

6. STREAM ANALYSIS FOR TRACE ELEMENTS AND OTHER POTENTIAL POLLUTANTS

6.1 General

One of the areas of coal conversion that is the most difficult to evaluate is the control of pollution by trace elements in coal and by trace organic compounds formed during conversion operations. The main difficulty is the paucity of analytical data from streams in coal conversion plants. A fair amount of data is available on trace elements in coal (1) but the fate of these elements in a gasification or liquefaction plant is largely unknown. Some qualitative data are available on carbon containing compounds formed in coal conversion, but little quantitative data are available. From the data available on trace elements and other trace compounds in coal conversion systems, it is difficult to decide if a problem with these materials exists. Information that has been collected under this contract together with a test plan to determine the fate of trace materials in coal conversion are presented in this section.

6.2 The Fate of Trace Elements in Coal Conversion

6.2.1 Trace Elements in Coals

A large amount of data has been accumulated on coals and coal ash under U.S. Bureau of Mines (USBM), U. S. Geological Survey (USGS), and the Illinois State Geological Survey (USGS). This material as well as that from other sources was surveyed and summarized in an early phase of this project. The data are summarized here in figure 4 for elements by regions. (A represents the Appalachian region, IE and IW are the Interior Eastern and Interior Western regions, N refers to the Great Northern Plains region, W indicates the Western region and SW symbolizes the Southwestern area of the Western region.)

In figure 4, USBM data for ppm on ash are shown at the top, and the USGS data on a coal basis at the bottom. The bar graphs for coal are the 90+% ranges, the dotted lines (---) are the extremes listed, and the regional average (●) is for the total region as given by USGS. This average is usually near the middle of the bar or may exceed it when there are many extremes, as for copper or zinc. Ranges which start below the limit of detection are shown by a broken bar line below 1 ppm in figure 4. Shorter dotted lines (--) represent values outside the 90+% range which were included in the USGS average but excluded here because they were for beds less than 75% analyzed. Artificially high specimen sample values for mercury are indicated by a 0, and Δ shows the high values for weathered samples, not included in the averages.

The bar graphs for most elements, thus adjusted, lie within the range of 1 to 50 ppm, and mostly close to 5-10 ppm on coal. The only elements significantly higher than this are boron and fluorine, in the range from 10 to 200 ppm. Beryllium is lower in all regions by an order of magnitude, at about 0.1 to 5 ppm, and Hg by two orders of magnitude, at about 0.01 to 0.5 ppm on coal.

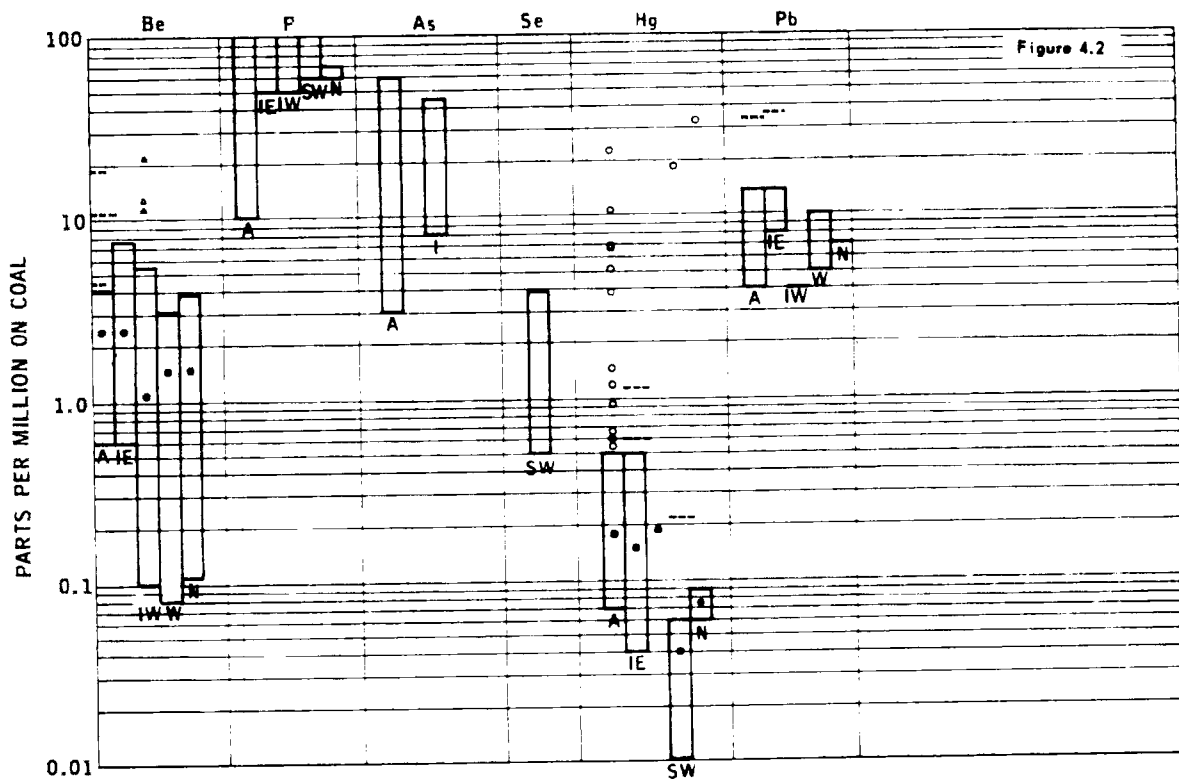
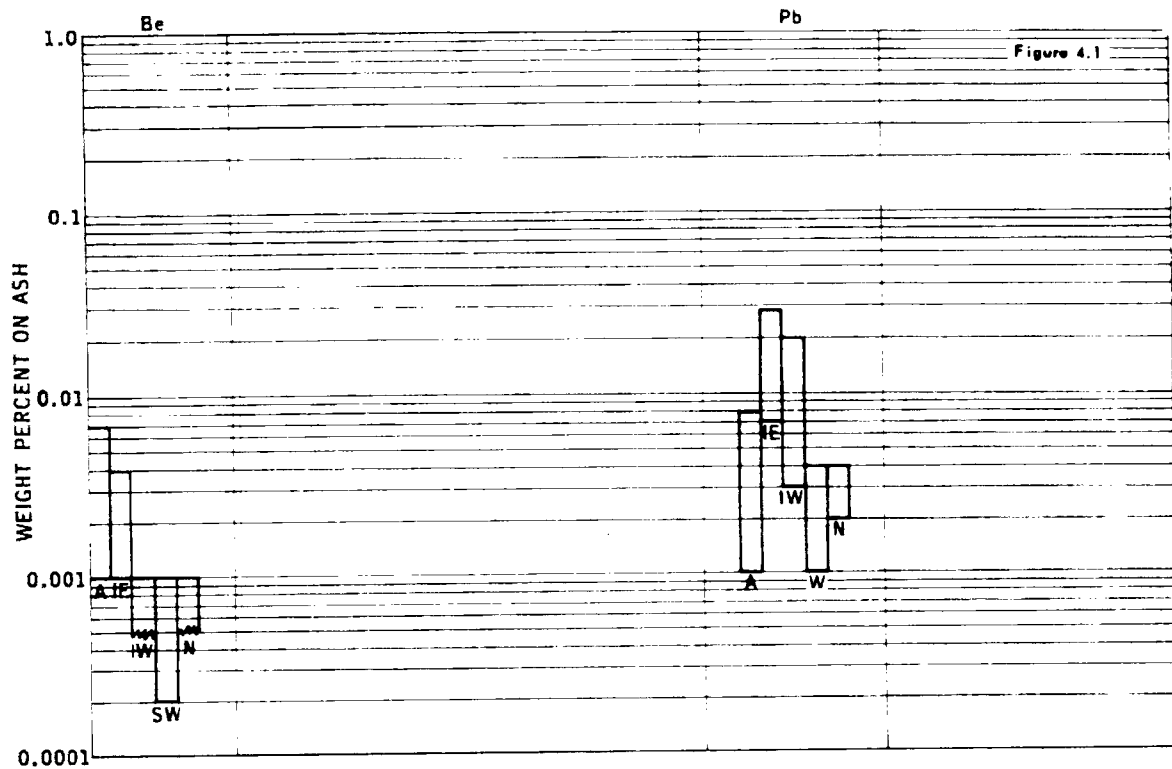


Figure 4

Trace Elements in U.S. Coals

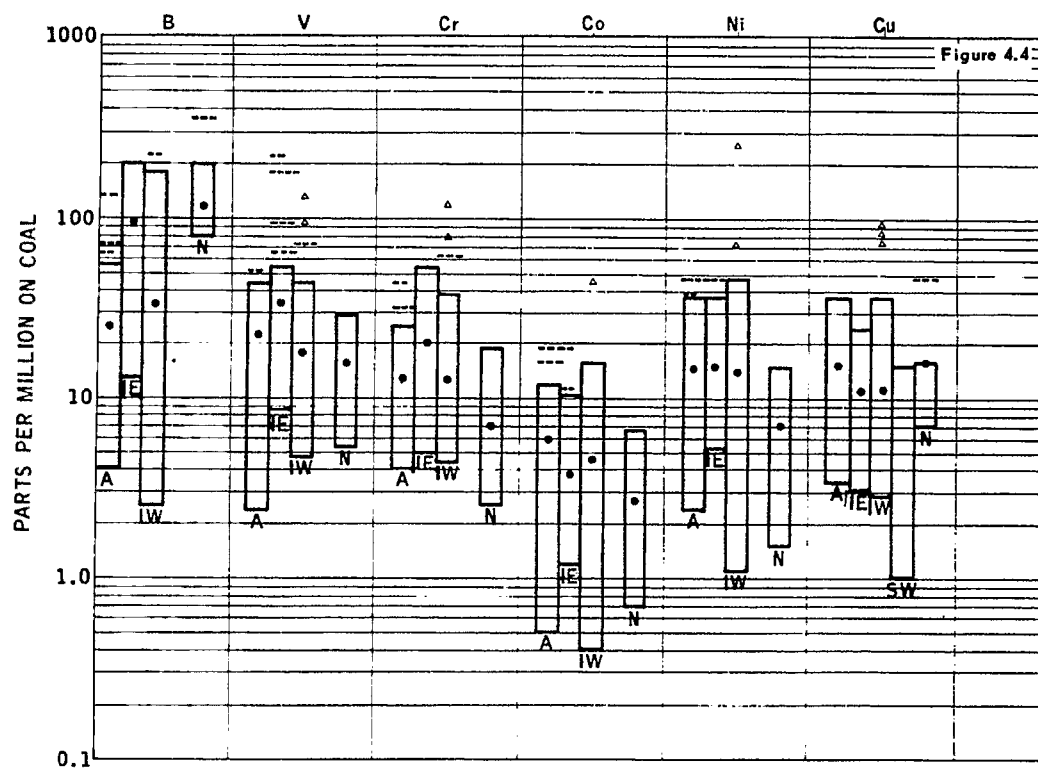
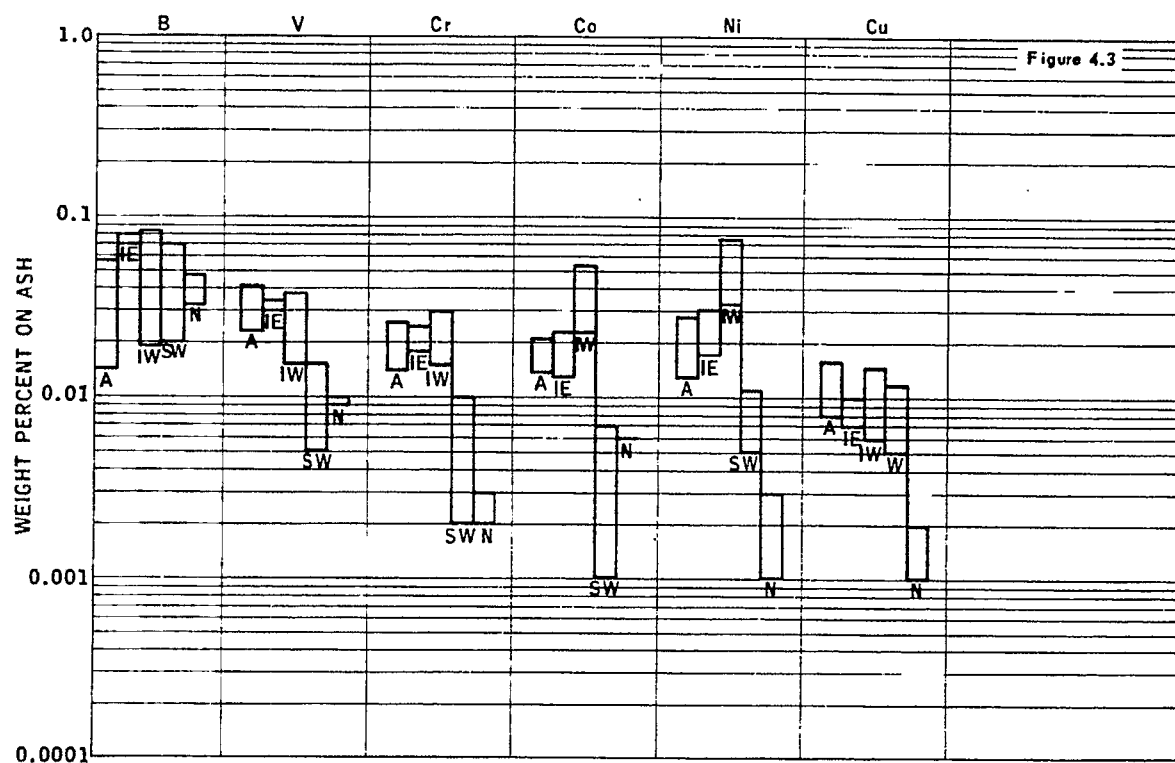


Figure 4 (Cont'd)

Trace Elements in U.S. Coals

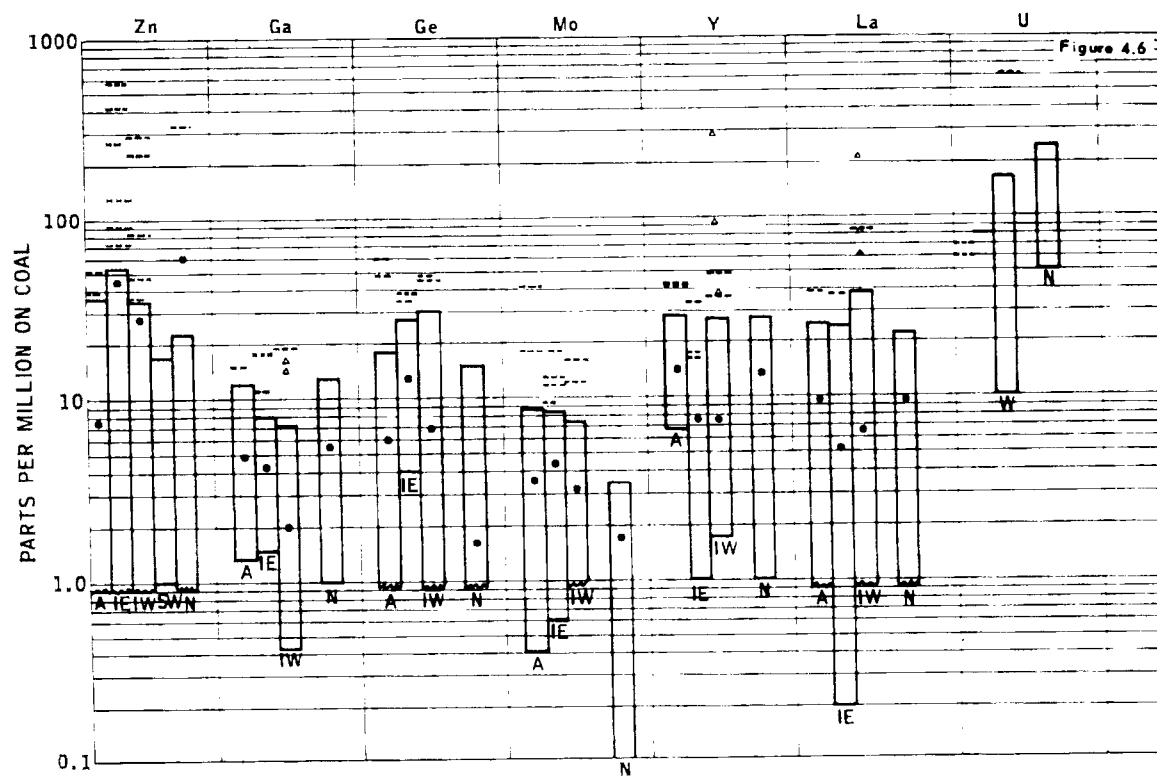
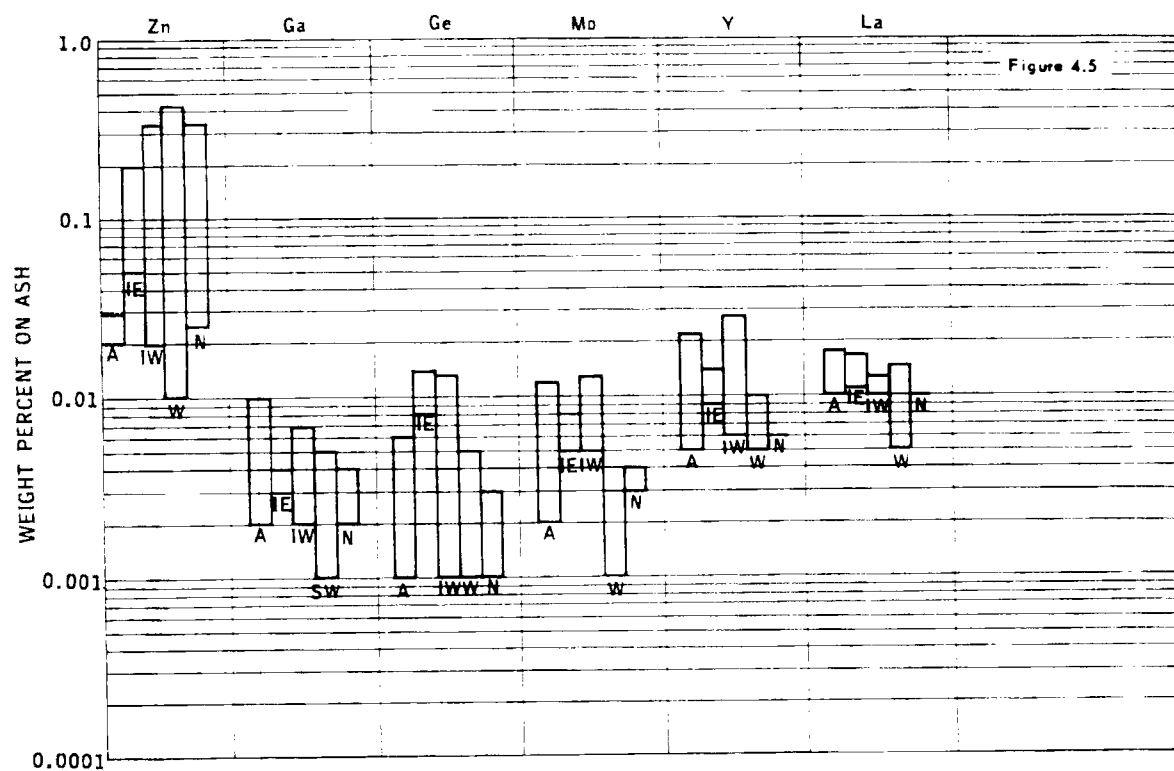


Figure 4 (Cont'd)

Trace Elements in U.S. Coals

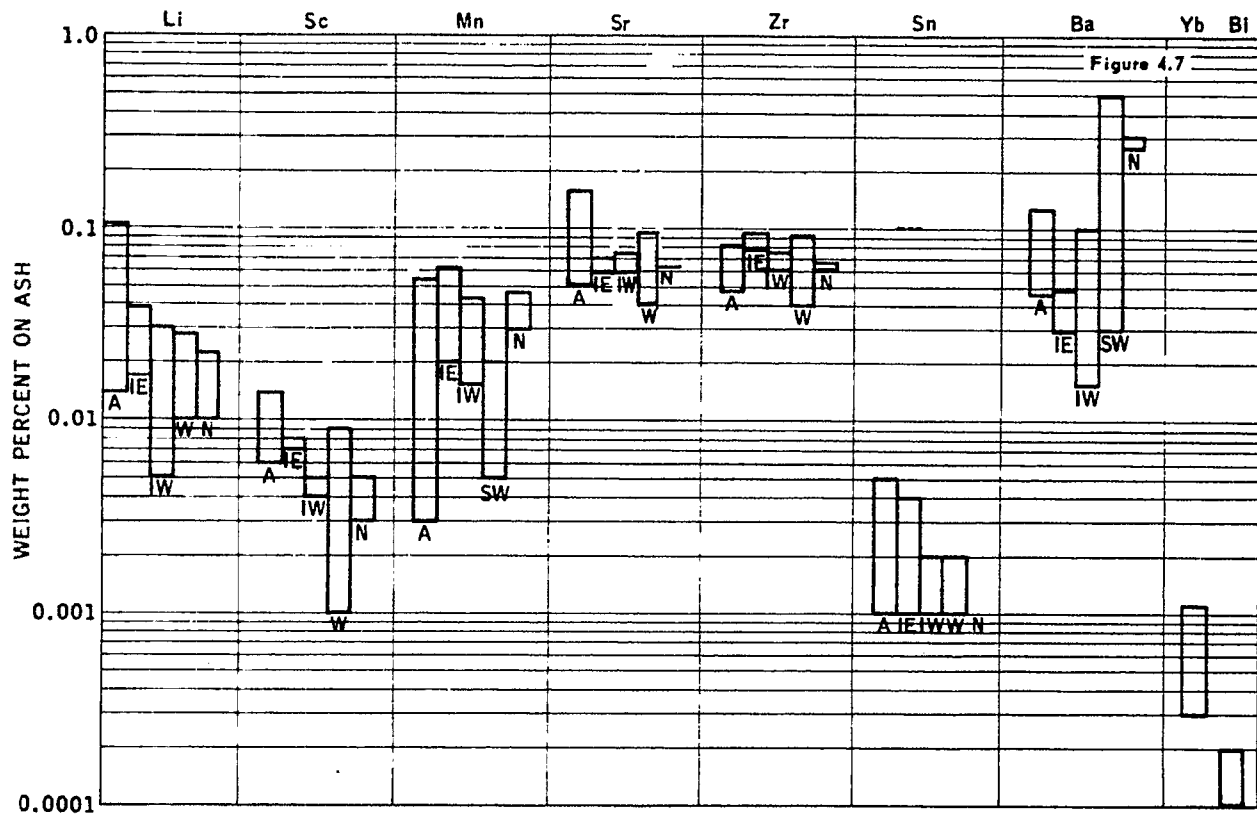


Figure 4 (Cont'd)
Trace Elements in U.S. Coals

The following are correlations indicated by the data obtained in this study:

1. Sulfur in coals appears in moderate amounts in the Appalachian region, higher in the Interior region (East and West), and less in all the Western coals.
2. Trace element concentration as a whole correlates only moderately with geographical location, and not at all with coal rank. Boron, which is high in lignites and lower in high rank coals, is an exception.
3. The amount of some trace elements is commonly highest in the top and bottom few inches of a bed, and at the edges of a coal basin (Ge, Be, Ga, and B at bottom only). These variations are frequently greater than the differences between the averages for different beds. Other elements (Cu, Ni, Co) show no such correlation.
4. Different elements tend to be concentrated at different parts of the bed or basin, depending on the geochemical processes involved in the formation of the coal.
5. Those elements which tend to be concentrated in coals (S, Ge, Be, B, Ga) are associated primarily with the organic portion of the coal. They also show the largest variance in average concentrations between different major producing areas: e.g., for germanium, which is high in Illinois.
6. The usual amount of some 20 trace elements present is about 5-10 ppm, in the range 1-50 ppm. B and F are higher, about 10-200 ppm, and Hg is lower, about 0.01-0.5 ppm.
7. Most trace elements are present in concentrations which fall within a narrow range, varying by a factor of 3 or less in the averages for different basins or areas. This range is close to their average crustal abundance, which usually lies between the concentration of the element in coal and its concentration in ash. Boron and germanium in coal are high compared to crustal abundance, and only a few elements such as manganese are low.
8. The selection of a completely "non-polluting" coal is not possible, in the general case. For a given amount of ash, coals which are low in any group of elements must be correspondingly high in others. The definition of non-polluting depends directly on the decision as to which elements are of concern, and which are not.
9. Trace element variations between coals in different areas often reflect differences in the source rocks which contributed the elements to the coal-forming swamps, and the distance of the source rocks from the swamp. In certain areas, e.g., the Illinois basin, this shows an instructive geographical pattern.

10. Surface outcrops or samples weathered otherwise by exposure may not be indicative of trace element concentrations in the coal at depth. Surface oxidation creates active sites on the coal, with which minor elements in flowing water can selectively react.
11. The elements present in largest amount, as minor components of the coal rather than as traces only, are the common constituents of surface waters and rocks: silicon, aluminum, iron, sulfur, phosphorus, sodium, potassium, calcium, and magnesium. These are present throughout the coal but they are often enriched in the top layer, where they have apparently been leached out of enclosing sediments.
12. Anomalous amounts of specific elements may be found in beds contiguous to mineral ore bodies of the same element. This is regularly the case for coals having a mercury, lead, zinc or uranium content higher than the usual range, and may be equally true for other elements including copper, tin and arsenic.

6.2.2 Trace Elements in Coal Feed to Processes in this Study

The trace elements in coals assumed as feeds for the various processes were given in each process report when information was available. Generalizations concerning trace elements in feeds are not possible; each prospective coal must be examined individually to determine what trace elements of interest are present and to what degree they will affect pollution control. Figure 4 is an indication of the ranges that must be considered.

6.2.3 Fate of Trace Elements in Coal

Although there is considerable information available, as indicated in Section 6.2.2, on the trace element composition of coals, much less is known concerning the fate of these elements during gasification and liquefaction. What goes into the plant must reappear somewhere. Thus, if 20,000 tons per day of coal is used as feed and this coal contains 1 wppm of a trace element, then 40 pounds per day of that element must appear in streams in the plant.

The fate of trace elements during combustion was determined in a study of both experimental and industrial furnaces (45). Some 85-90% of the mercury in coal leaves in the flue gas, and is not retained in the ash. Neither is it removed with the fly ash in an electrostatic precipitator. A large portion of the cadmium and lead are also vaporized during the combustion process, but the indications are that these will be retained with the fly ash and can be separated, for example, by an electrostatic precipitator on the stack gas. This work also shows that some elements appear in higher concentrations in the high density fractions of coal, so that coal cleaning may be effective in some cases for control.

Mass balances were made for 34 elements on a coal fired power station (46). More than 80% of the mercury and much of the selenium leave as a vapor. The electrostatic precipitator was about 98% efficient for removing fly ash and the elements associated with it. Other studies on furnaces have been described in references 47-49.

One study has been made on the trace element content of coal solids after various stages of treatment (50). The results are shown in Table 57. A very recent attempt has been made to make a material balance on trace elements in coal gasification (51). The recovery was variable, ranging from 17 to over 100 percent. Some information is available on the trace element content of liquid products from the SRC process (42).

It is obvious that all materials entering the plant must also leave via the effluent or product streams. Many of the trace elements volatilize to a small or large extent during processing, and many of the volatile components can be highly toxic. This is especially true for mercury, selenium, arsenic, molybdenum, lead, cadmium, beryllium, and fluorine.

The fate of trace elements in coal conversion operations such as liquefaction or gasification can be very different than experienced in conventional coal fired furnaces. One reason is that the conversion operations take place in a reducing atmosphere, whereas in combustion the conditions are always oxidizing. This maintains the trace elements in an oxidized condition such that they may have more tendency to combine or dissolve in the major ash components such as silica and alumina. Furthermore, the reducing atmosphere present in coal conversion may form compounds such as hydrides, carbonyls, or sulfides which may be more volatile.

Consideration must also be given to trace metals that are not volatilized and leave in the solid effluents from the plant, one of which is the slag or ash from the coal fired furnace and from gasification. Undesirable elements might be leached out of this slag since it is handled as a water slurry or will ultimately be exposed to leaching by ground water when it is disposed of as land fill or to the mine. Sufficient information is not now available to evaluate the potential problems and the situation on gasifiers may be quite different from the slag rejected from coal fired furnaces since it is produced in a reducing rather than an oxidizing atmosphere. Background information on slag from blast furnaces used in the steel industry may be pertinent from this standpoint, since the blast furnace operates with a reducing atmosphere. However, a large amount of limestone is also added to the blast furnace, consequently the nature of the slag will be different.

Other possible sources of trace element emissions from the plant need to be evaluated. Thus, additives such as chromates may be used in the cooling water circuit and appear in the blowdown stream. Depending upon the amount present and the particular plant location, it may be desirable to provide for chromium removal, for example using lime precipitation. Similarly, trace elements may be present in chemical purge streams such as from acid gas removal systems where arsenates etc. may be used as additives, or from absorption/oxidation sulfur plants using catalysts such as vanadates.

Table 57

Trace Element Concentration Of Pittsburgh No. 8 Bituminous Coal At
Various Stages Of Gasification

Calculated on the Raw Coal Basis (From Ref. 50)

	<u>Feed Coal</u>	<u>After Pretreat</u>	<u>After Hydro- Gasifier</u>	<u>After Electro Thermal Gasifier</u>	<u>% Overall Loss for Element</u>
Max. Temp. of Treat, °C	-	430	650	1000	
Element:	_____ppm_____				
Hg	0.27	0.19	0.06	0.01	96
Se	1.7	1.0	0.65	0.44	74
As	9.6	7.5	5.1	3.4	65
Te	0.11	0.07	0.05	0.04	64
Pb	5.9	4.4	3.3	2.2	63
Cd	0.78	0.59	0.41	0.30	62
Sb	0.15	0.13	0.12	0.10	33
V	33	36	30	23	30
Ni	12	11	10	9.1	24
Be	0.92	1.0	0.94	0.75	18
Cr	15	17	16	15	0

It can be concluded that, until more information is available as to what streams trace elements appear in, what form they are in, and in what quantities they appear, little can be decided on how to prevent their movement into the environment or even whether or not they present a problem if they do.

6.3 Trace Elements in Petroleum and Shale

A major survey was made to determine the trace elements in petroleum and shale. The results of this survey were reported in detail in reference 1 but are summarized in Appendix D for information purposes. Correlations found in the data and new data required are indicated below.

6.3.1 Correlations Indicated

Correlations indicated and conclusions drawn from the data and information presented herein are given below.

1. The sulfur and nitrogen levels of crudes consumed in the U.S. are well characterized while the levels for other trace elements are not.
2. Vanadium and nickel analyses are qualitatively correct but different methods of analysis produce somewhat different results. Values for other trace elements are more questionable.
3. Part (or even all) of the quantity reported for certain elements present in trace concentrations in a sample may have been introduced inadvertently by well piping, transportation systems, preparation of the sample for analysis, etc.
4. Analytical data on elements contained in crudes as suspended material or dissolved in associated water cannot have the same impact as data obtained from elements present as an intimate part of the organic matrix.
5. Samples must be completely identified as to their origin if data are to be meaningful.
6. Correlations have been developed between crude oil trace element concentrations and the geological occurrence of the oil. This is especially true for sulfur. These correlations may aid in locating crudes possessing low concentrations of trace elements.
7. The increasing demand for crude oil by the U.S. coupled with declining domestic production means that the developing crude oil gap will be met by imports.
8. Imports of crude from the Middle East can be expected to increase substantially. Imports from Canada and Venezuela already at high levels will change proportionally less.

9. Crude from the Middle East is of lower quality than much of U.S. production. The consumption of increasing quantities of Middle Eastern crude will decrease the overall quality of crudes processed in the U.S. This can require additional refining complexity in those refineries processing these crudes.
10. Trace element data are factors which contribute towards the establishment of a price for a given crude.

6.3.2 New Data Required

Based upon these conclusions it is apparent that a number of unmet needs exist related to crude oil trace element data. These unmet needs are listed below.

1. Far more extensive data are required for potentially hazardous elements present in trace concentrations in crude oil. This information should be obtained first on those crudes consumed in the greatest amounts in the U.S. Data from oil fields which can be expected to contribute to U.S. needs in the future (such as underdeveloped fields in the Middle East) would also be of value.
2. Referee methods must be developed in order to determine those trace elements that cannot be analyzed reliably at present. Several programs are underway to accomplish this. The methods developed should be widely promulgated as a first step in making crude oil trace element data more widely available.
3. It must be determined at which point a sample of oil should be obtained if the elemental analysis is to yield the maximum amount of information. In addition, it must be determined if it is desirable to remove extraneously introduced matter such as water and suspended particulates.
4. Further correlations should be developed between trace element data and geological information to aid in the search for high quality crude oils, i.e., those crudes possessing low levels of significant trace elements.

6.4 Trace Compounds Formed in Coal Conversion

In addition to the trace elements originally present in coal, it is also necessary to be concerned with the trace materials formed during processing. Some idea of the broad spectrum of chemicals produced in coal conversion is indicated in reference 52. Components in the gasifier gas, analyses of benzene-soluble tar, and by-product water analyses are shown in Tables 58, 59 and 60.

Table 58

Components In Gasifier Gas (From Ref. 52)
(ppm)

	<u>Pittsburgh Seam Coal</u>	<u>Illinois No. 6 Coal</u>
H ₂ S	860	9,800
COS	11	150
Thiophene	42	31
Methyl Thiophene	7	10
Dimethyl Thiophene	6	10
Benzene	1,050	340
Toluene	185	94
C ₈ Aromatics	27	24
SO ₂	10	10
CS ₂	--	10
Methyl Mercaptan	8	60

Table 59

Mass Spectrometric Analyses Of
Benzene-Soluble Tar
From Synthane Gasification (Ref. No. 52)
(Vol. %)

Structural type; includes alkyl derivates	HP-118 ^{a/} #118 <u>Pittsburg</u>	HP-1 ^{a/} #92 <u>Illinois</u>
Benzenes	1.9	2.1
Indenes	6.1 ^{b/}	8.6 ^{b/}
Indanes	2.1	1.9
Napthalenes	16.5	11.6
Fluorenes	10.7	9.6
Acenaphthenes	15.8	13.5
3-ring aromatics	14.8	13.8
Phenylnapthalenes	7.6	9.8
4-ring peri-condensed	7.6	7.2
4-ring cata-condensed	4.1	4.0
Phenols	3.0	2.8
Napthols	<u>b/</u>	<u>b/</u>
Indanols	0.7	0.9
Acenaphthenols	2.0	--
Phenanthrols	--	2.7
Dibenzofurans	4.7	6.3
Dibenzothiophenes	2.4	3.5
Benzonaphthothiophenes	--	1.7
N-heterocyclics ^{c/}	(8.8)	(10.8)
Average mol. wt.	202	212

^{a/} Spectra indicate traces of 5-ring aromatics.

^{b/} Includes any naphthol present (not resolved in these spectra).

^{c/} Data on N-free basis since isotope corrections were estimated.

Table 60

By-Product Water Analysis^{1/} From Synthane Gas (Ref. No. 52)

	<u>Pittsburgh</u> <u>Seam</u>	<u>Illinois</u> <u>No. 6</u>	<u>Coke</u> <u>Plant</u>
pH	9.3	8.6	9
Suspended Solids	23	600	50
Phenol	1,700	2,600	2,000
COD	19,000	15,000	7,000
Thiocyanate	188	152	1,000
Cyanide	0.6	0.6	100
NH ₃	11,000	8,100 ^{2/}	5,000
Chloride		500	
Carbonate		6,000 ^{3/}	
Bicarbonate		11,000 ^{3/}	
Total S		1,400 ^{4/}	

^{1/} Mg/liter (except pH)

^{2/} 85% free NH₃

^{3/} Not from same analysis

^{4/} S⁼ 400

SO₃⁼ 300

SO₄⁼ 1,400

S₂O₃⁼ 1,000

Compounds formed in coal conversion may cause environmental problems, but, unfortunately, little information is available as to the concentration of such materials in plant effluents. As a first step in obtaining the necessary information, an analytical test plan was constructed to guide in obtaining the necessary data. This plan is described in the next section.

6.5 Data Acquisition

No systematic study of a coal gasification or liquefaction plant is available that shows the fate of trace elements and trace organic compounds. It is impossible to estimate the concentrations of these materials and therefore sampling of the necessary streams with subsequent analysis of the samples is necessary to determine what controls are necessary. As part of the present program, an Analytical Test Plan (ATP) was devised for obtaining the needed information (53). This ATP is summarized here and for more information, the reader is referred to the original report.

6.5.1 Analyses to be Made

In selecting the possible pollutants for analysis in the selected plant streams, five factors were considered. These were: 1) the potential impact of the pollutant on the environment, 2) available data regarding the composition of commercial coal gasification and liquefaction plant streams, 3) the minor and trace constituents of coals, 4) various process considerations, and 5) lists supplied by the EPA of materials which are considered potential environmental hazards.

On the basis of this literature, the materials listed in Table 61 were selected for analysis. In addition to these materials other analyses were deemed desirable to include in the test plan because some environmental insight might be gained of the process in general; these analyses are listed in Table 62.

6.5.2 Analytical Techniques

The types of samples were classified as: 1) aqueous samples, 2) coal and coal-related solid samples, 3) gas and ambient air samples, and 4) coal liquid samples. Metals were discussed separately. Methods were referenced and discussed for analysis of each material contained in the sample classes. Techniques were given for sampling streams falling into the various classes. Sample preservation was indicated, where needed.

6.5.3 Coal Conversion Streams to be Sampled

Figure 5 shows the block flow diagram of the model gasification plant used in preparing the ATP. Table 63 lists those streams that should be sampled and analyzed. The ATP gives the methods for sampling and analyzing these streams. Successful analysis of these streams will give the disposition of the pollutants in gasification, but errors may occur due to faulty sampling, interfering substances, or others. It may then be necessary to analyze other streams to check the first analyses. If this is the case, it will be advisable to analyze the streams indicated below.

Table 61

Possible Pollutants From Coal Processing

<u>Metals</u>	<u>Gases</u>	<u>Polynuclear Aromatics</u>
As	AsH ₃	Benzo(k)fluoranthene
Ba	H ₂ Se	Benzo(b)fluoranthene
Be	Fe, Co and Ni Carbonyls	Benzo(a)pyrene
Ca	SO ₂ /SO ₃	Benzo(e)pyrene
Cd	NO _x	Perylene
Cr	COS	Benzo(ghi)perylene
Fe	H ₂ S	Coronene
Hg	CH ₃ SH	Chrysene
Li	NH ₃	Fluoranthene
Mn	H ₂	Pyrene
Na	CO	Benzo(ghi)fluoranthene
Ni	CO ₂	Benz(a)anthracene
Pb	CH ₄	Triphenylene
Sb		Benzo(j)fluoranthene
Se		
V		

Other Organic Materials

Thiophene
CS₂
phenols
benzene
toluene
xylene
oil
acids
aldehydes

Inorganic Ions

CN⁻ Cl⁻
SCN⁻ Phosphates
F⁻
S⁼
CO₃⁼

Particulates

Table 62

Other Analyses

Coal Analysis

Moisture
Ash
Volatile Matter
Fixed C
S
O
C
H
N
Calorific Value
Fusibility of Ash

Water Quality Indicators

Specific Conductance
pH
COD
BOD
TOC
Residue
Dissolved Oxygen
Suspended solids
Dissolved solids
Turbidity
Color
Oils

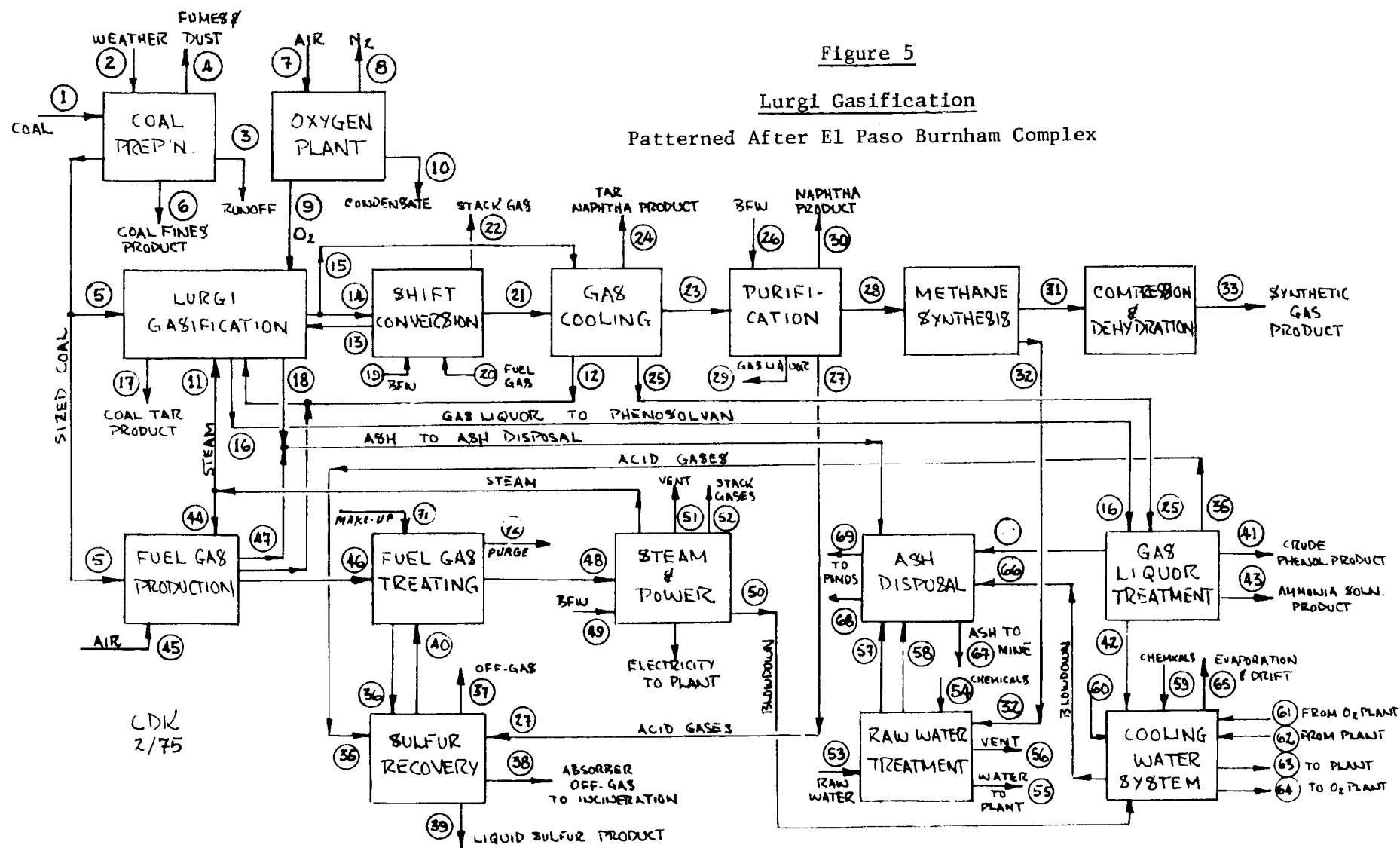


Table 63

Summary Of Effluent Streams To Be Analyzed

Coal Gasification

Lurgi Process Model

<u>Stream No.</u>	<u>Stream Name</u>	<u>Analysis For</u>
4	Dust and Fumes in Coal Preparation Area	Atmosphere in enclosed spaces, discrete stack emissions from enclosed spaces and from dust collection equipment, and atmosphere in vicinity of coal piles, open conveying and handling equipment, and coal fines collection system to be analyzed for particulates.
5	Sized Coal to Gasifiers and to Fuel Production	Complete coal analysis including trace elements.
17	Coal Tar Product*	Trace Sulfur Compounds Trace Elements
22	Shift Startup Heater Stack Gas	Stack Gas Analysis Trace Sulfur Compounds Particulates
24	Tar-Oil-Naphtha Product*	Sulfur Trace Elements
30	Naphtha Product*	Sulfur Trace Elements

Table 63 (Cont'd)

Summary Of Effluent Streams To Be Analyzed

Coal Gasification

Lurgi Process Model

<u>Stream No.</u>	<u>Stream Name</u>	<u>Analysis For</u>
33	Synthetic Gas Product	Trace Sulfur Compounds Metal Carbonyls
37	Absorber and Oxidizer Off-Gases and Incinerator Stack Gases	Trace Sulfur Compounds
38		Particulates (V, Ni, Na, etc.)
39	Liquid Sulfur Product*	Trace Elements
41	Crude Phenol Product*	Total Sulfur Trace Elements
43	Aqueous Ammonia Solution Product*	Trace Sulfur Compounds Trace Elements
51	Deaerator Vent Gases	Particulates
52	Boiler Stacks and Heaters (multiple stacks are involved, including heaters in shift conversion and gas compression areas	Stack Gas Analysis Trace Sulfur Compounds Particulates
53	Raw Water to Process	Complete Water Analysis
56	Degasser Vent Gases	Trace Sulfur Compounds Hydrocarbons

Table 63 (Con'd)

Summary Of Effluent Streams To Be Analyzed

Coal Gasification

Lurgi Process Model

<u>Stream No.</u>	<u>Stream Name</u>	<u>Analysis For</u>
65	Evaporation and Drift from Cooling Towers	Atmosphere in vicinity of cooling towers to be sampled for: Trace Sulfur Compounds Trace Elements Hydrocarbons and PNA
67	Wet Ash to Mine	Complete coal solids analysis and complete water analysis.
68	Ash Water Effluent to Evaporation Ponds*	As for Stream 67
69	Wet Fine Ash Slurry to Evaporation Ponds*	As for Stream 67

* Atmosphere over all evaporation and holding ponds and vicinity of all storage tankage to be sampled and analyzed for hydrocarbons and trace sulfur compounds.

- Coal Preparation

Streams 2 and 3; it would be appropriate to determine the concentration of organic and inorganic materials in the run-off from the coal area as a function of the quantity of rainfall.

- Gas Cooling

Streams 15, 21; into gas cooling and streams 12, 23, and 25 from gas cooling would have to be analyzed to check the analysis of stream 24.

- Gas Purification

Streams 23 and 26 into gas purification and streams 27, 28, and 29 from the purification must be analyzed to check stream 30.

- Sulfur Recovery

In order to check streams 37, 38, and 39 it will be necessary to analyze streams 27, 35, and 36 into the low-pressure Stretford unit and stream 40 out of the unit.

- Fuel Gas Treating

It would be wise to analyze stream 72 (solution purge) from the high-pressure Stretford unit. How this is done is difficult to predict as this purge may be continuous, intermittent, or in some cases, none at all.

- Cooling Water System

This is one of the most critical units for overall material balance. Good sampling of evaporation and drift losses are difficult and other factors may make the cooling towers research projects in themselves. To get a material balance, it may be necessary to analyze streams 42, 59, 60, 61, and 62 into the system and streams 63, 64, and 66 out of the system. Even this may not be sufficient as trace pollutants can be trapped in slime in the towers. This also may have to be analyzed and its quantity estimated. Whether or not these analyses will check the analysis of stream 65 is uncertain due to the sampling problems mentioned above.

- Ash Disposal

The streams into ash disposal should probably be analyzed and compared with effluent streams 67, 68, and 69 to be sure no air pollutants are escaping. This would entail analyses of streams 18, 39, 47, 57, 58, and 66.

All of the above would require 28 to 29 more streams to be analyzed than the 20 indicated in Table 63. If satisfactory results were not obtained, then it may be necessary to analyze all 72 streams of Figure 5.

A block flow diagram of the COED process is shown in Figure 6. This process was used as a model for liquefaction. Streams to be sampled and analyzed are given in Table 64. If it is necessary to check the analyses for each unit, then it will be necessary to analyze the additional streams listed below.

Coal Preparation - Streams 2 and 4.

Stages 2,3,4 Pyrolysis - Streams 13, 14, 15, 16, 17, 18, 19
21, 22, and 39.

Oil Filtration - Streams 25, 27, 28, 29, 30, and 31.

Hydrotreating - Streams 30, 32, 33, 34, 36, 37, and 39.

Sulfur Recovery - 45 and 51, 53 and 54.

Power and Steam Generation - 20, 46, 58, 59, 60, and 64.

Cooling Water - Streams 68, 71, 72, 73, and 75.

The above would require 37 to 38 more streams to be analyzed than the 23 listed in Table 64.

6.6 Analysis of Streams from Commercial and Development Scale Gasification Plants

The tables in this section are provided as an indication of the limits of information available and to provide a frame of reference for the magnitude of the concentrations of the various streams. These data were obtained from trips to commercial coal plants and from the literature. The stream numbers in the tables refer to stream numbers of Figure 5.

Table 65 gives analyses of the feed coals as well as pertinent information on other coals. Table 66 presents analyses of materials in ash disposal. Table 67 contains information on liquor streams from various plants while Table 68 shows what information is available on streams in gas purification. Table 69 gives analyses on organic hydrocarbon by-products.

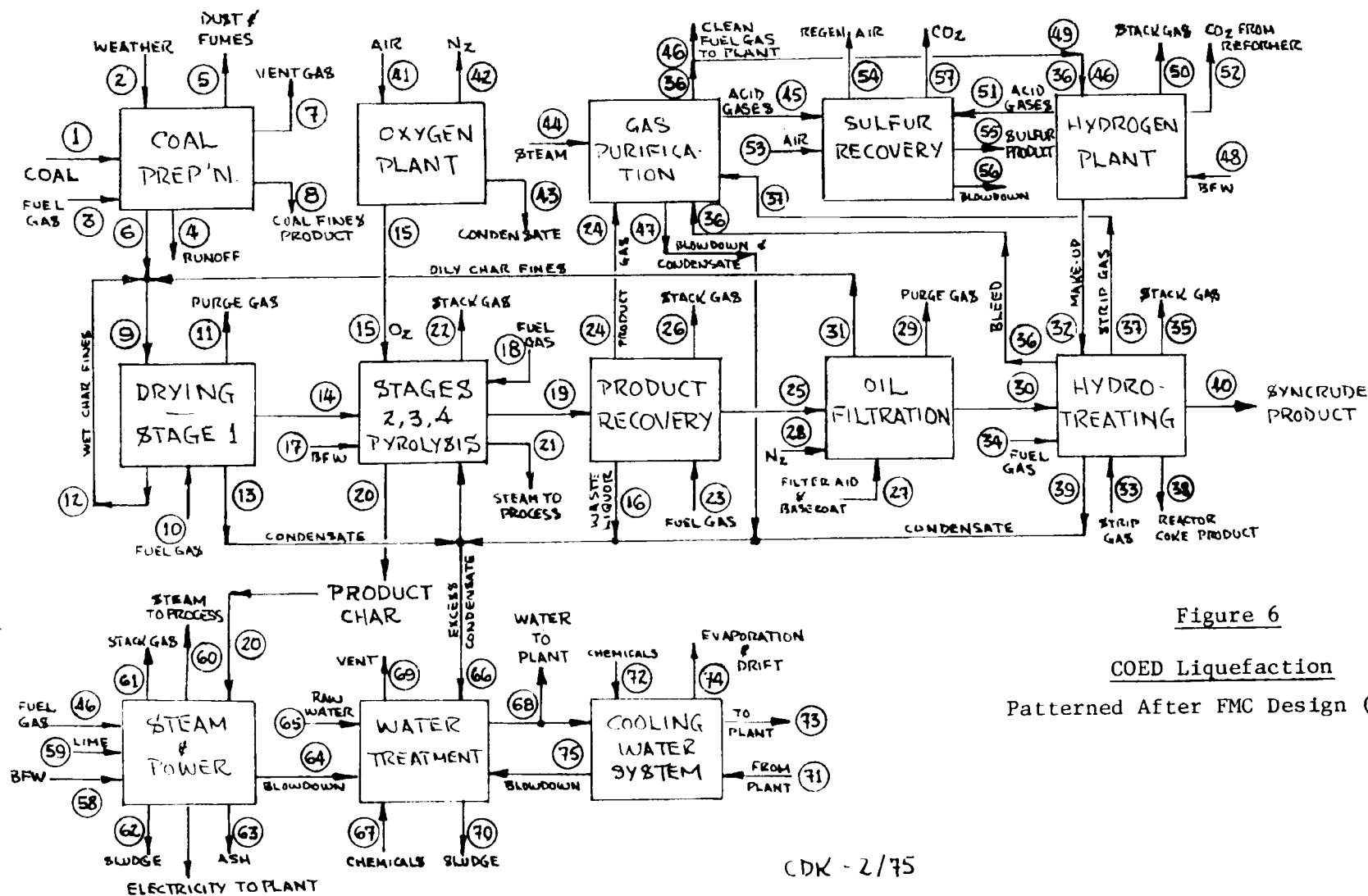


Figure 6

COED Liquefaction

Patterned After FMC Design (1974)

CDK - 2/75

Table 64

Summary Of Effluent Streams To Be Analyzed

Coal Liquefaction

COED Process Model

<u>Stream No.</u>	<u>Stream Name</u>	<u>Analysis For</u>
5	Dust and Fumes in Coal Preparation	Atmosphere in enclosed spaces, discrete stack emissions from enclosed spaces and from dust collection equipment, and atmosphere in vicinity of coal piles, open conveying and handling equipment, and coal fines collection system to be analyzed for particulates.
6	Sized Coal to Pyrolysis	Complete coal analysis including trace elements.
7	Coal Dryer Vent Gas	Stack Gas Analysis Trace Sulfur Compounds Particulates
11	Purge Gas from Stage 1 Pyrolysis	Stack Gas Analysis Trace Sulfur Compounds Particulates
20	Product Char	Complete Coal Analysis Including Trace Elements
22	Stack Gas from Superheaters	Stack Gas Analysis Trace Sulfur Compounds Particulates

Table 64 (Con'd)

Summary Of Effluent Streams To Be Analyzed

Coal Liquefaction

COED Process Model

<u>Stream No.</u>	<u>Stream Name</u>	<u>Analysis For</u>
26	Stack Gas from Transport Gas Heater	Stack Gas Analysis Trace Sulfur Compounds Particulates
35	Stack Gas from Preheater	Stack Gas Analysis Trace Sulfur Compounds Particulates
38	Hydrotreating Reactor Coke Product	Complete Coal Analysis Including Trace Elements
40	Syncrude Product	Sulfur Trace Elements
47	Benfield Blowdown	Complete coal solids analysis and complete water analysis.
50	Stack Gas from Hydrogen Plant Heaters	Stack Gas Analysis Trace Sulfur Compounds Particulates
52	Separated CO ₂ from Steam Reforming	Stack Gas Analysis Trace Sulfur Compounds Particulates
55	Sulfur Product	Trace Elements

Table 64 (Con'd)

Summary Of Effluent Streams To Be Analyzed

Coal Liquefaction

COED Process Model

<u>Stream No.</u>	<u>Stream Name</u>	<u>Analysis For</u>
56	Stretford Blowdown	Complete coal solids analysis and complete water analysis.
57	Sulfur Plant Off Gas	Trace Sulfur Compounds Particulates (V, Ni, Na, etc.)
61	Boiler Stacks and Heaters (Multiple Stacks are Involved)	Stack Gas Analysis Trace Sulfur Compounds Particulates
62	Lime Sludge from Flue-Gas Treatment	Complete coal solids analysis and complete water analysis
63	Char Ash from Boilers	Complete coal solids analysis and complete water analysis.
65	Raw Water to Process	Complete Water Analysis
69	Degasser Vent Gases	Trace Sulfur Compounds Hydrocarbons
70	Sludges from Water Treatment	Complete coal solids analysis and complete water analysis.
74	Evaporation and Drift from Cooling Towers	Atmosphere in vicinity of cooling towers to be sampled for: Trace Sulfur Compounds Trace Elements Hydrocarbons and PNA

Table 65

Analyses of Streams in Gasification

(ppm, unless noted otherwise)

Unit Stream No. and Identification Stream Material	Coal Storage and Preparation					Coal*	Hydrogasifier*
	2 and 5					Pretreatment	5b - Coal After
	ROM Coal and Feed Coal					5a - Coal After	Pretreatment
	U.S. Coals From Ref. 1	Navajo Coal From Ref. 21	Illinois No. 6 From Ref. 42	Pittsburgh No. 8 From Ref. 50	Sasol Plant From Ref. 57	Pittsburgh No. 8 From Ref. 50	Pittsburgh No. 8 From Ref. 50
Aluminum	--	--	12,000	--	--	--	--
Antimony	--	0.3-1.2	<4-10.6	0.15	<0.05-<0.5	0.13	0.12
Arsenic	3-60	0.1-3	19	9.6	2-5	7.5	5.1
Barium	--	--	50	--	--	--	--
Beryllium	0.08-11	--	<10	0.92	2-3	1.0	0.94
Bismuth	--	0-0.2	<5	--	--	--	--
Boron	2.7-370	60-150	200	--	100	--	--
Bromine	--	0.4-18	7.2	--	1	--	--
Cadmium	--	0.2-0.4	1.5-<33	0.78	<0.05-<0.1	0.59	0.41
Calcium	--	--	3400-4800	--	--	--	--
Cerium	--	--	--	--	150-200	--	--
Chlorine	--	--	--	--	70	--	--
Cobalt	0.4-20	--	<10-17	--	--	--	--
Copper	1-50	--	31-78	--	--	--	--
Chromium	2.7-20	--	--	15	--	17	16
Fluorine	10-100	200-780	300	--	100	--	--
Gallium	0.4-20	0.5-8	--	--	--	--	--
Germanium	0.4-50	0.06-0.5	<10	--	--	--	--
Gold	--	--	<10	--	--	--	--
Iron	--	--	20,000-24,000	--	--	--	--
Lanthanum	<1-90	--	--	--	--	--	--
Lead	4-33	1.4-4	8-<10	5.9	10-20	4.4	3.3
Lithium	--	--	7.4	--	--	--	--
Magnesium	--	--	550-890	--	--	--	--
Manganese	--	--	39-75	--	500	--	--
Mercury	0.01-1.2	0.2-0.35	0.05	0.27	<0.1	0.19	0.06
Molybdenum	0.1-41	--	49	--	--	--	--
Niobium	--	--	<44	--	--	--	--
Nickel	1-50	3-30	29-120	12	30-50	11	10

* Not from Figure 5

Table 65 (Continued)

Analyses of Streams in Gasification

Unit Stream No. and Identification	Coal Storage and Preparation					Coal*	Hydrogasifier*
	2 and 5					Pretreatment	5b - Coal After
	ROM Coal and Feed Coal					5a - Coal After Pretreatment	Hydrotreating
Stream Material	U.S. Coals From Ref. 1	Navajo Coal From Ref. 21	Illinois No. 6 From Ref. 42	Pittsburgh No. 8 From Ref. 50	Sasol Plant From Ref. 57	Pittsburgh No. 8 From Ref. 50	Pittsburgh No. 8 From Ref. 50
Potassium	--	--	1,300-1,790	--	--	--	--
Samarium	--	--	1.9	--	--	--	--
Selenium	0.5-4.0	0.08-0.21	7	1.7	--	1.0	0.65
Silicon	--	--	18,000	--	--	--	--
Silver	--	--	0.8	--	--	--	--
Sodium	--	--	166-320	--	--	--	--
Strontium	--	--	<20	--	--	--	--
Sulfur	--	--	--	--	--	--	--
Tantalum	--	--	<50	--	--	--	--
Tellurium	--	--	5.8	0.11	--	0.07	0.05
Thorium	--	--	<20	--	--	--	--
Tin	--	--	40-104	--	--	--	--
Titanium	--	--	460-600	--	--	--	--
Tungsten	--	--	<30	--	--	--	--
Uranium	10-600	--	<100	--	--	--	--
Vanadium	2.3-190	--	200	33	300-500	36	30
Ytterbium	--	--	0.51	--	--	--	--
Yttrium	1-50	--	--	--	--	--	--
Zinc	<1-600	1.1-27	42	--	--	--	--
Zirconium	--	--	6.3-35	--	--	--	--
Coal Analysis, %							
Moisture	--	16.5	2.7 after drying	--	8	--	--
Fixed C	--	--	51.70	--	--	--	--
Volatile Matter	--	--	38.47	--	--	--	--
Ash	--	17.3	7.13	--	31.6 Dry	--	--
C	--	76.72 MAF	70.75	--	52.4 Dry	--	--
H	--	5.71 MAF	4.69	--	2.6 Dry	--	--
N	--	1.37 MAF	1.07	--	1.2 Dry	--	--
S	--	0.95 MAF	3.38	--	0.43 Dry	--	--
O	--	15.21 MAF	10.28	--	11.7 Dry	--	--
Heating Value, Btu/lb	--	7,500-10,250	12,821	--	8,890	--	--
Gross Streams, lb/hr							
Solid	--	2,162,135	1,041,667	--	560,000	--	--

* Not from Figure 5

Table 66

Analyses of Streams in Gasification Plants: Ash Disposal

Unit Stream No. Identification	Ash Disposal		
	18		
	Dry Ash, %		
	From Westfield After Quench From Ref. 56	From Sasol From Ref. 57	From Azot Sanayii From Ref. 58
<u>Stream Materials</u>			
SiO ₂	54.60	52	42-65
Al ₂ O ₃	32.66	28	16-19
Fe ₂ O ₃	4.71	5	13-15
CaO	3.58	7	6-10
C	--	3	--
MgO	1.28	1.7	5-7
K ₂ O	--	0.5	1-3
Na ₂ O	--	0.7	0.3-1.0
SO ₄	--	0.2	(SO ₃) 5-6
PO ₄	--	0.3	--
TiO ₂	--	--	0.2-0.8
Trace Elements	--	--	--
Loss on Ignition	2.82	--	--
Cr, Co, Ni, Mn	Trace		

Table 67

Analyses of Streams in Gasification: Gas Liquor

Unit Stream No.	Gas Liquor				Phenosolvan Treated Liquor
	16 + 25				39
Identification	Sasol From Ref. 57	Synthane From Ref. 55	Westfield From Ref. 56 Tar Liquor	Oil Liquor	Sasol From Ref. 57
<u>Stream Material</u>					
CN ⁻	6 ppm	0.1-0.6 mg/l	7.8 ppm	2.6 ppm	1 ppm
Fe(CN) ₆	--	--	4.2 ppm	10.5 ppm	--
SCN ⁻	--	21-200 mg/l	NIL	41.2 ppm	--
H ₂ S	--	--	--	--	12 ppm
F ⁻	--	--	--	--	56 mg/l
SO ₄ ⁼	--	--	90.6 ppm	74.1 ppm	--
S ⁼	223 ppm	total sulfur: 1,400 mg/l	0.7 ppm	177 ppm	--
S ₂ O ₃ ⁼	--	--	9.0 ppm	15.8 ppm	--
CO ₃ ⁼	--	17,000 mg/l	1,128 ppm	17,655 ppm	--
Cl ⁻	--	35-500 mg/l	4.3 ppm	11.3 ppm	25 ppm
Na ⁺	53 ppm	--	--	--	--
Phosphates	--	--	--	--	2.5 ppm
Particulates	--	--	--	--	--
Conductivity	--	--	--	--	1,000-1,800 μ Siemens/cm
pH	--	7.9-9.3	9.4	8.0	8.4
Ammonia (free)	10,600 ppm	Total NH ₃ :	--	--	--
Ammonia (fixed)	150-200 ppm	2,500-11,000 mg/l	Total NH ₃ 1,795 ppm	Total NH ₃ 9,597 ppm	215 ppm
COD	--	1,700-38,000 mg/l	--	--	1,126 ppm
BOD	--	--	--	--	--
TOD	--	--	--	--	--
Phenols	3250-4000 ppm	200-6600 mg/l	5,781 ppm	5,047 ppm	Steam Volatile 1 ppm Bound 160 ppm
TDS	--	--	--	--	875 ppm
Fatty Acids	0.03%	--	696 ppm	228 ppm	560 ppm
Suspended Solids	--	23-600 mg/l	100 ppm	340 ppm	21 ppm
Tar + Oil	5000 ppm	--	1,000-5,000 ppm	100-500 ppm	--
Quantity	--	--	--	--	594,000 lb/h

Table 68

Analyses of Streams in Coal Gasification: Gas Purification

Unit Stream No. and Identification	Sasol From Ref. 57					Raw Gas 23 From Synthane From Ref. 55
	23	28	27			
	Raw Gas to Purification	Pure Gas From Purification	High Pressure	Low Pressure	Expansion Gases Atmospheric Pressure	
Stream Material						
SO ₂ /SO ₃	--	--	--	--	--	1-10 ppm
NO _x	--	--	--	--	--	--
COS	≤ 10 ppm	--	--	--	--	2-150 ppm
H ₂ S	3,220 mg/m ³ _n	not detected	4,500 mg/m ³ _n	7,000 mg/m ³ _n	12,600 mg/m ³ _n	186-9,800 ppm
Thiophenes	--	--	--	--	--	1.3-55 ppm
CH ₃ SH	RSH, 20 ppm	total sulfur:	--	--	--	0.1-60 ppm
CS ₂	--	0.05 mg/m ³ _n	--	--	--	10 ppm
NH ₃	--		--	--	--	--
HCN	--	--	--	--	--	20 ppb
H ₂	40.05 mol %	57.30 mol %	21.4 mol %	2.6 mol %	0.14 mol %	--
CO	20.20 mol %	28.40 mol %	18.2 mol %	4.8 mol %	0.0 mol %	--
CO ₂	28.78 mol %	0.93 mol %	46.7 mol %	83.4 mol %	97.2 mol %	--
Inert	1.59 mol %	1.77 mol %	1.5 mol %	0.8 mol %	0.03 mol %	--
CH ₄	8.84 mol %	11.38 mol %	11.4 mol %	7.2 mol %	0.9 mol %	--
C ₂ ⁺	0.54 mol %	--	0.7 mol %	1.1 mol %	0.7 mol %	--
Flow Rate	381,000 m ³ _n /h	263,000 m ³ _n /h	4,600 m ³ _n /h	15,000 m ³ _n /h	98,000 m ³ _n /h	--
Btu	--	--	--	--	--	--

* m³_n at 0°C and 760 mm Hg; 1 lb mol = 10.167 m³_n

Table 69

Analyses of Streams in Coal Gasification:
Organic Liquid By-Products

(ppm unless otherwise indicated)

Unit Stream No.	Coal Gasification and Gas Liquor Separation						
	Coal Tar to Storage			Oil From Gas Cooling		Naphtha From Gas Purification	
	17			24		30	
	Benzene Soluble Tar From Ref. 55	Westfield From Ref. 56	Sasol From Ref. 57	Westfield From Ref. 56	Sasol From Ref. 57	Westfield From Ref. 56	Sasol From Ref. 57
<u>Identification</u>							
<u>Stream Material</u>							
Antimony	--	--	0.8-1.0	--	0.5-0.6	--	--
Arsenic	0.7	--	3.1-5.0	--	23-30	--	--
Beryllium	--	--	0.6-1.0	--	<0.6	--	--
Boron	--	--	50	--	0.5-0.6	--	--
Bromine	--	--	<0.3	--	Not Detected	--	--
Cadmium	--	--	<0.03-<0.05	--	<0.3	--	--
Cerium	--	--	<0.3-5.0	--	<0.3	--	--
Chlorine	--	--	1.6-10	--	0.5-1.2	--	--
Fluorine	--	--	<0.5-5.0	--	<0.6	--	--
Lead	--	--	50	--	0.5-1.2	--	--
Manganese	--	--	1.6-4.1	--	0.2-0.3	--	--
Mercury	--	--	0.3-0.5	--	<0.1-0.15	--	--
Nickel	--	--	1.6-4.1	--	1-1.4	--	--
Sulfur	0.5-2.7 wt.% of tar	0.77%	0.3 wt.%	0.29%	0.25 wt.%	0.078%	0.34 wt.%
Vanadium	--	--	1.8-8.2	--	0.1-0.3	--	--
Polynuclear Aromatics	Percent of benzene soluble tar						
	Indenes, 1.5-8.6	--	--	--	--	--	--
	Indans 1.9-4.9	--	--	Naphthalene, 7.6%	--	Naphthalene, 1.4%	--
	Naphthalenes 11.6-19.0	--	--	--	--	Indan, 1.43%	--
	Fluorenes 7.2-10.7	--	--	--	--	Indene, 5.37%	--
	Acenaphthenes 11.1-15.8	--	--	--	--	--	--
	3-ring Aromatics 9.0-14.8	--	--	--	--	--	--
	Phenyl naphthylenes 3.5-9.8	--	--	--	--	--	--
	4-ring pericondensed 3.5-7.6	--	--	--	--	--	--
	4-ring catacondensed 1.4-4.1	--	--	--	--	--	--

Table 69 (Cont'd)

Unit Stream No.	Coal Gasification and Gas Liquor Separation			Oil From Gas Cooling		Naphtha From Gas Purification	
	Coal Tar to Storage			24		30	
Identification	Benzene Soluble Tar From Ref. 55	Westfield From Ref. 56	Sasol From Ref. 57	Westfield From Ref. 56	Sasol From Ref. 57	Westfield From Ref. 56	Sasol From Ref. 57
Stream Material							
Other Organics	Percent of benzene Soluble tar						
Thiophene	Thiophenes 1.0-5.2	--	--	--	--	Other Thiophenes, 1.77%	--
CS ₂	--	--	--	--	--	--	--
(CH ₃) ₂ S	--	--	--	--	--	--	--
Phenol	Phenols 2.8-13.7	--	--	--	--	--	--
Pyridine Bases	--	--	--	1.3%	--	--	--
Other Phenols	2.7-16.6	--	--	--	--	--	--
Benzene	All benzenes 1.9-4.1	--	--	--	--	19.56%	--
Toluene	--	--	--	--	--	28.40%	--
Xylene	--	--	--	--	--	C ₈ Aromatics, 15.77%	--
	N-Heterocyclics 3.8-10.8	--	--	--	--	Other substituted benzenes, 14.5%	--
Acids	Furans 4.7-9.2	7.1%	--	16.5%	--	1:2 Benzofuran, 1.09%	--
Aldehydes	--	--	--	--	--	--	--
%	(Tar analysis Illinois No. 6), %						
Moistures	--	--	--	--	--	--	--
Fixed C	--	--	--	--	--	--	--
Volatile Matter	--	--	--	--	--	--	--
Ash	--	0.16%	--	--	--	--	--
C	82.5	--	--	--	--	--	--
H	6.6	--	--	--	--	--	--
N	1.1	--	--	--	--	--	--
S	2.8	0.77%	--	--	--	--	--
O	2.9 (by diff.)	--	--	--	--	--	--
Heating Value, Btu/lb	--	--	16,000-18,000	--	16,000-18,000	--	16,000-18,000
Gross Streams							
lb/hr	--	--	902-946	--	2,485-2,552	--	1,937
Liquid	--	--	--	--	--	--	--