability of cells to utilize oxygen can cause damage to other organs as well.

Hydrogen sulfide is also a potent local irritant. Eye exposure results in conjunctivitis, keratitis, and palpebral edema, although corneal ulceration is rare. Photophobia and lacrimation have also been reported. However, no reports of lasting eye damage were found in the literature (NIOSH, 1977b). Respiratory tract irritation produces rhinitis, pharyngitis, bronchitis, pneumonia, and hemorrhagic pulmonary edema.

Effects of chronic exposure to low concentrations of hydrogen sulfide have not been documented. Cough, disturbed sleep, fatigue, headache, nausea, vomiting, and diarrhea have all been reported at a wide range of concentrations.

NIOSH recommends a ceiling concentration for hydrogen sulfide no greater than 10 ppm; the OSHA standard is a ceiling value of 20 ppm with a maximum peak of 50 ppm for a maximum duration of 10 minutes one time only.

#### Carbon Monoxide

In coal gasification, the dry, raw product gas from the gasifier contains up to 20 percent carbon monoxide (CO). This concentration is further increased by gas purification processes which remove carbon dioxide and hydrogen sulfide.

The most acute and obvious effect of exposure to large amounts of CO is CNS depression, with accompanying symptoms of headache, dizziness, drowsiness, nausea, vomiting, coma, and death from respiratory arrest. These symptoms all result from hypoxia caused by the replacement of normal oxyhemoglobin by carboxyhemoglobin and a resultant decrease in the oxygen-carrying capacity of the blood.

Because carbon dioxide blood levels are not affected and therefore do not trigger a respiratory stimulation response, unconsciousness usually precedes awareness of distress. NIOSH (1978c) defines the IDLH concentration as 1,500 ppm. This represents the maximum level from which one could escape

within 30 minutes without any escape-impairing symptoms or any irreversible health effects. The OSHA standard is 50 ppm.

Once an exposure is terminated, complete recovery is the rule unless hypoxia has produced cell damage. Surviving victims who have experienced prolonged unconsciousness may have permanent damage, especially to the CNS basal ganglia and subthalamus. A relapse or delayed toxicity has been reported in some patients regaining consciousness. In these cases, CNS deterioration and death occur within a few weeks of apparent recovery.

The results of chronic, long-term exposure to low levels of carbon monoxide are less well documented but of increasing concern. Neurologic, behavioral, and cardiac effects have all been reported and refuted. Exposure to carbon monoxide increases blood carboxyhemoglobin in proportion to the CO air concentration as well as the length of exposure and individual ventilation rate (increased during work). A rough correlation of air concentrations and 8-hour equilibrium levels of carboxyhemoglobin are shown below:

<u>ppm</u>	<u>% Carboxyhemoglobin</u>
10	2
20	3.7
30	5

Table C-6 summarizes the major toxicological effects and target organs for the groups of chemicals studied in the five coal liquefaction plants.

Table C-6. Major Toxicological Effects of Chemicals Sampled  
at Coal Conversion Facilities

Chemical	Major Organs at Risk	Indicator of Exposure
PNAs	Skin (cancer) Lung (cancer)	
Aromatic Amines	Lung (cancer) Urinary Tract (cancer)	
Naphthalene	Blood (methemoglobinemia, hemolysis)	
Aniline	CNS Liver	
Benzene	CNS (depressant) Blood-forming elements (depression, cancer)	Urinary phenols
Toluene	CNS (depressant) Skin (sensitization)	Urinary hippuric acid
Xylene	CNS (depressant)	Urinary hippuric acid
Phenolics	CNS (depressant) Cardiovascular System Respiratory System Liver Kidney "all organs" (NIOSH, 1977) (cancer promoter)	Urinary or serum phenol
Cresol	Skin (sensitization)	
Carbon Monoxide (CO)	CNS (depressant) Heart (stress)	Blood carboxyhemoglobin
Hydrogen Sulfide (H <sub>2</sub> S)	CNS (depressant, respiratory arrest)	

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