NIOSH

TECHNICAL REPORT

POTENTIAL HEALTH HAZARDS INVOLVED with COAL GASIFICATION

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

POTENTIAL HEALTH HAZARDS
INVOLVED WITH COAL GASIFICATION

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CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

TABLES

No.

TABLES (Continued)

No.

ILLUSTRATIONS

ILLUSTRATIONS (Continued)

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Chapter 1

INTRODUCTION

Out of magic, mysticism, and trial-and-error, he had evolved the scientific method. Its aim is prediction, which is the essence of control.

Felton, Newman, & Read 1964

1.0 BACKGROUND

Although recent studies indicate that the Chinese may have used coal for fuel in small amounts before the year 1000, the use of coal as a major source of energy did not begin until about the twelfth century. Around that time, the inhabitants of the northeast coast of England discovered that certain "black rocks" found along the seashore would burn (Zahradnik 1975).

Coal was the principal energy source in America from the 1880's until shortly after World War II, although consumption began to decline around 1910 (University of Oklahoma 1975). This is shown pictorially in Figure 1. The decreased demand for coal resulted primarily from several major consumers switching to other fuels. Railroads converted to diesel fuel, and households, commercial consumers, and electric utilties converted to natural gas or fuel oil (University of Oklahoma 1975). About one-half of our electric power is generated from natural gas and low-sulfur fuel oil or petroleum (Yavorsky 1975). Currently, as shown in Table 1, petroleum and natural gas account for over 75 percent of energy consumption, although they represent less than 8 percent of our domestic fossil fuel reserves (Synfuels Interagency Task Force 1975a). In contrast, coal accounts for 75 percent of the nation's fossil fuel resources while accounting for less than 20 percent of energy consumption (Cochran 1976).

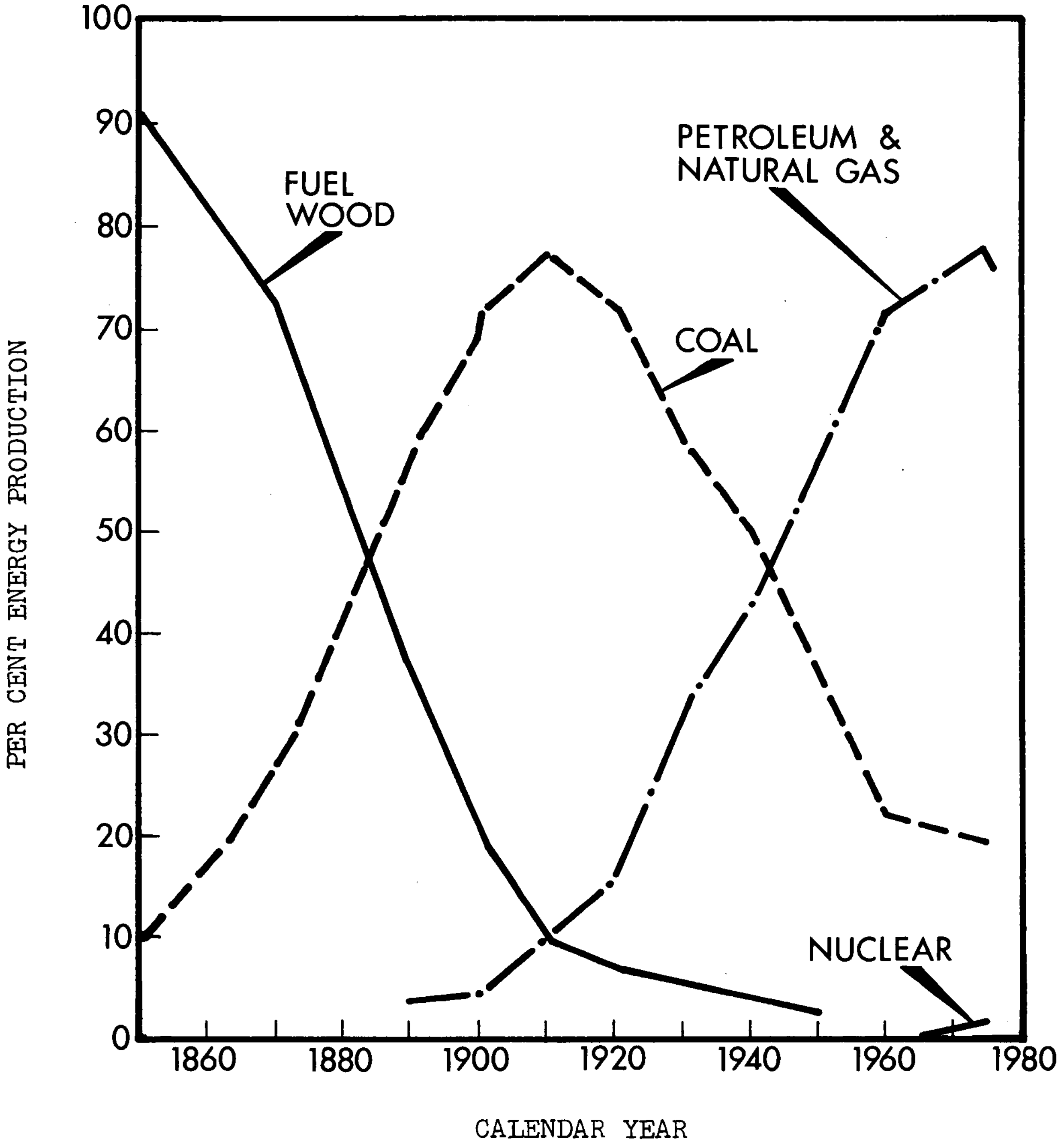


Figure 1

U.S. ENERGY CONSUMPTION PATTERNS

Source: Energy Research and Development Administration 1975

Table 1

DOMESTIC FOSSIL ENERGY CONSUMPTION AND SUPPLY*

(QUADS OR 10^{15} B.T.U.)

Fossil Fuel Sources	Consumption 1974	Reserves**	Recoverable Resources**
Coal	13.0	5,200 - 10,400	12,000 - 33,000
Oil (Inc. Nat. Gas Liq.)	33.8	250 - 410	800 - 1,100
Gas	22.3	230 - 430	775 - 1,100
Shale (25 gal/ton)	0.0	460 - 1,160	1,200 - 2,300
Total (Fossil)	69.1	6,140 - 12,400	14,775 - 37,500
All Other	4.1		
Total	73.2		

* Estimates from U.S. Geological Survey, June 1975

** Entries correspond to full energy content of resources and do not take account of efficiencies of utilization.

Source: Synfuels Interagency Task Force 1975a

The direct consumption of coal is virtually ruled out in transportation and seems unlikely to expand much in industrial, commercial and residential markets because of air pollution restrictions and distribution problems. Therefore, success in exploiting the nation's huge coal reserves depends on a developmental program of coal conversion. These processes take a dirty, bulky, inconvenient solid fuel and transforms it into a clean, easily transportable solid, liquid, or gaseous fuel. In general, the work has been directed to basic process development, including hardware development and yield improvement (Kalfadelis et al. 1975). Few developers of conversion processes have seriously addressed the occupational health aspects of their process, although experience in the 1950's at a large coal hydrogenation pilot plant revealed several industrial health problems. The most serious of these was skin cancer resulting from contact with polycyclic aromatic hydrocarbons. If coal conversion is developed on the mammoth scale required to satisfy an appreciable fraction of domestic demand for hydrocarbon fuels, the occupational health problems associated with this technology will affect substantial numbers of people.

1.1 PURPOSE

The objective of the research effort described in this report was to develop an inventory of specifically identified, potentially hazardous contaminants which may be generated in synthetic fuel plants, which are likely to become commercially viable within the next decade. An additional objective was to prepare a review of the toxicological and epidemiological information on the more important substances.

1.2 APPROACH

As a first step in identifying and quantifying the fate of pollutants in coal conversion processes, it is necessary to understand the structure and composition of coal (Rhodes 1975). Thus, a brief overview of coal has been included. In general, a strategy for process development evolves from laboratory work to a commercial facility. Thus, a review of these various stages was warranted.

The unit operations approach was chosen for our evaluation of coal gasification. The three basic steps involved in this analysis are:

- Define the overall chemical process and reactions of basic chemical compounds.
- Define the input and output streams of each unit and speculate on chemical compounds formed.
- Define within this unit all sources of possible leaks, vents, or discharges of gases, solids, and liquids to the atmosphere.

Following this approach it is obvious that a basic understanding of the process technology is necessary. This can be accomplished by compiling, summarizing and evaluating the existing engineering process literature.

1.3 SCOPE OF THE EFFORT

This study does not present complete solutions to occupational problems of coal conversion facilities. It does summarize the potential contaminants that may be generated, and review the relevant toxicological and epidemiological information on the more important substances. The remaining elements of the industrial hygiene tripartite--evaluation and control, are being addressed in other studies. Other research needs include determining the extent of worker exposure in coal gasification plants. Where excessive exposures exist, appropriate engineering controls should be implemented. It should be obvious that the development of either conversion technology or environmental control technology, without proper consideration of the other, is both unacceptable and unworkable.

Chapter 2

COAL CHARACTERISTICS

2.0 INTRODUCTION

As a first step in identifying and quantifying the fate of pollutants in coal conversion processes, it is necessary to understand the structure and composition of coal (Rhodes 1975). The purpose of this chapter is to present a brief overview of the present knowledge of coal from the existing literature, including the origin, classification, and chemical and physical character of coal.

2.1 ORIGIN

Coal is a carbonaceous, nonhomogeneous, highly variable fossilized material (Braunstein 1977). It is derived from partly decayed plant material laid down in the vast swamps which once covered large areas of the northern hemisphere (NIOSH 1978a). The material include woody parts of trees, leaves, spores, pollen, some charcoal like substances from wood charred in forest fires, and some ill-defined amorphous material (Given 1974). This decayed material was then subjected to a variety of microbiological, geological, and geochemical conditions which varied not only from one swamp to another, but also showed marked variations within a given local region (NIOSH 1978a).

2.2 RANK

Coal was formed through an apparently continuous series of alterations: living plants > peat > lignite subbituminous coal > bituminous coal > anthracite. This process is referred to as metamorphosis; the degree of metamorphosis is called rank (Ensminger 1977). Figure 2 shows the linear progression of coal through the stages of development and some of the associated properties. The carbon content of the material increases from 60 percent at the peat stage to 90 percent at the low-volatile bituminous stage. Reflectance, which is used in identifying coal constituents, also increases with increase in rank and carbon content. Volatile matter, which decreases with increasing rank, consists of gaseous substances which are driven off by heat (Ensminger 1977).

As indicated in Table 2, approximately 70 percent of all U.S. coal resources is bituminous or subbituminous, while only about one percent is anthracite (University of Oklahoma 1975).

2.3 CLASSIFICATION

Coals are classified on the basis of specific compositional characteristics, such as carbon content, heating value, and impurities (University of Oklahoma 1975). Anthracite and bituminous coals are primarily classed on the basis of fixed carbon content (Figure 3). Subbituminous coals and lignite are classified on the basis of heating value (Figure 4).

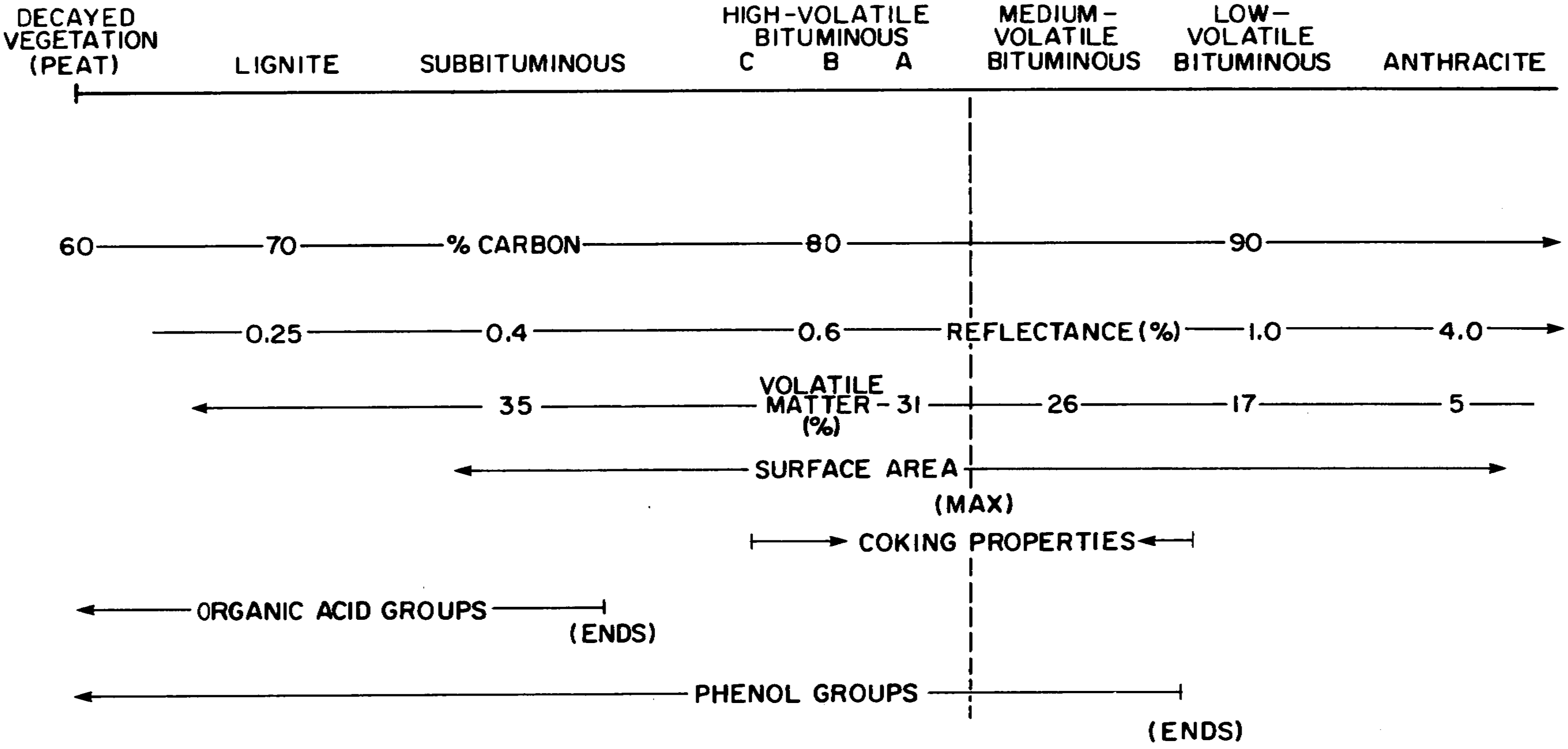


Figure 2

THE COAL SERIES

Source: Ensminger 1977

Table 2

RANK OF IDENTIFIED U.S. COAL RESOURCES

Rank		Identified Resources (billions of tons)	Percent of Total Reserve
Anthracite		21	1.3
Bituminous		686	43.5
Subbituminous		424	26.8
Lignite		449	28.4
	Total	1,580	100.0

Source: Modified from University of Oklahoma 1975

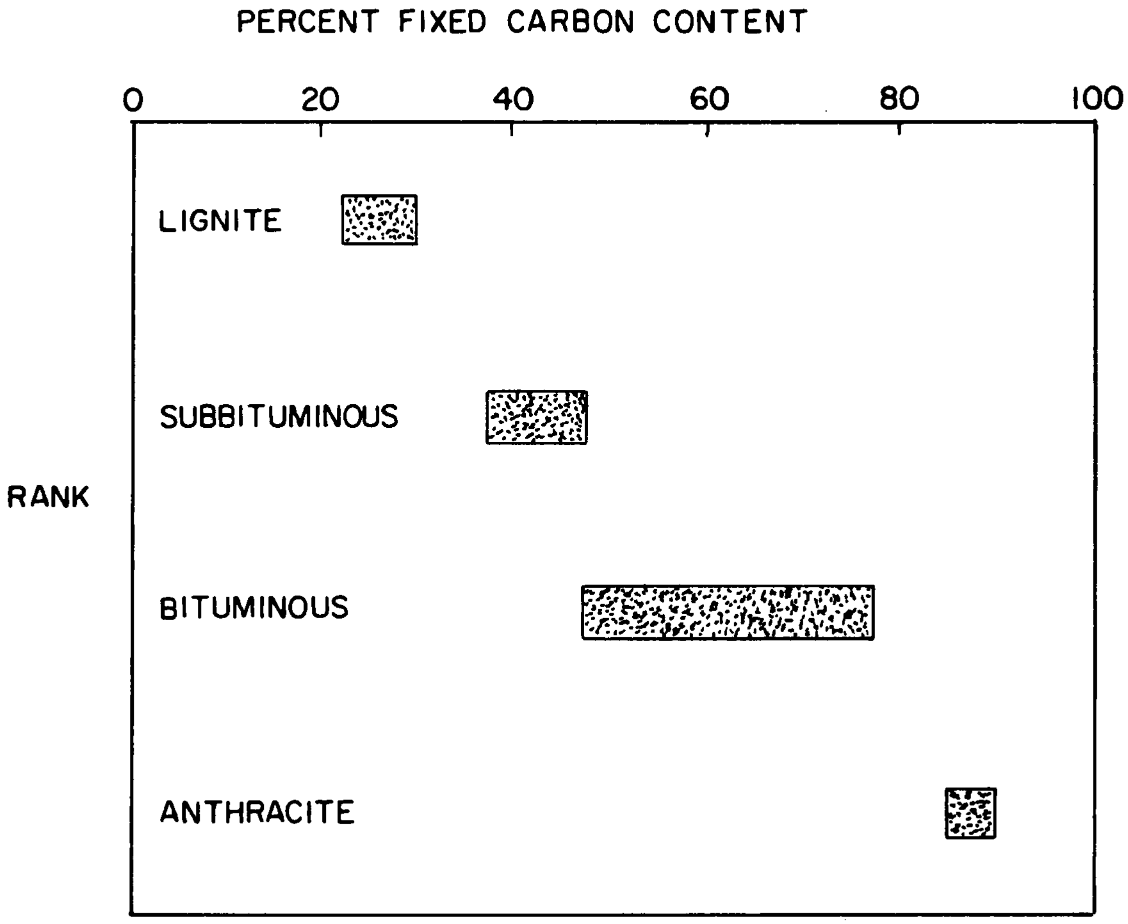


Figure 3

FIXED CARBON CONTENT OF MAJOR COALS RANKS

Source: University of Oklahoma 1975

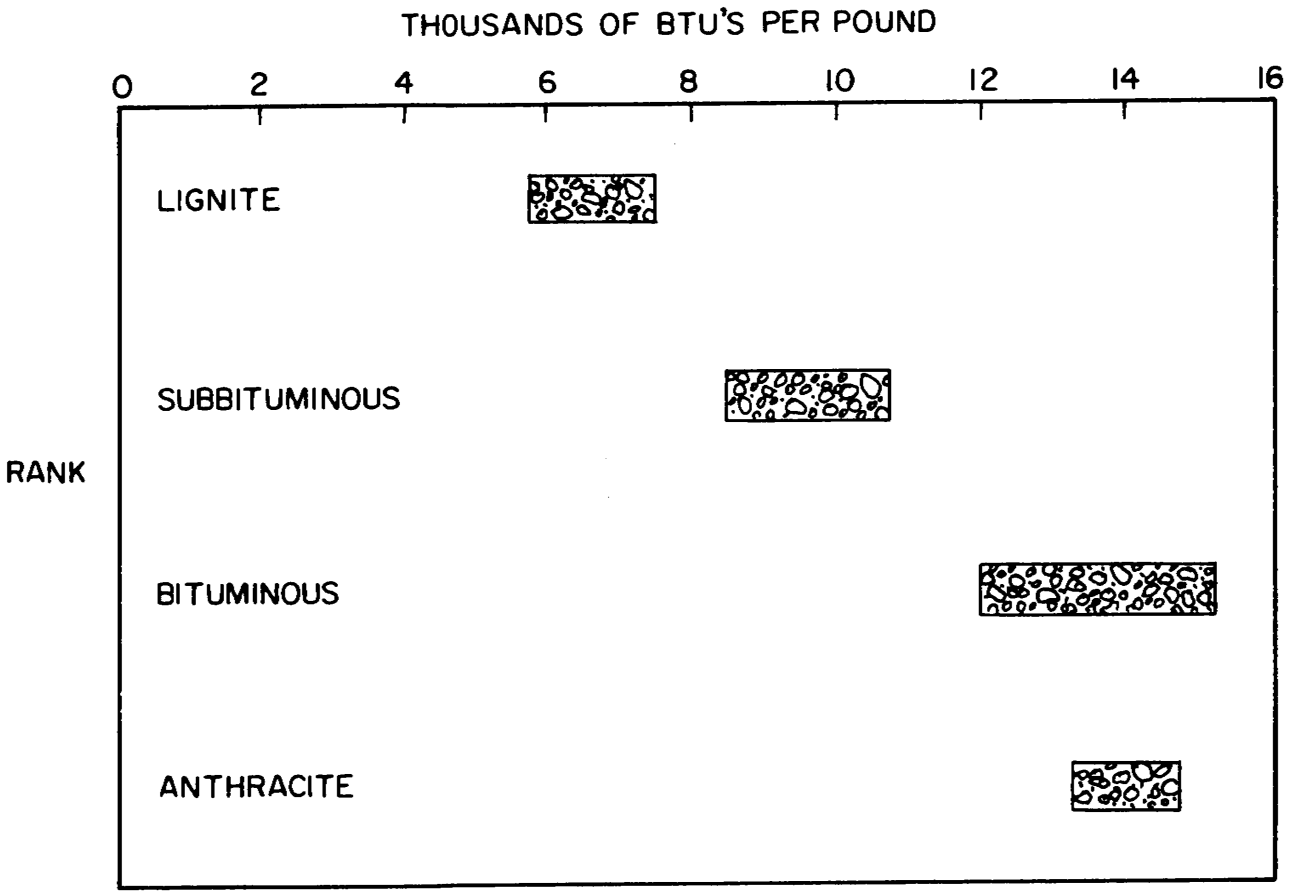


Figure 4

HEAT CONTENT OF MAJOR COAL RANKS

2.4 COAL-PRODUCING REGINS

There are five major coal-producing regions capable of supplying the coal required for commercial production of synthetic fuels (Synfuels Interagency Task Force 1975b). These regions include two having bituminous deposits, two having subbituminous deposits, and one having lignite deposits (Hittman Associates 1975). Identification of the five regions is shown in Table 3.

2.5 ANALYSIS

The analyses used for evaluating coal are the "proximate analysis" and the "ultimate analysis". The ultimate analysis gives the exact chemical composition of a fuel without describing the physical form. Such an analysis gives the data needed for combustion calculations (Perry, Chilton, and Kirkpatrick 1963). An ultimate analysis of coal by region is given in Table 4.

Proximate analysis is the simplest means of classifying coal for industrial use (Hittman Associates 1975). It includes:

- Percentage of moisture
- Percentage of ash
- Percentage of volatile matter
- Percentage of fixed carbon

These percentages add to 100 (Perry, Chilton, Kirkpatrick 1963). Within each region, variations in the properties

Table 3

COAL-PRODUCING REGIONS

Region	States Wholly or Partially Included	Coal Rank
Appalachian Region	Pennsylvania Ohio West Virginia Virginia Maryland Kentucky Tennessee Alabama	Bituminous
Eastern Interior	Illinois Indiana Kentucky	Bituminous
Fort Union	North Dakota South Dakota Montana	Lignite
Powder River Region	Montana Wyoming	Subbituminous
Four Corners	New Mexico Colorado Utah Arizona	Subbituminous

Source: Hittman Associates 1975

Table 4

AVERAGE ULTIMATE ANALYSIS OF COAL BY REGION*

Region	Moisture	Ash	C	H	O	N	S
Appalachian	3.40	7.70	76.37	4.45	5.27	1.01	1.80
Eastern Interior	11.20	9.40	64.32	4.15	6.15	1.28	3.50
Fort Union	37.50	6.20	41.13	2.73	11.03	0.81	0.60
Powder River	19.10	5.30	56.70	4.00	13.00	1.30	0.60
Four Corners	11.40	14.10	58.29	3.90	10.29	1.32	0.70

* In percent

Source: Hittman Associates 1975

reported in Table 5 occur. For example, lignite from the Fort Union Region can contain as little as 20 percent or as much as 43 percent moisture.

2.6 CHEMICAL PROPERTIES

2.6.1 Structure

The true structure of coal is presently unknown; most researchers agree that the structure is so complicated and variable that it is impossible to form an accurate model (Ensminger 1977). However, it has been observed that aromatic rings are joined together in a variety of patterns--single rings, condensed double rings, condensed triple rings, etc. Clusters thus formed are believed to be held together by bridges:

- Short aliphatic groups, principally methylene, probably not many longer than four carbon atoms
- Ether linkages
- Sulfide and disulfide
- Biphenyl types

The short aliphatic groups are probably the most common (Ensminger 1977).

The diagram shown in Figure 5 is an attempt by Wiser to use the present knowledge of coal to represent an average bituminous coal molecule in a single plane. It shows polycyclic aromatic clusters linked into large molecules by carbon bridges and by heter-atom groups (Oak Ridge National Laboratory 1976 and Ensminger 1977). The

Table 5

AVERAGE PROXIMATE ANALYSIS OF COAL BY REGION

Region	Coal Rank	Heating Value Btu/lb	Moisture* %	Volatile Matter %	Fixed Carbon %	Ash %	Sulfur** %
Appalachia	Bituminous	13570	3.4	30.6	56.5	7.7	1.8
Eastern Interior	Bituminous	11630	11.2	35.2	40.7	9.4	3.5
Fort Union	Lignite	6870	37.5	27.6	28.1	6.2	0.6
Powder River	Subbituminous	9780	19.1	34.4	40.6	5.3	0.6
Four Corners	Subbituminous	10160	11.4	33.8	40.0	14.1	0.7

* As received basis.

** Sulfur is distributed between the volatile matter as organic sulfur and the ash (or mineral matter) as pyrite.

Source: Hittman Associates 1975

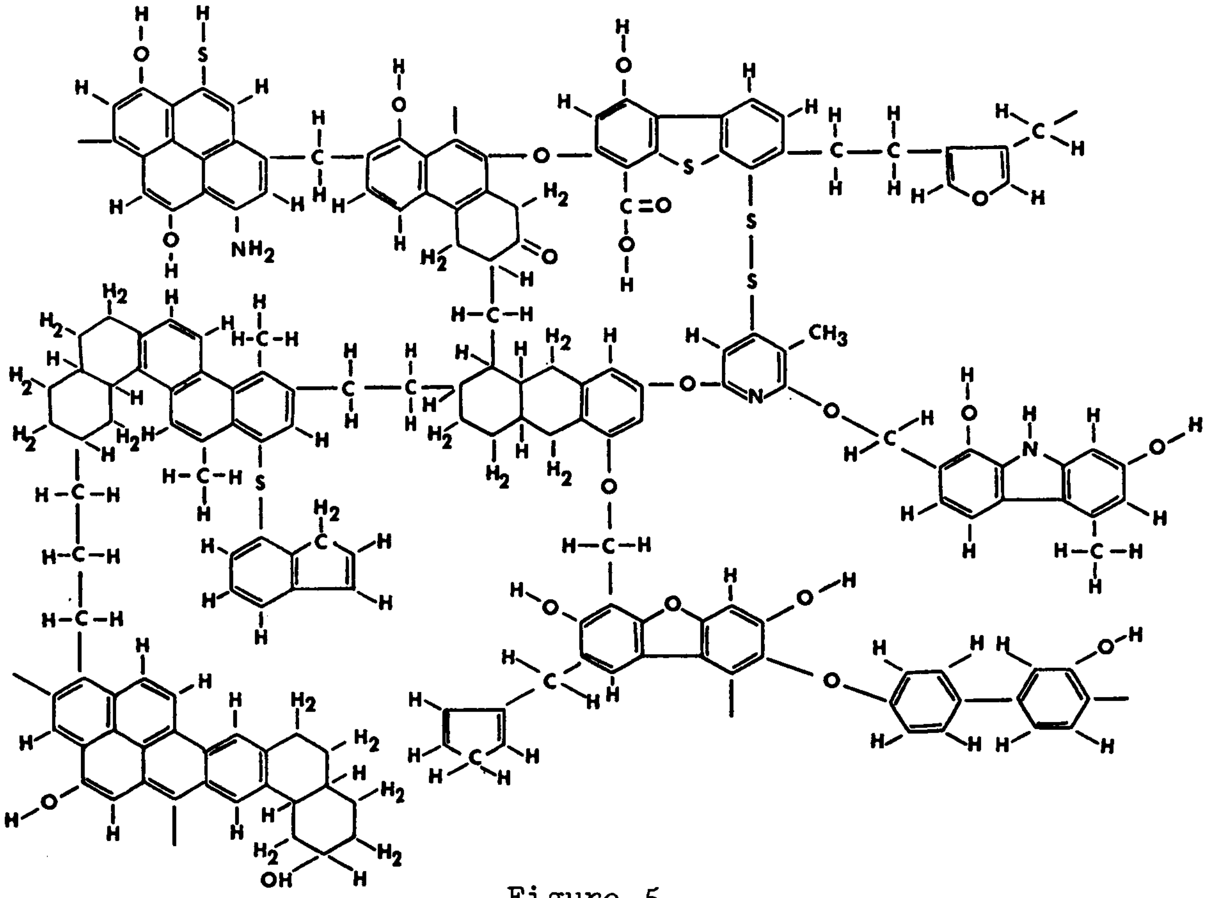


Figure 5

A HYPOTHETICAL COAL MOLECULE

Source: Oak Ridge National Laboratory 1976 molecular weights of coal species are thought to be within the range of 2,000-12,000 (Koppenaal and Manahan 1976).

2.6.2 Functional Groups

To understand the organic chemistry of coal, it is helpful to become familiar with the "functional groups"--reactive oxygen, nitrogen, and sulfur groups (Ensminger 1977).

Oxygen-containing Groups

As metamorphosis proceeds, reactive oxygen groups are lost. The methoxy groups are lost first, then the carboxyl and the carbonyl groups decreases rapidly (van Krevelen 1961). At greater than 92 percent carbon content, almost all oxygen is in nonreactive, stable forms. These nonreactive stable oxygen structures are mostly hydroxyl and carbonyl groups (Given and Peover 1960). The structure of some oxygen-containing compounds commonly encountered in coal analysis are shown in Figure 6.

Sulfur-containing Groups

The sulfur in coal may be present in either an organic or an inorganic form. The organic compounds consist primarily of thiophene and benzothiophene derivatives and constitute the principal sulfur fraction of low-sulfur coals. The inorganic sulfur is present principally as iron

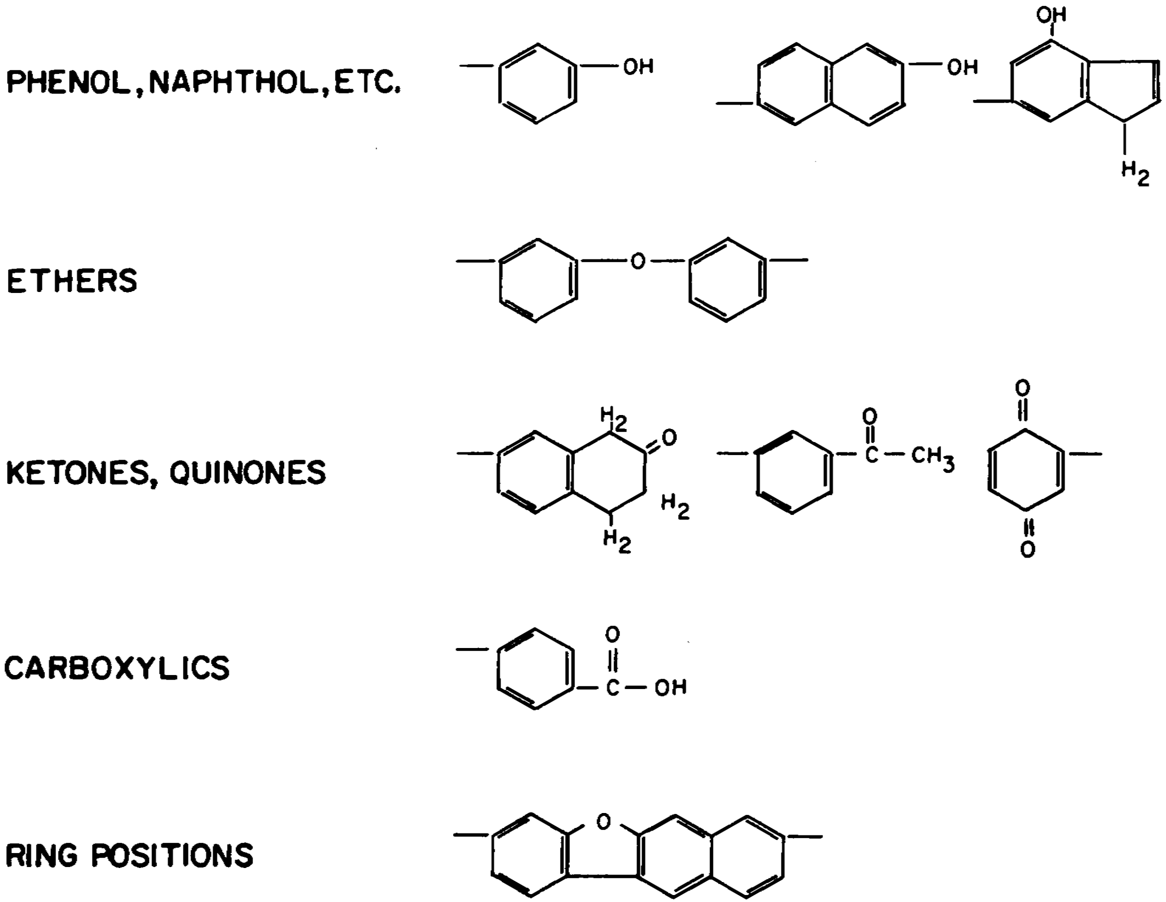


Figure 6

TYPES OF OXYGEN STRUCTURES IN COAL

Source: Ensminger 1977

disulfide (FeS_2) in its mineral configuration of pyrite or marcasite, though lesser amounts appear as sulfates ($CaSO_4$) or $MgSO_4$) (Glaser, Hershaft, and Shaw 1974). Concentrations of the various forms of sulfur and the total sulfur content of 172 coals are given in Table 6. One hundred and fourteen of the 172 samples are from the Illinois Basin. The remaining samples are from other coal-producing areas of the United States (Gluskoter et al. 1977).

Nitrogen-containing Groups

The nitrogen content of most coals is generally below 2 percent (Ensminger 1977). Francis and Wheeler (1925) observe that nitrogen in coal is almost completely in cyclic structures. Some major nitrogen structures in coal are shown in Figure 7.

2.7 PETROGRAPHY

Coal is composed basically of two types of material--inorganic crystalline minerals and phytogenic noncrystalline macerals. Both occur in coals as grains, particles, and fragments ranging in size from 2 μm^3 to several cubic centimeters and larger (Ensminger 1977).

2.7.1 Macerals

Macerals are the fragmentary organic remains of plants that died, were altered to peat by partial decay, and

Table 6

SULFUR ANALYSES OF WHOLE COAL SAMPLES
(percent, moisture-free whole coal basis)

Sample	Organic	Pyritic	Sulfate	Total
C12059				3.14
C12495	1.62	2.67	0.06	4.35
C12831	1.28	1.29	0.03	2.60
C12942	1.38	2.42	0.12	3.92
C13039	1.60	2.41	0.01	4.02
C13046	1.66	3.02	0.01	4.69
C13324	1.59	2.69	0.02	4.30
C13433	0.85	2.17	0.01	3.03
C13464	1.75	1.63	0.67	4.04
C13854	0.66	1.27		1.93
C13895	2.12	2.43	0.02	4.57
C13975	0.71	1.82	0.01	2.54
C13983	1.78	2.47	0.02	4.27
C14194	1.29	2.26	0.08	3.63
C14574	1.20	0.94	0.04	2.18
C14609	1.07	1.81	0.04	2.92
C14613	0.77	0.65	0.01	1.43
C14630	0.63	0.57	0.02	1.22
C14646	2.07	2.72	0.04	4.83
C14650	1.32	3.38	0.11	4.81
C14684	1.33	1.44	0.02	2.79
C14721	1.94	1.76	0.03	3.73
C14735	1.65	2.34	0.02	4.01
C14774	2.24	1.42	0.02	3.68
C14796	0.58	0.74	0.02	1.34
C14838	2.56	1.66	0.03	4.25
C14970	2.19	2.02	0.04	4.25
C14982	2.12	1.57	0.01	3.70
C15012	1.11	2.04	0.02	3.17
C15038	0.53	0.99	0.01	1.53
C15079	1.78	2.13	0.07	3.98
C15117	1.86	2.26	0.08	4.20
C15125	2.02	1.42	0.01	3.45
C15208	2.03	1.96	0.07	4.06
C15231	2.59	1.69	0.03	4.31
C15263	0.85	2.27	0.04	3.16
C15278	1.65	1.60	0.10	3.35
C15331	1.75	3.78	0.06	5.59
C15384	1.63	2.13	0.14	3.90
C15418	0.42	0.54	0.02	0.98
C15432	0.71	0.98	0.05	1.74
C15436	1.89	1.37	0.07	3.33
C15448	2.26	2.56	0.12	4.94

Table 6 (continued)

SULFUR ANALYSES OF WHOLE COAL SAMPLES
(percent, moisture-free whole coal basis)

Sample	Organic	Pyritic	Sulfate	Total
C15456	2.03	2.36	0.06	4.45
C15496	2.34	1.28	0.05	3.67
C15566	1.42	3.38	0.05	4.85
C15678	2.10	3.21	0.05	5.36
C15717	2.56	1.59	0.04	4.19
C15791	0.72	1.14	0.02	1.88
C15868	0.56	0.29		0.85
C15872	1.82	1.81	0.05	3.68
C15943	1.26	3.02	0.05	4.33
C15944	0.91	2.27	0.02	3.20
C15999	1.44	1.79	0.08	3.31
C16030	1.60	1.87	0.04	3.51
C16139	2.46	2.27	0.11	4.84
C16264	2.14	2.33	0.05	4.52
C16265	1.94	1.22	0.04	3.20
C16317	1.95	0.97	0.33	3.25
C16408	1.07	3.78	0.05	4.90
C16501	1.15	1.21	0.01	2.37
C16543	1.91	1.20	0.04	3.15
C16564	2.10	1.67	0.03	3.80
C16729	0.83	2.30	0.04	3.17
C16741	1.96	1.54	0.05	3.55
C16787	0.54	1.10	0.03	1.66
C16919	0.37	0.76	0.10	1.23
C16993	1.50	1.75	0.90	4.15
C17001	1.51	2.62	0.02	4.14
C17016	2.59	2.87	0.10	5.84
C17045	0.31	0.10	0.02	0.44
C17046	0.56	0.53	0.03	1.11
C17047	0.70	1.16	0.02	1.88
C17053	1.78	1.97	0.02	3.77
C17054	0.49	0.31	0.03	0.83
C17089	0.56			0.56
C17092	1.41	2.37	0.16	3.94
C17095	1.42	2.59	0.19	4.20
C17096	0.40	0.24	0.05	0.69
C17097	0.46	0.07	0.02	0.55
C17098	0.46	1.01	0.05	1.53
C17099	1.01	1.82	0.21	3.04
C17215	1.41	2.67	0.10	4.18
C17243	1.32	2.41	0.42	4.15
C17244	0.69	1.85	0.12	2.66
C17245	1.05	2.39	0.24	3.68
C17246	0.74	0.19	0.02	0.96

Table 6 (continued)

SULFUR ANALYSES OF WHOLE COAL SAMPLES
(percent, moisture-free whole coal basis)

Sample	Organic	Pyritic	Sulfate	Total
C17278	3.20	1.47	0.18	4.84
C17279	3.09	1.95	0.18	5.22
C17303	0.75	0.48	0.06	1.29
C17304	2.09	1.52	0.51	4.13
C17305	1.44	2.00	1.06	4.50
C17307	1.84	3.65	0.98	6.47
C17309	0.34	0.06	0.01	0.42
C17601	1.28	2.35	0.18	3.81
C17721	0.88	1.37	0.01	2.26
C17970				
C17984	0.57	1.50	0.01	2.09
C17988	0.80	1.35	0.01	2.17
C18009	0.72	0.27	0.08	1.07
C18040	2.11	1.74	0.01	3.86
C18044	1.85	1.85	0.01	3.71
C18304	1.55	2.63	0.07	4.25
C18320	1.83	1.83	0.05	3.71
C18349	1.81	2.88	0.03	4.72
C18350	2.15	3.46	0.04	5.64
C18351	1.21	2.72	0.03	3.96
C18355	0.93	3.76	0.03	4.72
C18368	2.08	1.84	0.02	3.94
C18389	2.01	2.46	0.11	4.58
C18392	1.58	1.81	0.04	3.43
C18395	1.99	1.28	0.26	3.52
C18398	2.39	1.84	0.34	4.57
C18401	0.90	0.83	0.18	1.92
C18404	1.70	2.31	0.22	4.24
C18407	1.84	1.60	0.08	3.52
C18408	1.71	1.64	0.26	3.62
C18411	1.57	2.77	0.28	4.62
C18415	1.88	2.08	0.12	4.09
C18419	1.54	2.40	0.16	4.10
C18421	1.45	1.64	0.42	3.51
C18433	1.13	0.13	0.09	1.35
C18436	0.68	0.20	0.05	0.92
C18437	0.71	0.91	0.02	0.74
C18440	0.47	0.01	0.03	0.51
C18441	0.36	0.08	0.03	0.47
C18444	0.64	0.07	0.09	0.79
C18445	0.60	0.23	0.02	0.84
C18446	0.31	0.01	0.01	0.34
C18449	0.56	0.13	0.02	0.72

Table 6 (continued)

SULFUR ANALYSES OF WHOLE COAL SAMPLES
(percent, moisture-free whole coal basis)

Sample	Organic	Pyritic	Sulfate	Total
C18450	0.52	0.09	0.04	0.64
C18451	0.56	0.01	0.03	0.59
C18454	0.30	0.05	0.22	0.58
C18457	0.25	0.17	0.07	0.50
C18458	0.28	0.12	0.01	0.41
C18462	0.91	0.32	0.01	1.24
C18463	0.44	0.45	0.07	0.95
C18464	0.62	0.03	0.05	0.69
C18465	0.58	0.02	0.05	0.65
C18493	0.78	1.07	0.04	1.88
C18560	1.87	4.56	0.02	6.45
C18572	1.94	3.60	0.52	6.06
C18573	1.97	5.01	0.91	7.88
C18574	2.30	4.87	0.72	7.88
C18581	0.45	2.35	0.02	2.81
C18590	1.35	2.58	0.05	3.98
C18594	1.63	2.49	0.08	4.20
C18684	1.29	2.51	0.06	3.86
C18685	1.69	2.91	0.06	4.66
C18689	1.52	1.49	0.05	3.06
C18693	2.05	3.21	0.15	5.41
C18697	1.93	2.02	0.08	4.03
C18701	1.69	1.92	0.08	3.69
C18816	0.45	0.54	0.01	1.00
C18820	0.51	0.26	0.03	0.80
C18824	0.54	0.43	0.01	0.98
C18825	0.58	1.03	0.13	1.74
C18829	1.11	2.60	0.09	3.80
C18830	0.58	0.36	0.09	1.03
C18831	0.96	0.68	0.01	1.65
C18832	0.79	0.58	0.02	1.38
C18833	0.66	0.06		0.72
C18837	0.63	1.24	0.03	1.90
C18841	2.51	2.48	0.03	5.02
C18844	1.16	1.14	0.03	2.33
C18848	0.50	0.04	0.01	0.55
C18849	0.35	1.21	0.07	1.62
C18853	1.42	1.87	0.10	3.40
C18857	2.42	2.51	0.09	5.02
C18992	0.62	0.10		0.71
C18993	0.56	0.14	0.02	0.72
C19000	0.52	0.08		0.61

Source: Gluskoter et al. 1977

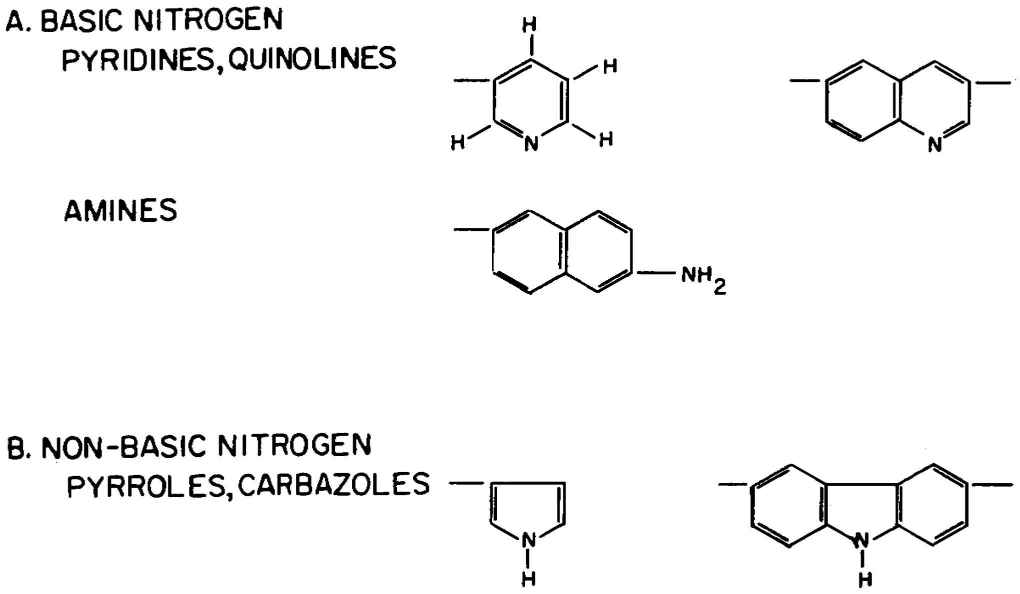


Figure 7

TYPES OF NITROGEN STRUCTURES IN COAL

Source: Ensminger 1977

because of exposure to heat in the earth's crust through time, were converted to their present state in coal (Ensminger 1977). The carbonaceous, combustible fraction of coal is made up of macerals; thus, by definition, macerals comprise more than half of the coal mass. Probably the most widely used method of determining the maceral content of coal is by measurement of reflected light.

2.7.2 Mineral Matter

The ash-forming mineral constituents in coal have originated from:

- original plant ash,
- sedimentary deposition,
- deposits from percolating ground waters, or
- material from the roof or floor of the mine added during the mining process.

The principal ingredients present are slate, clay, sandstone, shale, carbonates, pyrite, and gypsum (Perry, Chilton, and Kirkpatrick 1963). The relative amounts of mineral constituents present determine the characteristics of the ash and impose certain limitations on the utilization of the coal (Perry, Chilton, and Kirkpatrick 1963).

2.7.3 Trace Elements

Trace elements are usually defined as those elements that are present in the earth's crust to the extent of 0.1

percent (1,000 ppm) or less (Hall, Varga, and Magee 1974). Nearly all trace elements show an enrichment in coal relative to their abundance in the earth's crust (Hall, Varga, and Magee 1974 and Glaser, Hershaft, and Shaw 1974). Actually, out of 92 known non-transuranic elements, only 16 have not yet been found in coal (O'Hara et al. 1976). See Figure 8.

Gluskoter et al. (1977) did an extensive study of 172 coals; 114 were taken from the Illinois Basin, and 58 were collected from other states. Mean values resulting from their analysis are shown in Tables 7, 8 and 9.

1 H 1.00797 ± 0.00001																1 H 1.00797 ± 0.00001	▨ 2 He 4.0026 ± 0.00005
3 Li 6.939 ± 0.0005	4 Be 9.0122 ± 0.00005											5 B 10.811 ± 0.003	6 C 12.01115 ± 0.00005	7 N 14.0067 ± 0.00005	8 O 15.9994 ± 0.0001	9 F 18.9984 ± 0.00005	▨ 10 Ne 20.183 ± 0.0005
11 Na 22.9898 ± 0.00005	12 Mg 24.312 ± 0.0005											13 Al 26.9815 ± 0.00005	14 Si 28.086 ± 0.001	15 P 30.9738 ± 0.00005	16 S 32.064 ± 0.003	17 Cl 35.453 ± 0.001	▨ 18 Ar 39.948 ± 0.0005
19 K 39.102 ± 0.0005	20 Ca 40.08 ± 0.005	21 Sc 44.956 ± 0.0005	22 Ti 47.90 ± 0.005	23 V 50.942 ± 0.0005	24 Cr 51.996 ± 0.001	25 Mn 54.9380 ± 0.00005	26 Fe 55.847 ± 0.003	27 Co 58.9332 ± 0.00005	28 Ni 58.71 ± 0.005	29 Cu 63.54 ± 0.005	30 Zn 65.37 ± 0.005	31 Ga 69.72 ± 0.005	32 Ge 72.59 ± 0.005	33 As 74.9216 ± 0.00005	34 Se 78.96 ± 0.005	35 Br 79.909 ± 0.002	▨ 36 Kr 83.80 ± 0.005
37 Rb 85.47 ± 0.005	38 Sr 87.62 ± 0.005	39 Y 88.905 ± 0.0005	40 Zr 91.22 ± 0.005	41 Nb 92.906 ± 0.0005	42 Mo 95.94 ± 0.005	▨ 43 Tc (99)	▨ 44 Ru 101.07 ± 0.005	45 Rh 102.905 ± 0.0005	46 Pd 106.4 ± 0.05	47 Ag 107.870 ± 0.003	48 Cd 112.40 ± 0.005	49 In 114.82 ± 0.005	50 Sn 118.69 ± 0.005	51 Sb 121.75 ± 0.005	52 Te 127.60 ± 0.005	53 I 126.9044 ± 0.00005	▨ 54 Xe 131.30 ± 0.005
55 Cs 132.905 ± 0.0005	56 Ba 137.34 ± 0.005	57 *La 138.91 ± 0.005	72 Hf 178.49 ± 0.005	73 Ta 180.948 ± 0.0005	74 W 183.85 ± 0.005	▨ 75 Re 186.2 ± 0.05	▨ 76 Os 190.2 ± 0.05	▨ 77 Ir 192.2 ± 0.05	78 Pt 195.09 ± 0.005	79 Au 196.967 ± 0.0005	80 Hg 200.59 ± 0.005	81 Tl 204.37 ± 0.005	82 Pb 207.19 ± 0.005	83 Bi 208.980 ± 0.0005	84 Po (210)	▨ 85 At (210)	86 Rn (222)
▨ 87 Fr (223)	88 Ra (226)	▨ 89 Ac (227)	90 Th 232.038 ± 0.0005	▨ 91 Pa (231)	92 U 238.03 ± 0.005												

*Lanthanum Series

58 Ce 140.12 ± 0.005	59 Pr 140.907 ± 0.0005	60 Nd 144.24 ± 0.005	▨ 61 Pm (147)	62 Sm 150.35 ± 0.005	63 Eu 151.96 ± 0.005	64 Gd 157.25 ± 0.005	65 Tb 158.924 ± 0.0005	66 Dy 162.50 ± 0.005	67 Ho 164.930 ± 0.0005	68 Er 167.26 ± 0.005	▨ 69 Tm 168.934 ± 0.0005	70 Yb 173.04 ± 0.005	71 Lu 174.97 ± 0.005

Figure 8

PERIODIC TABLE OF THE ELEMENTS
(The elements shaded have not been found in Coal.)

Source: O'Hara et al. 1976b

Table 7

MEAN ANALYTICAL VALUES FOR 45 TRACE ELEMENTS IN 114 WHOLE COAL SAMPLES FROM THE ILLINOIS BASIN COAL FIELD

Element	Mean	Standard Deviation	Range
Antimony, ppm	1.3	1.4	0.1 - 8.9
Arsenic, ppm	14	20	1.0 - 120
Barium, ppm	100	110	5.0 - 750
Beryllium, ppm	1.7	0.82	0.5 - 4.0
Boron, ppm	110	50	12 - 230
Bromine, ppm	13	7.4	0.6 - 52
Cadmium, ppm	2.2	7.4	0.1 - 65
Cerium, ppm	14	7.5	4.4 - 46
Cesium, ppm	1.4	0.73	0.5 - 3.6
Chromium, ppm	18	9.7	4.0 - 60
Cobalt, ppm	7.3	5.3	2.0 - 34
Copper, ppm	14	6.6	5.0 - 44
Dysprosium, ppm	1.1	0.42	0.5 - 3.3
Europium, ppm	0.26	0.12	0.1 - 0.87
Fluorine, ppm	67	26	29 - 140
Gallium, ppm	3.2	1.2	0.8 - 10
Germanium, ppm	6.9	6.4	1.0 - 43
Hafnium, ppm	0.54	0.25	0.13 - 1.5
Indium, ppm	0.16	0.11	0.01 - 0.63
Iodine, ppm	1.7	2.0	0.24 - 14
Lanthanum, ppm	6.8	2.8	2.7 - 20
Lead, ppm	32	42	0.8 - 220
Lutetium, ppm	0.09	0.06	0.02 - 0.44
Manganese, ppm	53	41	6.0 - 210
Mercury, ppm	0.2	0.19	0.03 - 1.6
Molybdenum	8.1	5.4	0.3 - 29
Nickel, ppm	21	10	7.6 - 68
Phosphorus, ppm	64	60	10 - 340
Rubidium, ppm	19	9.9	2.0 - 46
Samarium, ppm	1.2	0.55	0.4 - 3.8
Scandium, ppm	2.7	1.1	1.2 - 7.7
Selenium, ppm	2.2	1.0	0.4 - 7.7
Silver, ppm	0.3	0.02	0.02 - 0.08
Strontium, ppm	35	23	10 - 130
Tantalum, ppm	0.15	0.06	0.07 - 0.3
Terbium, ppm	0.22	0.14	0.04 - 0.65
Thallium, ppm	0.66	0.31	0.12 - 1.3
Thorium, ppm	2.1	0.87	0.71 - 5.1
Tin, ppm	3.8	8.8	0.2 - 51
Tungsten, ppm	0.82	0.69	0.04 - 4.2
Uranium, ppm	1.5	0.93	0.31 - 4.6
Vanadium, ppm	32	13	11 - 90
Ytterbium, ppm	0.56	0.21	0.27 - 1.5
Zinc, ppm	250	650	10 - 5300
Zirconium, ppm	47	27	12 - 130

Source: Adapted from Gluskoter et al. 1977

Table 8

MEAN ANALYTICAL VALUES FOR 44 TRACE ELEMENTS IN 23 WHOLE COAL SAMPLES FROM APPALACHIAN COAL FIELDS

Element	Mean	Standard Deviation	Range
Antimony, ppm	1.6	1.7	0.25 - 7.7
Arsenic, ppm	25	27	1.8 - 100
Barium, ppm	200	110	72 - 420
Beryllium, ppm	1.3	0.56	0.23 - 2.6
Boron, ppm	42	32	5.0 - 120
Bromine, ppm	12	7.6	0.71 - 26
Cadmium, ppm	0.24	0.18	0.10 - 0.60
Cerium, ppm	25	9.1	11 - 42
Cesium, ppm	2.0	1.6	0.40 - 6.2
Chromium, ppm	20	16	10 - 90
Cobalt, ppm	9.8	7.8	1.5 - 33
Copper, ppm	18	7.3	5.1 - 30
Dysprosium, ppm	2.3	0.94	0.74 - 3.5
Europium, ppm	0.52	0.22	0.16 - 0.92
Fluorine, ppm	89	31	50 - 150
Gallium, ppm	5.7	2.6	2.9 - 11
Germanium, ppm	1.6	1.7	0.10 - 6.0
Hafnium, ppm	1.2	0.45	0.58 - 2.2
Indium, ppm	0.23	0.08	0.13 - 0.37
Iodine, ppm	1.7	1.1	0.33 - 4.9
Lanthanum, ppm	15	5.3	6.1 - 23
Lead, ppm	5.9	4.0	1.0 - 18
Lutetium, ppm	0.22	0.12	0.04 - 0.40
Manganese, ppm	18	16	2.4 - 61
Mercury, ppm	0.20	0.12	0.05 - 0.47
Molybdenum, ppm	4.6	6.3	0.10 - 22
Nickel, ppm	15	5.7	6.3 - 28
Phosphorus, ppm	150	300	15 - 1500
Rubidium, ppm	22	15	9.0 - 63
Samarium, ppm	2.6	1.0	0.87 - 4.3
Scandium, ppm	5.1	2.4	1.6 - 9.3
Selenium, ppm	4.0	2.0	1.1 - 8.1
Silver, ppm	0.02	0.01	0.01 - 0.06
Strontium, ppm	130	130	28 - 550
Tantalum, ppm	0.33	0.28	0.12 - 1.1
Terbium, ppm	0.34	0.17	0.06 - 0.63
Thorium, ppm	4.5	2.1	1.8 - 9.0
Tin, ppm	2.0	2.4	0.20 - 8.0
Tungsten, ppm	0.69	0.31	0.22 - 1.2
Uranium, ppm	1.5	0.73	0.40 - 2.9
Vanadium, ppm	38	14	14 - 73
Ytterbium, ppm	0.83	0.35	0.18 - 1.4
Zinc, ppm	25	24	2.0 - 120
Zirconium, ppm	45	18	8.0 - 88

Source: Adapted from Gluskoter et al. 1977

Table 9

MEAN ANALYTICAL VALUES FOR 44 TRACE ELEMENTS IN 28 WHOLE COAL SAMPLES FROM THE WESTERN UNITED STATES

Element	Mean	Standard Deviation	Range
Antimony, ppm	0.58	0.61	0.18 - 3.5
Arsenic, ppm	2.3	2.6	0.34 - 9.8
Barium, ppm	500	320	160 - 1600
Beryllium, ppm	0.46	0.34	0.10 - 1.4
Boron, ppm	56	32	16 - 140
Bromine, ppm	4.7	7.3	0.50 - 25
Cadmium, ppm	0.18	0.13	0.10 - 0.60
Cerium, ppm	11	8.0	2.8 - 30
Cesium, ppm	0.42	0.82	0.02 - 3.8
Chromium, ppm	9.0	4.2	2.4 - 20
Cobalt, ppm	1.8	1.5	0.60 - 7.0
Copper, ppm	10	5.9	3.1 - 23
Dysprosium, ppm	0.63	0.32	0.22 - 1.4
Europium, ppm	0.20	0.17	0.07 - 0.80
Fluorine, ppm	62	28	19 - 140
Gallium, ppm	2.5	1.4	0.80 - 6.5
Germanium, ppm	0.91	0.92	0.10 - 3.0
Hafnium, ppm	0.78	0.33	0.26 - 1.3
Indium, ppm	0.10	0.07	0.01 - 0.25
Iodine, ppm	0.52	0.25	0.20 - 1.0
Lanthanum, ppm	5.2	3.0	1.8 - 13
Lead, ppm	3.4	2.3	0.70 - 9.0
Lutetium, ppm	0.07	0.09	0.01 - 0.43
Manganese, ppm	49	49	1.4 - 220
Mercury, ppm	0.09	0.11	0.02 - 0.63
Molybdenum, ppm	2.1	5.6	0.10 - 30
Nickel, ppm	5.0	3.2	1.5 - 18
Phosphorus, ppm	130	130	10 - 510
Rubidium, ppm	4.6	6.6	0.30 - 29
Samarium, ppm	0.61	0.29	0.22 - 1.4
Scandium, ppm	1.8	1.1	0.50 - 4.5
Selenium, ppm	1.4	0.59	0.40 - 2.7
Silver, ppm	0.03	0.02	0.01 - 0.07
Strontium, ppm	260	140	93 - 500
Tantalum, ppm	0.15	0.08	0.04 - 0.33
Terbium, ppm	0.21	0.15	0.06 - 0.58
Thorium, ppm	2.3	1.5	0.62 - 5.7
Tin, ppm	1.9	3.8	0.10 - 15
Tungsten, ppm	0.75	0.65	0.13 - 3.3
Uranium, ppm	1.2	0.65	0.30 - 2.5
Vanadium, ppm	14	10	4.8 - 43
Ytterbium, ppm	0.38	0.17	0.13 - 0.78
Zinc, ppm	7.0	4.9	0.30 - 17
Zirconium, ppm	33	31	12 - 170

Source: Adapted from Gluskoter et al. 1977

Chapter 3

HISTORICAL PERSPECTIVE

3.0 COAL GAS

The history of coal gasification can be traced back to 1691 when the Rev. John Clayton discovered that an inflammable vapor could be produced by distilling coal (Meade 1916, Wyer 1906, and Lewes 1907). However, it was not unitl 1779 that William Murdoch succeeded in manufacturing gas from coal in a crude retort and illuminated his home with a "wickless flame" (Lewes 1907). Murdoch, however, was not destined to reap the reward of his discovery, and in 1799 a Frenchman named Philippe Lebon took out a patent in Paris for making an illuminating gas from wood, and gave an exhibition in 1802 (Lewes 1907 and Meade 1916). It was seen by a German, named Winsor, who made Lebon an offer for his secret process for Germany. This offer was declined, and Winsor studied the subject and quickly succeeding, he exploited his invention in Germany. Winsor then came to England and gave lectures on gas lighting in 1804 and subsequently founded the first coal gas company, Gas Light and Coke Company in London in 1812 (Lewes 1907 and Meade 1916). This facility is depicted in Figure 9. The first U.S. company was chartered in Baltimore in 1816 (Perry 1974a).

By 1900, the coal gas plants had became more complex as shown in Figure 10. The coal was heated in D-shaped retorts in the absence of air. The gas from the retorts was passed through an atmospheric condenser where the

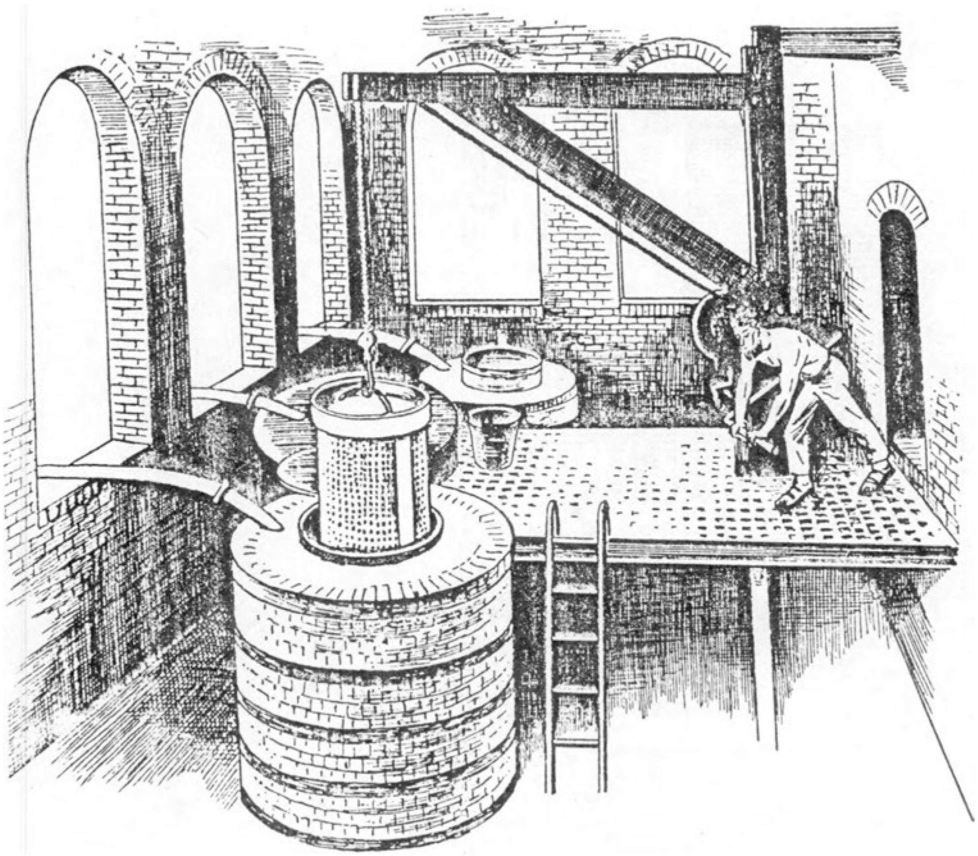


Figure 9

THE FIRST COAL GAS COMPANY (Circa 1812)

Source: Felton, Newman, and Read 1964

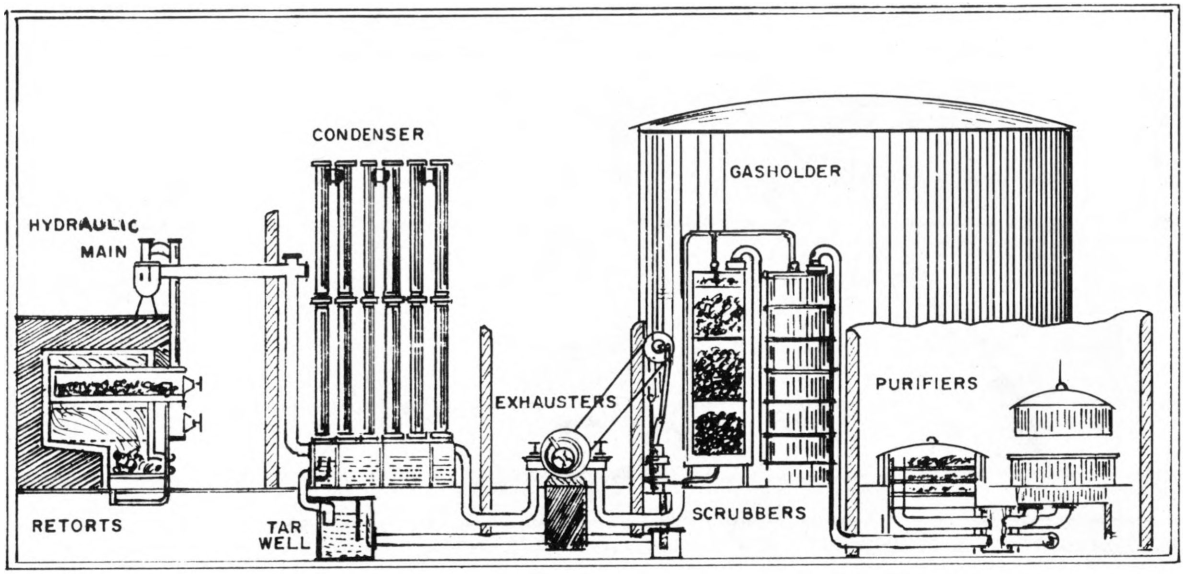


Figure 10

COAL GAS PLANT (Circa 1900)

Source: Lewes 1907

majority of the tar and ammoniacal liquor was condensed. The gas then passed through scrubbers where some H_2S and CS_2 were removed along with the final traces of tar and ammonia (Lewes 1907). The gas then passed on to the purifiers where the remaining sulfur compounds were removed (Thorp 1898). The purified gas was then stored in large tanks from which it was delivered to the street mains.

As the gas market grew, it became necessary to find ways to supplement the low yield from coal distillation. Over 70 percent of the coal remains a solid when it is heated, and this portion had to be sold if the price were to be competitive. When slot-type coke ovens became widely used in the steel industry, coke-oven gas was used as a supplement (Perry 1974b).

3.1 WATER GAS

In 1875, Lowe developed the carbureted water gas process which was used for the next half century (Evans 1976). A schematic diagram of Lowe's process is shown in Figure 11. A bed of noncaking coal or coke was brought to an acceptable temperature and blasted with air (Perry 1974a). The "blow reaction" was (Meade 1916)"

$$C + O_2 \longrightarrow CO_2$$

As the coal in the upper part of the bed became hot, the following reaction occurred (Perry 1974a and b):

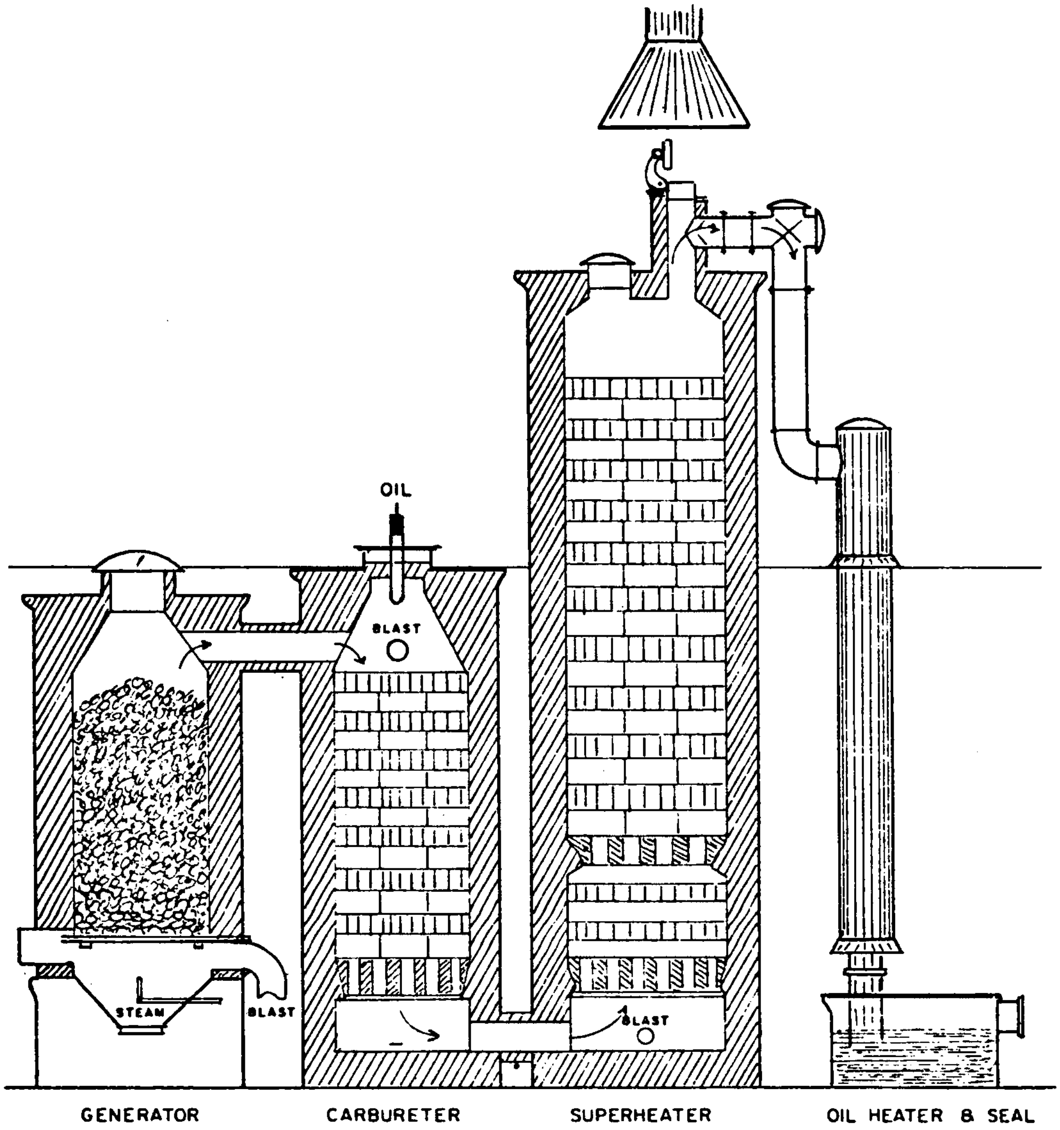


Figure 11

LOWE'S CARBURETED WATER GAS PROCESS

Source: Thorp 1898

$$CO_2 + C \rightarrow 2CO$$

After enough coal had been heated, the air blast was discontinued and steam was introduced, resulting in the following reaction (Perry 1974a):

$$C + H_2O \rightarrow H_2 + CO$$

The gas produced had a heating value of about 300 Btu/cu. ft. and had to be enriched to be compatible with coal gas (475-560 Btu/cu. ft.) (Perry 1974a).

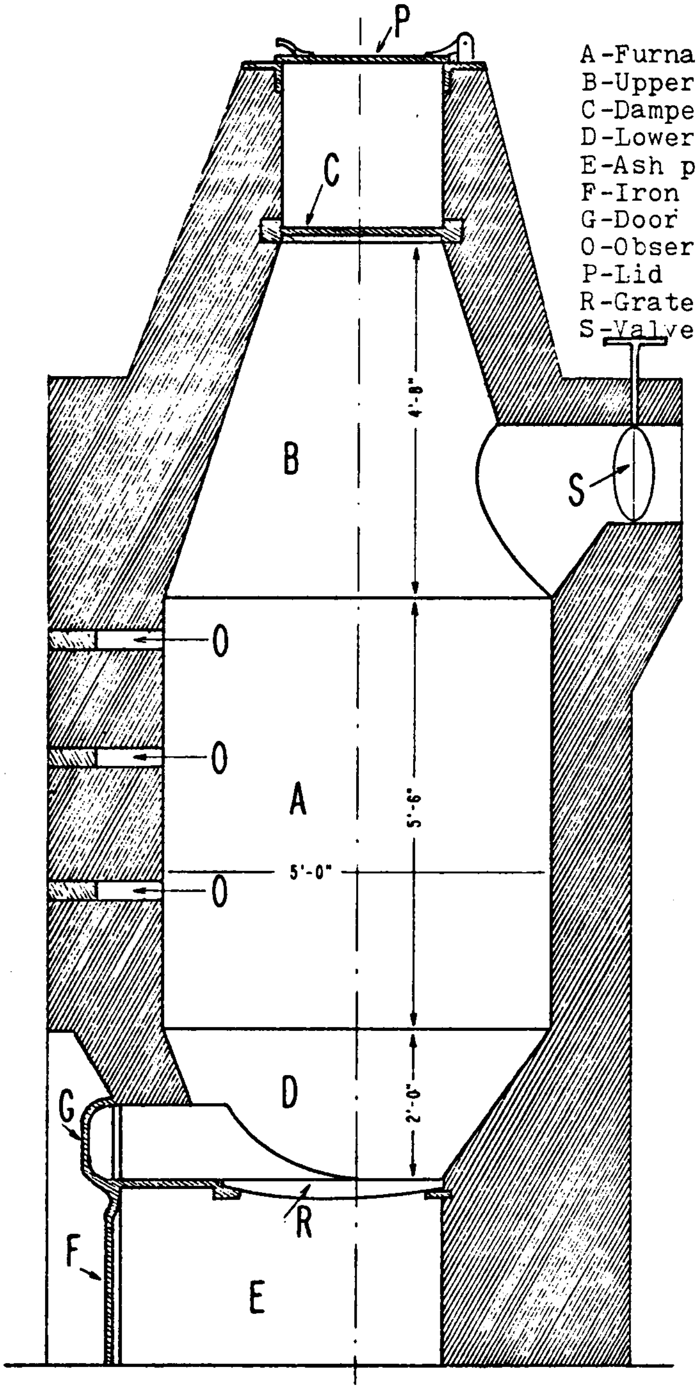
The enrichment process was also cyclical. Gases from the last part of the "blow" cycle were burned to heat refractory bricks enclosed in a "carburetor" vessel. When the bricks were hot enough, the gas was shut off and oil was sprayed on the bricks, where it was "cracked" into lower molecular weight hydrocarbons, including methane and propane. The resulting gas, which had a high heating value, was mixed with the gas made during the run period (Perry 1974a and b).

3.2 PRODUCER GAS

"Producer gas" was used extensively because "of its cheapness, cleanliness, and the regularity of the temperature obtained" (Thorp 1898). The conception of the producer gas process is credited to Wilhelm Frederich von Faber du Faur of Germany (Wyer 1906). However, because of sickness, he was not able to pursue his research and communicated his ideas to Abelmen and Bischof (Wyer 1906), who subsequently built the first gas producer in 1839 (Wyer 1906 and Lewes 1907). A diagram of this simple producer is shown in Figure 12. However, it was not until 1857 that Siemens incorporated a system of regeneration and developed the first commercially successful producer (Wyer 1906 and Lewes 1907). The Siemens producer is shown in Figure 13.

There are still three important points in the development of the gas producer (Wyer 1906). First, the introduction of the Dowson gas producer in 1878, this was the first producer that was successful for power purposes (Wyer 1906). By 1909, there was nearly 500 gas producer power plants operating in the United States (Fernald 1912). See Table 10. Second, the introduction of the Mond by-product process on a large scale in 1889. Third, the introduction of the Benier suction gas-producer in 1895, which was the first compact unit (Wyer 1906).

Gas producers may be divided into two types according to the method of supplying air and steam--suction or pressure (Walker et al. 1937). Producer gas was made in a continuous process wherein a bed of hot coal or coke was blasted with air or a mixture of steam and air. The final product necessarily contained nitrogen from the air and carbon dioxide resulting from the combustion of carbon with oxygen (Perry 1974a). Producer gas was used at industrial plants needing a clean source of fuel but for



LEGEND

A-Furnace body
B-Upper Furnace area
C-Damper
D-Lower furnace area
E-Ash pit
F-Iron plate with aperatures
G-Door
O-Observation ports
P-Lid
R-Grate
S-Valve

Figure 12

BISCHOF GAS PRODUCER

Source: Wyer 1906

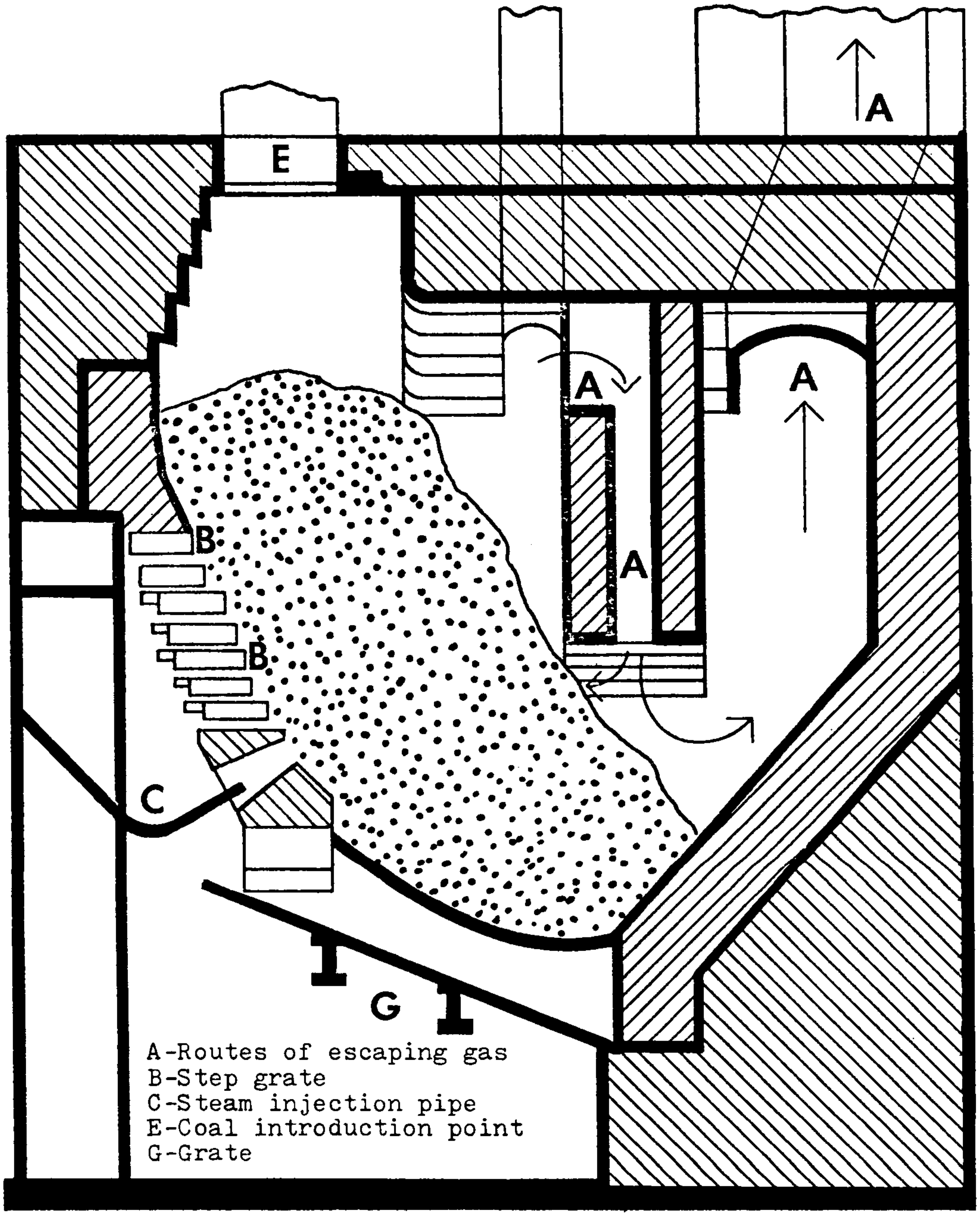


Figure 13

SIEMENS GAS PRODUCER

Source: Thorp 1898

Table 10

U.S. GAS PRODUCER POWER PLANTS OPERATING IN 1909

Fuel	No. of Plants	Horsepower Avg.	Horsepower Range
Anthracite			
over 500 hp	8	950	600-1500
500 hp or less	407	100	15- 500
Bituminous			
over 500 hp	20	2450	750-6000
500 hp or less	17	300	35- 500
Lignite			
over 500 hp	3	2430	525-3750
500 hp or less	19	90	25- 250
Total	474	235	15-6000

Source: Adapted from Fernald 1912

which the cost of transport and distribution of the gas was not important (Perry 1974b).

The technology of making water gas and producer gas was steadily improved in the United States (Perry 1974a). By the mid 1920's, there was 150 manufacturers of producers in the world and nearly 12,000 producers in the United States alone (Squires 1974). At that time, gasifiers fed gas to gas engines, heating furnaces, and kilns (EPA 1978). The residential gas market in the eastern United States was supplied mainly with manufactured gas as late as 1932 (Perry 1974b). But with the introduction of long-distance natural-gas pipelines during World War II, natural gas rapidly became more widely distributed, and by the end of the war, it was supplying nearly 90 percent of the market (Perry 1974b). By 1948, there was still 2,000 gasifiers in use; however, the number has since disminished so that no significant number of commercial gasifiers are presently used in the United States (EPA 1978). The reasons for disappearance of the gas producer were (Hottell and Howard 1971):

- Its production of dirty gas--high in dust, soot and tar--which was objectionable in many applications;
- Difficulties in bed clinkering from poor temperature control;
- Sensitivity to coal type, i.e., occasional need for hand poking when caking coals were used, even though the fuel bed was mechanially stirred;

- Sulfur content of the gas was objectionable in some applications even fifty years ago;
- Restriction to small size, with associated high cost of labor and equipment for large power usage;
- The increasing availability of cheap natural gas.

The real innovations in coal gasification technology started around 1920 in Europe, where coal was the principal source of energy and where there was an incentive to develop processes for making low-cost synthesis gas from coal for use in the production of ammonia and synthetic liquid fuels (Evans 1976). The basic concept of today's Lurgi coal gasification process were developed from the Lurgi coking operation. Other process developments include the Koppers-Totzek, Winkler, Galusha, Wellman-Lord and McDowell-Wellman processes. In a period of about 50 years, major advances in coal gasification have occurred; in the use of oxygen; in operation at high pressure; in the use of fluidized bed and particle suspension systems; in operation under slagging conditions; in the use of fluids, solids, and liquids as carriers of heat for the gasification reactions (Evans 1976). Today most of the development in coal gasification is being done in the United States, rather than in Europe as it was 40 to 50 years ago.

Chapter 4

STAGES OF PROCESS DEVELOPMENT

New processes and new sources of energy present occupational health problems of unprecedented complexity.

Senate Report 91-1282
accompaning the Occupational
Safety and Health Act of 1970

4.0 INTRODUCTION

In general, a strategy for process development evolves through the stages of (1) bench, (2) process development, (3) pilot plant, and (4) demonstration plant (AEC 1974a). The various scales of process development are shown in Table 11 in terms of capacity and capital cost. The developmental status of several coal conversion processes is shown in Table 12.

4.1 BENCH SCALE UNIT

The function of laboratory and bench scale units (BSU) is primarily to establish the scientific feasibility of a process. The work normally is conducted in batch or semi-continuous units that represent only the key steps of a potential process (AEC 1974a). A laboratory model of Battelle's Agglomerating Burner Process is shown in Figure 14.

4.2 PROCESS DEVELOPMENT UNIT

The function of a Process Development Unit (PDU) is to establish the engineering feasibility of a process. The PDU normally provides the first opportunity to evaluate engineering aspects such as component designs, materials of construction, and adaptability for scale-up (AEC 1974a). The PDU is the most economical size for the conduct of unit operation parametric studies, coal characterization and

Table 11

STAGES OF PROCESS DEVELOPMENT

Unit	Capacity (tons coal/day)	Capital Cost (1974 $, millions)
Bench(BSU)	< 1	< 1
Process Development(PDU)	1 - 10	4 - 10
Pilot Plant	50 - 125	15 - 30
Demonstration Plant	600 - 5,000	200 - 500
Pioneer Plant	10,000 - 20,000	600 - 900
Commercial Plant	35,000	1,000 - 1,500

Source: Modified from Atomic Energy Commission 1974a

Table 12

COAL CONVERSION DEVELOPMENT STATUS

Process	Company	Status
Agglomerating Burner	Battelle Columbus Laboratories	PDU
Atgas	Applied Technology Corp.	BSU
Bi-Gas	Bituminous Coal Research Inc.	Pilot Plant
CO_2 Acceptor	Consolidation Coal Co.	Pilot Plant
COED	FMC Corp.	Pilot Plant
Fischer-Tropsch	M.W. Kellogg Co.	Commercial
Consol Synthetic Fuel	Consolidation Coal Co.	Pilot Plant
Garrett's Coal Pyrolysis	Garrett Research & Development Co. Inc.	PDU
H-Coal	Hydrocarbon Research Inc.	Demonstration
Hydrane	U.S. Bureau of Mines	BSU
Lurgi	Lurgi Mineralotechnik G.m.b.H.	Commercial
Koppers-Totzek	Heinrich Koppers G.m.b.H. of Essen	Commercial
Hygas	Institute of Gas Technology	Pilot Plant
Molton Salt	M.W. Kellogg Co.	BSU
Solvent Refined Coal	Pittsburg & Midway Coal Mining Co.	Pilot Plant
Synthane	U.S. Department of Energy	Pilot Plant
Synthoil	U.S. Department of Energy	PDU
U-Gas	Institute of Gas Technology	BSU
Westinghouse	Westinghouse Research Laboratories	PDU
Wellman-Galusha	Wellman Engineering Co.	Commercial
Winkler	Davy Powergas Inc.	Commercial

Source: Adapted from Bodle and Vygas 1974

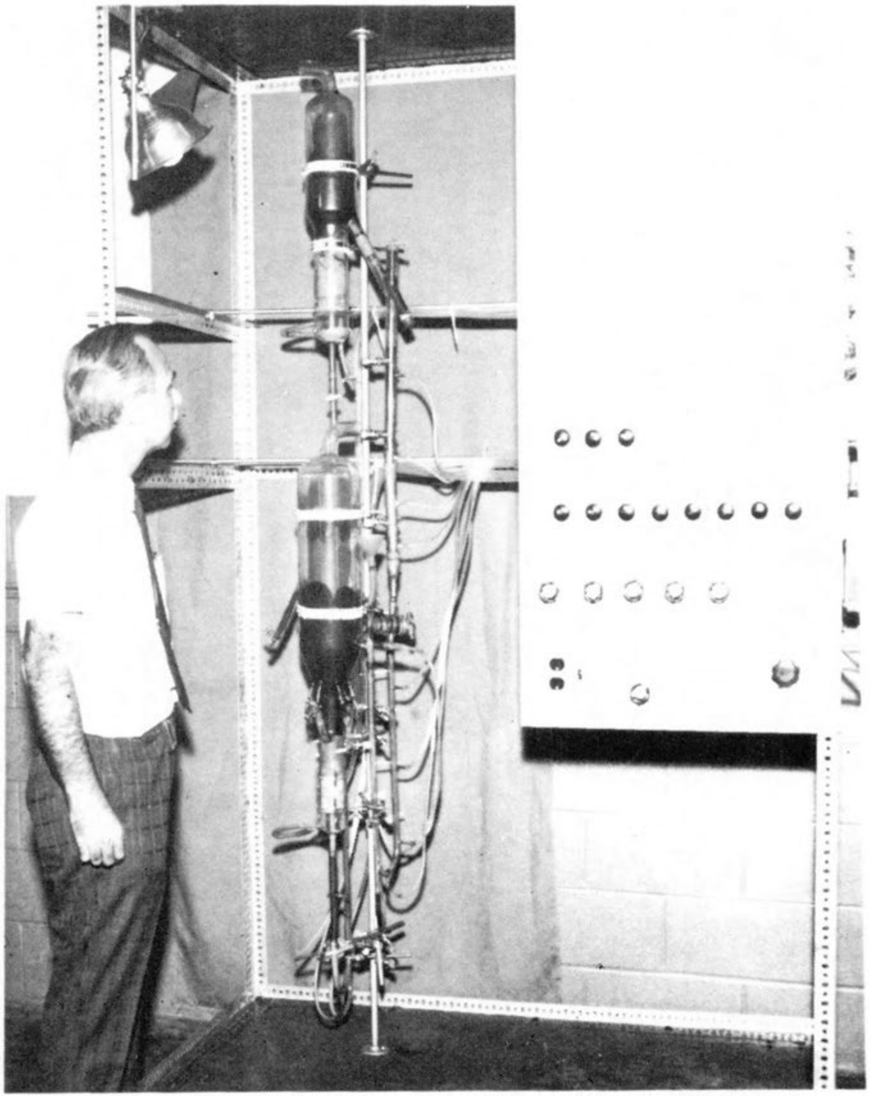


Figure 14

LABORATORY MODEL OF BATTELLE'S AGGLOMERATING BURNER PROCESS

(Photo courtesy of William G. Steedman)

other process related evaluations (ERDA 1976a). Westinghouse's 1,200 lb./hr. PDU for producing low Btu gas is pictured in Figure 15.

4.3 PILOT PLANT

The pilot plant is designed to test that portion of a process which is novel to determine scale-up problems and to define process limitations or problems and solutions under a reasonably wide range of conditions. The equipment used is generally that which is available on the market at the time the plant is designed. A good pilot plant will also test equipment, equipment lay-outs, refractory material, etc. Its prime product is data to be gained over a number of relatively short steady-state periods (i.e., 7 days maximum at the coal gasification pilot plants supported by ERDA) (Young and Evans 1976). In general, a pilot plant has to be scaled up by a factor of 10 to 100 to the first trains of commercial plants and may use the smallest sizes of commercial equipment (AEC 1974a).

An aerial view of the SRC 50 T/D pilot plant located at North Fort Lewis, Washington is shown in Figure 16. The plant site covers about 12 acres (Perrussel et al. 1976). Construction cost was approximately $20 million (Perrussel et al. 1976).

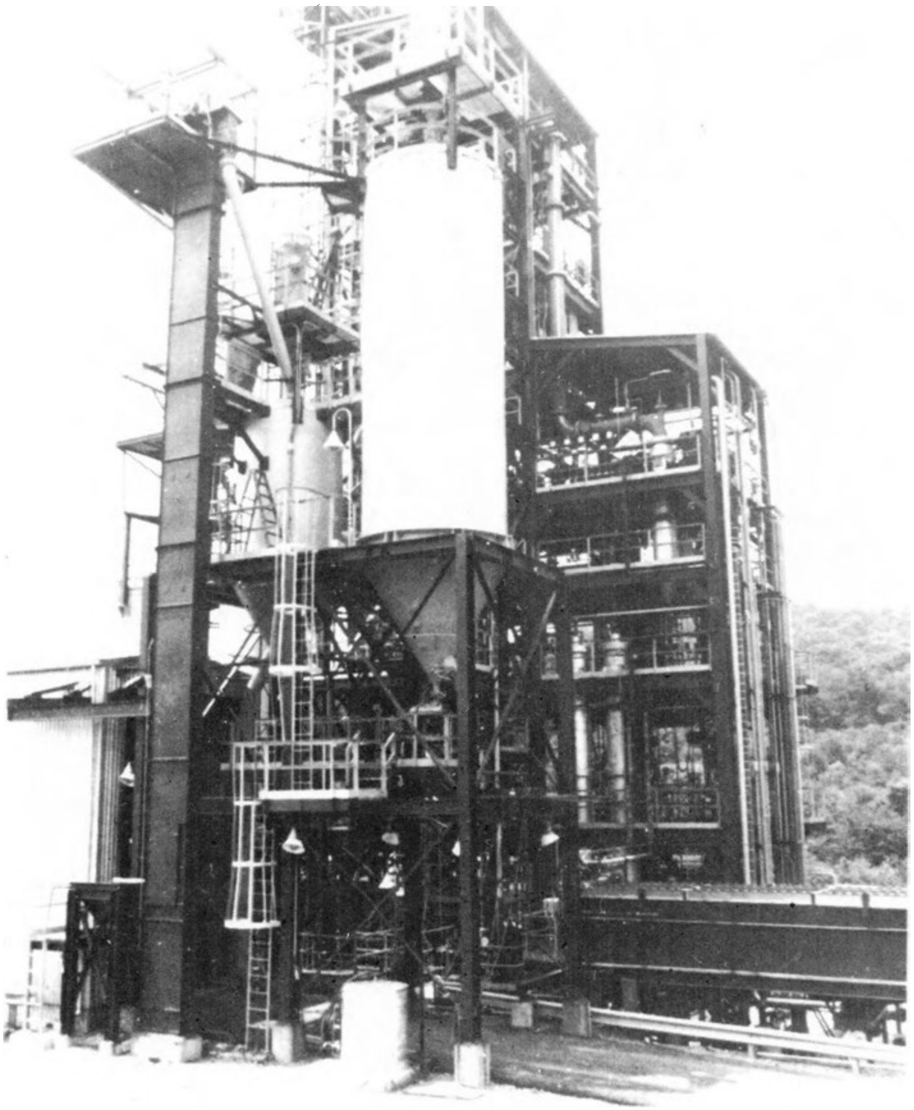


Figure 15

WESTINGHOUSE'S PDU PROCESS STRUCTURE
AND RAW MATERIALS STORAGE

(Photo courtesy of Edwin F. Vandergrift)

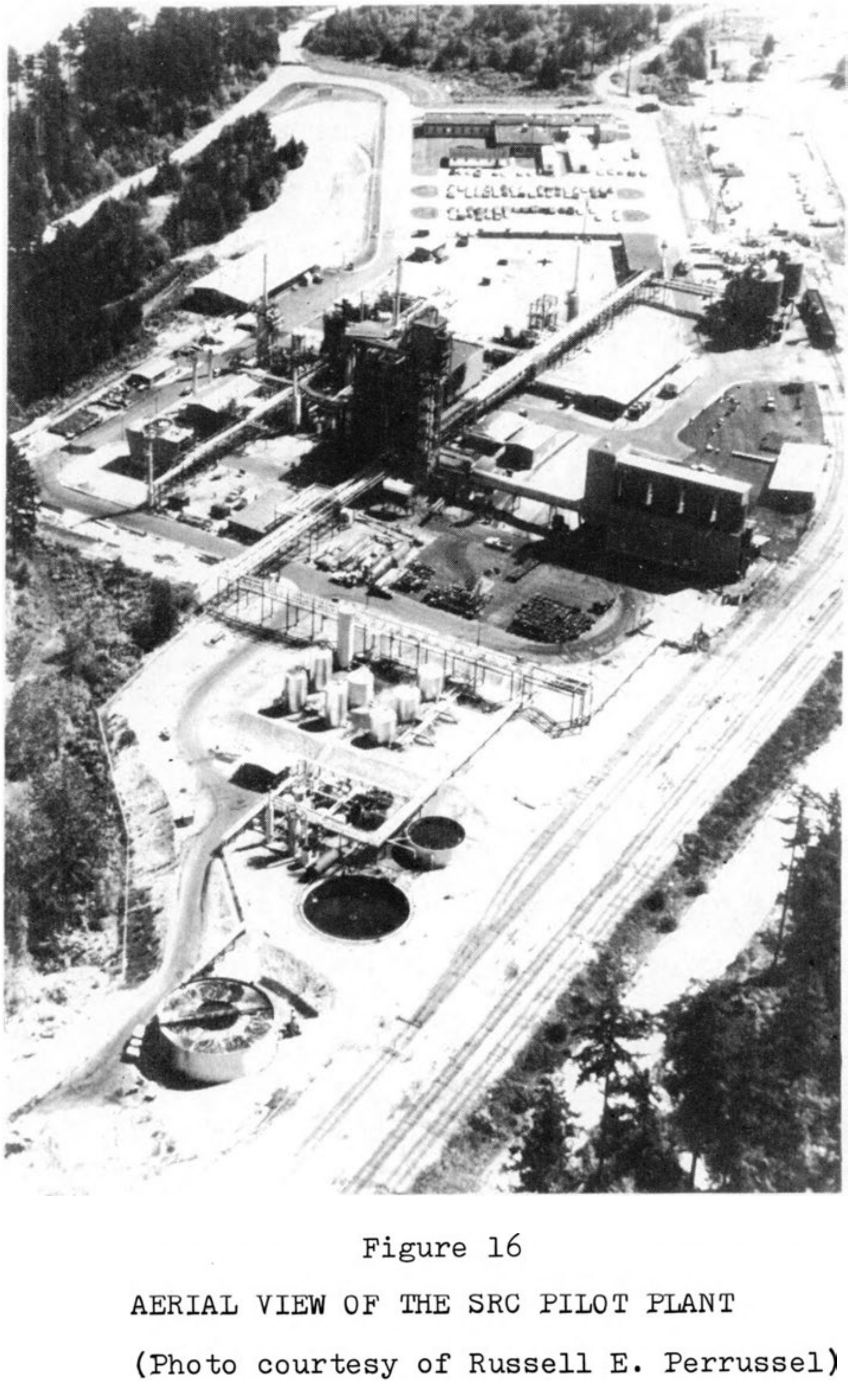


Figure 16

AERIAL VIEW OF THE SRC PILOT PLANT

(Photo courtesy of Russell E. Perrussel)

4.4 DEMONSTRATION PLANT

Demonstration plants and pioneer plants have the objective of establishing the economic viability of a process. The demonstration plants normally consist of a first process train that later may be replicated to provide for full commercial scale. A pioneer plant is the first commercial multitrain plant of a given process (AEC 1974a).

The estimated manpower requirements for a coal gasification plant converting 18,000 tons of coal per day into 250 million standard cubic feet of pipeline quality gas are shown in Table 13 (Synfuels Interagency Task Force 1975b).

Conceptual design criteria for a pioneer coal conversion plant have been published (O'Hara et al. 1976a). This facility would convert 34,700 tons of coal per day to 11,310 tons of low-sulfur fuel oil, 3,940 tons of SNG, 1,290 tons of naphtha, 940 tons of LPG, 1,250 tons of sulfur, and 90 tons of ammonia. Six hundred acres would be needed for the complex site alone (O'Hara et al. 1976b). An artist's concept of this Oil/Gas complex is shown in Figure 17.

4.5 COMMERCIAL FACILITY

Several commercial coal gasification plants based on Lurgi technology followed by methanation are being planned, although none have actually proceeded to con-

Table 13

OPERATIONAL MANPOWER REQUIREMENT FOR A UNIT HIGH-BTU PLANT

Labor Category	# of Workers
Operating	
Operator	50
Helper	38
Controlman	15
Pumper	13
Utilityman	7
Fireman, Stat.	7
Foreman	20
Maintenance	
Instrument Technician	35
Mechanic, Machine	28
Equipment Operator	32
Welder	38
Bricklayer	24
Bricklayer Helper	24
Electrician	35
Electrician Helper	35
Carpenter	25
Painter	24
Pipefitter	38
Pipefitter Helper	38
Mechanic	38
Mechanic Helper	38
Master Machinist	32
General Maintenance	76
Foreman	60

Labor Category	# of Workers
Service/Administration	
Management	18
Sales	7
Personnel Department	6
Accounting	9
Safety/Fireman	3
Medical	3
Maintenance Room	13
Security	18
Secretarial	13
Warehouseman	13
Office Service	6
Engineering and Technical	
Chemical	14
Electrical	14
Statistician	1
Computer Programmer	2
Chemist	13
Mechanical	11

Total Number of Workers 891

Source: Synfuels Interagency Task Force 1975b

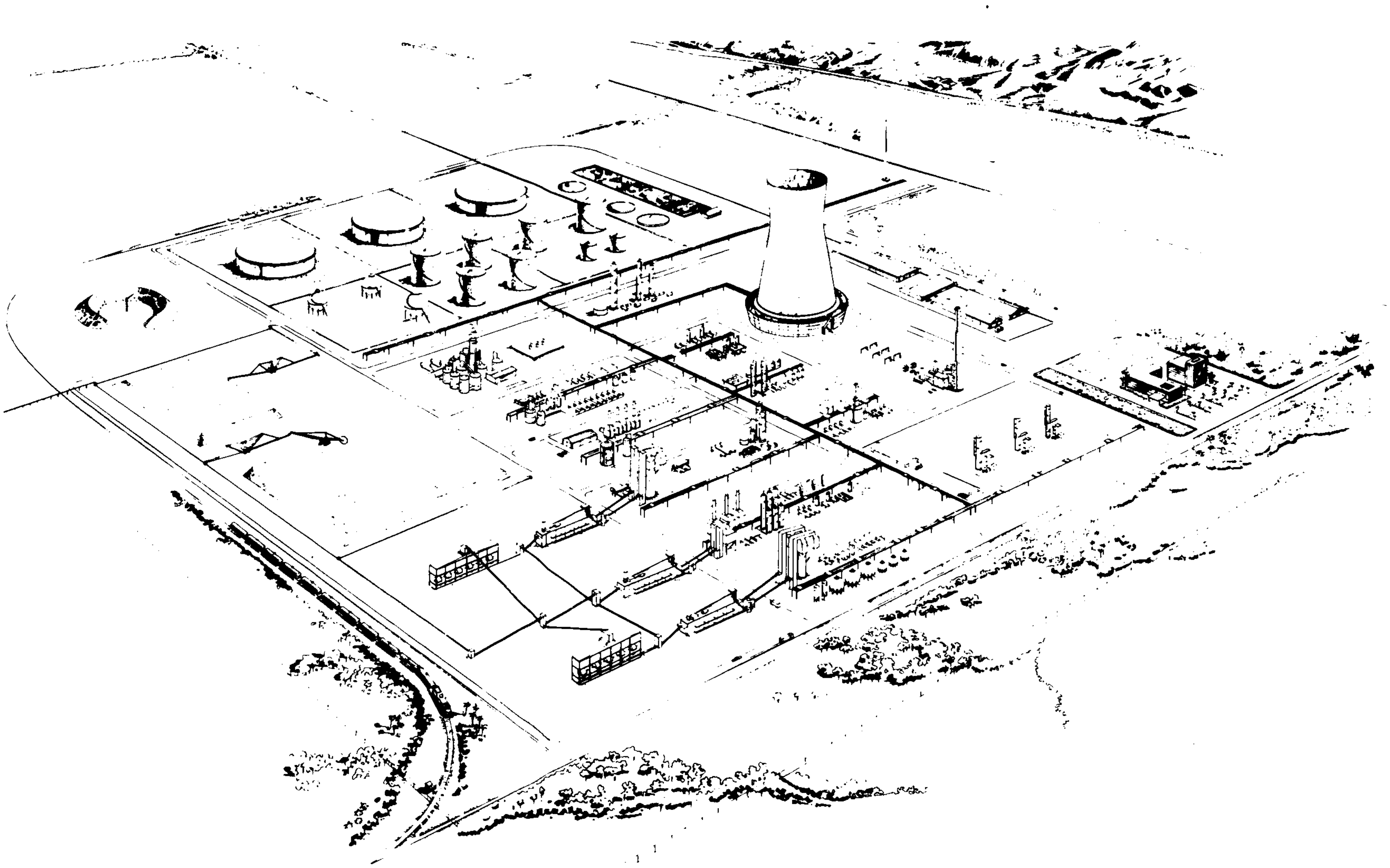


Figure 17

ARTIST'S CONCEPT OF AN OIL AND GAS PLANT
Source: O'Hara et al. 1976b

struction (Synfuels Interagency Task Force 1975a). The active projects and their status in 1975 are shown in Table 14. The output of future plants producing high-Btu gas from coal in the United States has been estimated recently by several organizations with the results shown in Table 15. Using the more recent projections of the Bureau of Mines, only one high-Btu plant is expected on stream by 1980. However, the projected increases through 2000 show rapid growth--a 620 percent increase in production in 20 years (EPA 1978). The 5,500 - 6,200 trillion Btu's projected for the year 2000 corresponds to 60-68 plants producing 250 billion Btu's (~270 million cubic feet) of SNG per day.

Table 14

ACTIVE HIGH BTU GAS FROM COAL PROJECTS

COMPANY	LOCATION	STATUS
Western Coal Gasification Co.	New Mexico, Public Land	Federal Power Commission has issued opinion approving project with certain qualifications. The company has requested a cost of service authorization.
Michigan-Wisconsin Pipeline Co.	North Dakota, Private Land	Application filed with Federal Power Commission, March 1975. Lignite reserves of 3.7 billion tons dedicated to project by North Coal Corp. Four plants planned. North Dakota has awarded conditional water permit.
El Paso Natural Gas	New Mexico, Public Land	Application before Federal Power Commission. Company has asked FPC to defer decision. Coal lease on Navajo Indian Reservation. Water application filed but not approved.
Panhandle Eastern Pipeline Co.	Wyoming, Private Land	Planning and design. Peabody Coal Co. has dedicated in excess of 500 million tons of coal. State has issued water permit.

Table 14 (Continued)

ACTIVE HIGH BTU GAS FROM COAL PROJECTS

Company	Location	Status
Natural Gas Pipeline Co. of America	North Dakota, Largely Private Land	Detail planning. Rights to 2.1 billion tons of lignite leased. Application for water submitted to North Dakota. Plans for eventual 4 plants with 250 million scf/d capacity each.
Cities Service Gas Northern Natural Gas	Montana-Wyoming	Study of coal gasification in Powder River Basin. Up to 1,000 million scf/d in four plants. Peabody Coal Co. has dedicated 500 million tons of coal.

Source: Synfuels Interagency Task Force 1975a

Table 15

Survey of Estimates of Future Supply of Pipleline Quality (High Btu) Gas Produced from Coal in the United States (Trillions of Btu's)

	Year				
Source	1980	1985	1990	1995	2000
FPC(a)	300	1100	3100	800	--
USDI(b)	700	2000	--	--	5500
USBM(c)	100	1300	3000	4000	6200

[a] Federal Power Commission

[b] U.S. Department of Interior

[c] U.S. Bureau of Mines

Source: EPA 1978

Chapter 5

CURRENT TECHNOLOGY

Even the most radical environmental and health scientists are not trying to scotch synfuel production entirely. They say that as long as in-plant environments are regulated and health hazards are given high research priority, the technology can be made safe.

Business Week 1976

5.0 INTRODUCTION

The major characteristics of three coal gasification processes are described. Using technology now available, first generation processes can be constructed by employing a conventional fixed-bed gasifier followed by catalytic methanation. The Lurgi coal gasification process was chosen as an example of this technology because it is a common commercial process, and because it is planned to be the major component of the first full scale high Btu gasification complex in the United States. Processes attainable in ten years are referred to as second-generation (Hottel and Howard 1971); these processes potentially will improve the economics (perhaps by about 20 percent) (AEC 1974b). The two leading pilot plants, HYGAS and CO_2 Acceptor, are described. These three processes illustrate the current state of the art.

5.1 LURGI PROCESS

The basic scheme for a high Btu gas production plant using a Lurgi gasifier is shown in Figure 18. This facility would consist of (Rudolph and Herbert 1975 and Haynes and Forney 1976):

- Coal gasification
- Shift conversion
- Rectisol sulfur removal
- Methanation

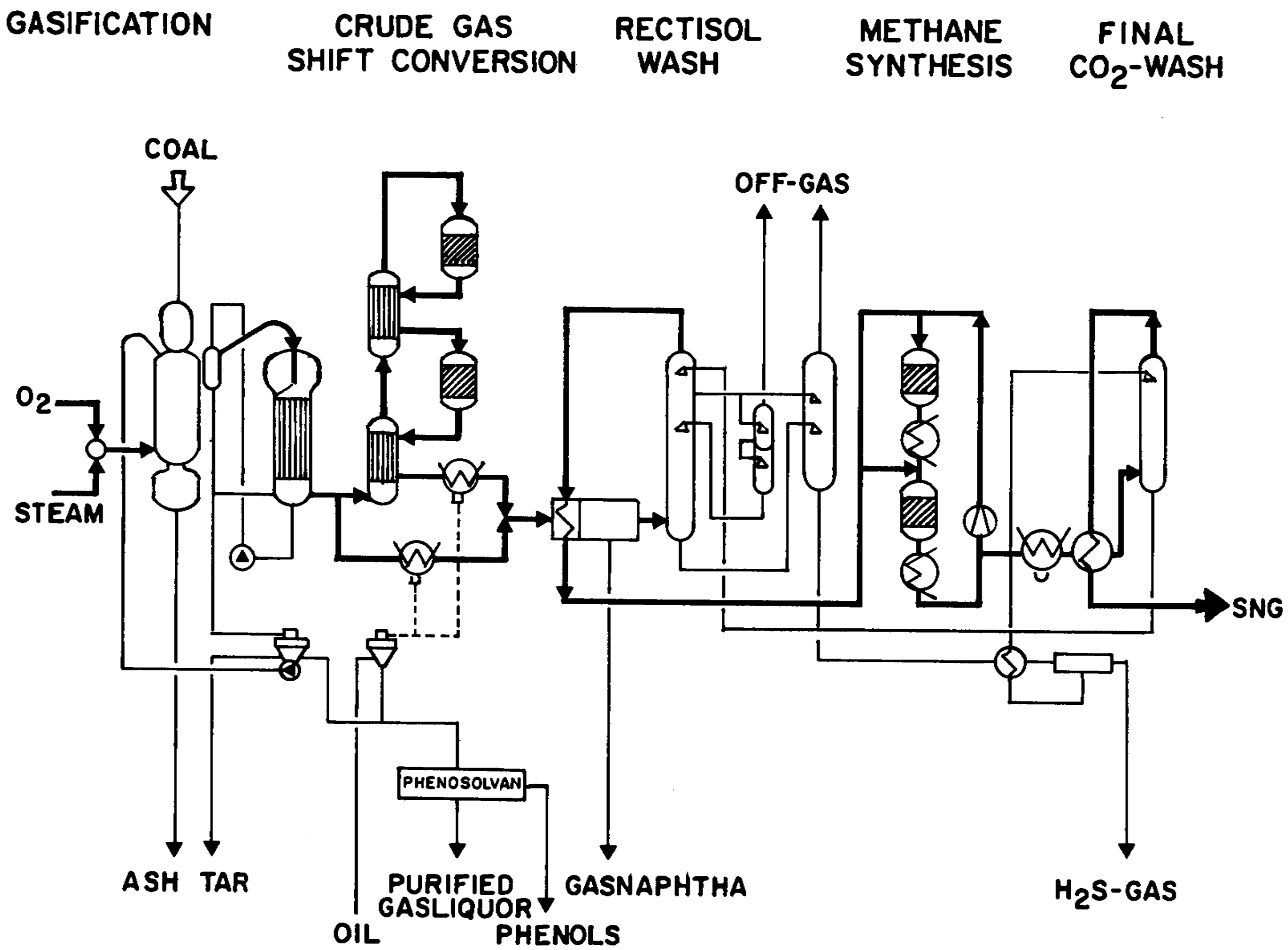


Figure 18

LURGI PROCESS TO PRODUCE SNG FROM COAL
Source: Haynes and Forney 1976

- Phenosolvan process

5.1.1 Coal gasification

The Lurgi gasifier, shown schematically in Figure 19 was first developed on lignite in 1931 by Lurgi Gesellschaft fur Warme und Chemetechnik mbH, Frankfurt, West Germany (Ball et al. 1974 and Howard-Smith and Werner 1976). Lurgi gasifiers have been widely used in other parts of the world, primarily utilizing an oxygen-steam gasifying medium for the production of town gas and synthesis gas for hydrocarbon products (Ball et al. 1974). The first commercial plant was constructed in 1936 and to date, fourteen plants (comprising 58 units) have been built with further plants, either with or without a methanation step, in the planning stages (Howard-Smith and Werner 1976). The most notable application is the world's largest coal gasification plant at Sasolburg, South Africa (Ball et al. 1974). The Sasol plant utilizes thirteen Lurgi gasifiers and consumes coal at the rate of 8,000 tons per day (McIver 1975). These gasifiers are 12 ft. I.D. and are the largest of their kind in commercial operation at present (McIver 1975).

The Lurgi gasifier utilizes a fixed-bed pressurized process with the gasifier operating under approximately 20 atmospheres of pressure (Ball et al. 1974). Pressurization requires coal feed and ash removal to be handled by lock hoppers at the top and bottom of the unit. The lock

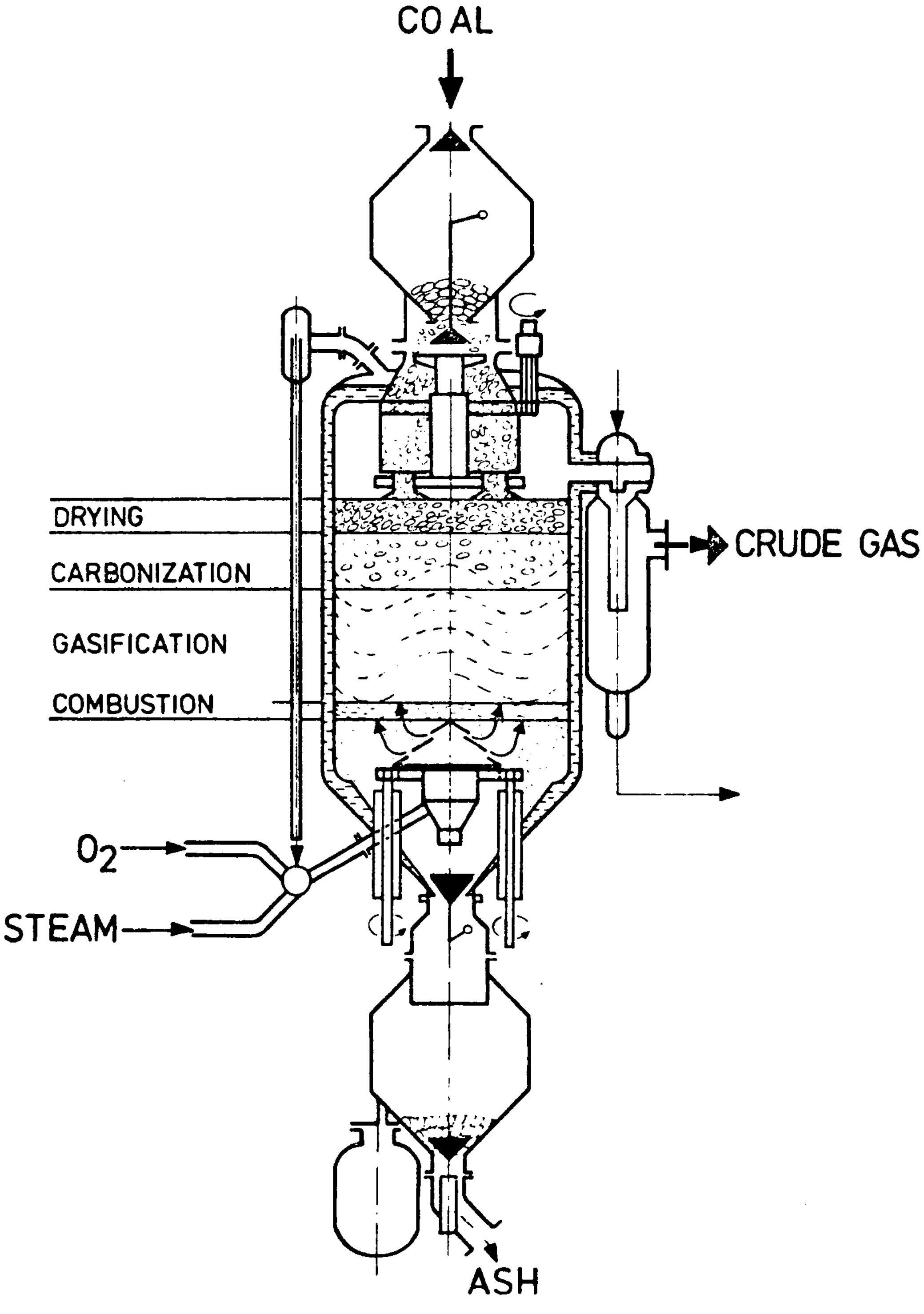


Figure 19

LURGI GASIFIER
Source: Ruldolph and Herbert 1975

hoppers allow coal and ash to be processed in and out of the unit intermittently without interrupting the process. The gasifying medium is introduced under pressure through a roating grate in the bottom of the unit and flows countercurrently through the coal bed, forming the fuel gas which is taken off at the top of the unit. The rotating grate also allows ash to fall into the bottom lock hopper for removal and serves to prevent agglomeration of the coal to insure an evenly distributed flow of the gasifying medium through the bed (Ball et al. 1974). At the top of the gasifier is a rotating horizontal arm that distributes the coal from the feed hopper evenly over the surface of the bed. The gasifier body itself consists of a water-cooled double-shelled cylinder with the water flowing in the jacket formed by the annulus of the two shells. Steam formed by the heat absorbed in the cooling water is capable of supplying approximately 20 percent of the process steam requirements of the unit (Ball et al. 1974).

In general there are three process zones in the gasifiers (Shaw and Magee 1974). The first zone devolatilizes the coal. As the coal drops down it is met with hot synthesis gas coming up from the bottom causing devolatilization, thus removing hydrocarbons and methane from the coal. As the coal drops lower to the second zone, gasification occurs by the reaction of carbon with steam. Finally as the coal approaches the grate, carbon is burned to produce the heat required for the gasification process. The chemical reactions associated with these zones are listed in Table 16.

The gas stream leaving the Lurgi gasifier contains coal dust, oil, naphtha, phenol, ammonia, tar oil, ash, char and other constituents (Shaw and Magee 1974). This mixture goes through a scrubbing and cooling tower to remove the tar. The raw gas stream then goes through a waste heat boiler where the raw gas is cooled to about 370°F. The raw gas stream after cooling is split into roughly two equal parts. Half of it goes through shift conversion to produce additional hydrogen which will be needed for methanation. The other half goes directly to the gas purification system (Shaw and Magee 1974).

5.1.2 Shift conversion

Only about one-half of the total crude gas is subjected to shift conversion (Glaser et al. 1974). Here, additional hydrogen is produced to adjust the H_2:CO ratio for proper feed to the methanator. In this process, the ratio of the combined, shifted gas is 3.7:1 because some CO_2 is also methanated (Glaser et al. 1974). Hot effluent gas from the exothermic shift reaction is cooled in countercurrent heat exchangers with the feed gas (Glaser et al. 1974).

Table 16

CHEMICAL REACTIONS IN LURGI GASIFIER

Devolatilization and Drying

$$\text{Coal} + \text{Heat} \rightarrow CH_4 + H_2O + \text{Organics}$$

Gasification

$$C + H_2O + 56{,}400 \text{ Btu/lb-mole} \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2 + 17{,}770 \text{ Btu/lb-mole}$$

$$C + CO_2 + 74{,}200 \text{ Btu/lb-mole} \rightarrow 2\,CO$$

$$C + H_2 \rightarrow CH_4 + 32{,}300 \text{ Btu/lb-mole}$$

Partical Combustion

$$C + \tfrac{1}{2}\,O_2 \rightarrow CO + 47{,}550 \text{ Btu/lb-mole}$$

$$C + O_2 \rightarrow CO_2 + 169{,}200 \text{ Btu/lb-mole}$$

Source: Shaw and Magee 1974

5.1.3 Rectisol sulfur removal

The original Lurgi Rectisol plant was built in Sasolburg, South Africa in 1955 and has operated since then at about 97 percent on-stream factor (EPA 1978). The Rectisol process uses one solvent (methanol) for removal of tar and oil, CO_2, sulfur compounds, ammonia, and phenol, as well as other compounds in smaller amounts. Carbon dioxide and hydrogen sulfide are removed from process gases by physical absorption in the cold methanol at approximately 40^oF. The Rectisol has selectivity for H_2S, which within reasonable limits permits concentrating H_2S in the regeneration section for feed to a Claus unit (EPA 1977). Normally H_2S and CO_2 are removed simutaneously from coal gas, since both gases require removal. The cold temperature and organic nature of the solvent also permits the Rectisol to remove tars, oils, ammonia, phenols and other condensables. Various liquid streams may be removed from the Rectisol for recovery of the more valuable by-products such as light oils, phenols, and ammonia. The disadvantages of the Rectisol are that some methanol loss to the product streams may occur and the ethane and ethylene loss from the main process stream to the Rectisol off-gas streams is significant (EPA 1978).

5.1.4 Methanation

The feed gas leaving the acid gas purification system is preheated with product gas leaving the methanation section (Shaw and Magee 1974). The chemical reactions involved in methanation are:

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O + 87{,}700\ \text{Btu/lb-mole}$$

and

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O + 71{,}000\ \text{Btu/lb-mole}$$

The heat of reaction that is generated by the synthesis of methane is removed by converting boiler feed water to process steam (Shaw and Magee 1974). This steam is used for gasification and in other parts of the plant.

The Westfield Lurgi Plant found excessive quantities of nickel carbonyl in its product gas (Shaw and Magee 1974). An active-carbon bed was installed to remove this material. The origin of the nickel carbonyl has not been established.

5.1.5 Phenosolvan process

The aqueous streams condensed from the coal gasification and gas processing areas by scrubbing and cooling the crude gas stream are called the gas liquor (Shaw and Magee 1974). Gas liquor is collected in one central area coming from gasification, shift, and gas purification. Before all of these aqueous streams are collected, all of the tar oil and naphtha will have been collected and stored for by-product value. Gas liquor streams will contain all of the ammonia and phenols that are produced in gasification

(Shaw and Magee 1974). In addition to these by-products, the gas liquor will also contain carbon dioxide, hydrogen sulfide, trace quantities of hydrogen cyanide, and other trace components.

The incoming gas liquor stream is filtered to remove suspended matter such as coal dust and ash. Disposition of the filtered solid material may be a problem as it will be contaminated with traces of materials from the gas liquor (Shaw and Magee 1974). The liquid is then mixed with an organic solvent (isopropyl ether) in an extractor in order to dissolve the phenol. The Phenolsolvan process (Lurgi proprietary process) is an integral part of the gas liquor treatment section. The phenol solvent mixture is collected and fed to solvent distillation columns where crude phenol is recovered as the bottom product, and the solvent as the overhead product (Shaw and Magee 1974). The solvent is then recycled to extractors after removing some of the contained water. The raffinate is stripped with fuel gas to remove traces of solvent which are picked up in the extraction step. The fuel gas is scrubbed with crude phenol product to recover the solvent. Finally, the phenol solvent mixture is distilled in the solvent recovery stripper to produce the crude phenol product, and the solvent is recycled to the extraction step (Shaw and Magee 1974).

5.2 HYGAS PROCESS

The HYGAS process is being developed by the Institute of Gas Technology (IGT) as part of the joint program of the Department of Energy (DOE) and the American Gas Association (AGA). DOE is providing two-thirds of the funds and AGA, one-third.

IGT's specific objectives include (ERDA 1976b):

- Development of a high-pressure hydrogasification process that uses all types of coal.
- Determination of the technical and economic feasibilities of utilizing the steam-oxygen and the electrothermal processes as hydrogen-generating systems for the HYGAS pilot plant.
- Perfection of the internal coal cycling system.
- Demonstration of the feasibility of ash agglomeration as a technique to increase carbon utilization.
- Demonstration of a methanation system.

5.2.1 History of the project

Development of the HYGAS process by IGT was initiated under the sponsorship of AGA in 1946, and continued under joint sponsorship with the Office of Coal Research in 1964 (ERDA 1976b). A state-of-the-art design and cost estimate for a 265 million scf/day facility was performed in 1965 (Tsaros et al. 1965). By 1967 a pilot plant flowsheet had been formulated; design and construction followed and initial reactor shakedown occurred in October 1971 (Schora 1975a). This pilot facility occupies three acres and has a capacity of producing 1.5 million cu. ft./day of synthetic pipeline gas from 75 tons/day of coal (Schora et al. 1973). Plant investment is approximately ten million dollars (Schora et al. 1973).

5.2.2 Process description

Hydrogasification is a key feature of the HYGAS process (ERDA 1976b). Hydrogasification is a direct reaction of hydrogen and steam on coal to produce methane without first producing carbon monoxide and hydrogen (Schora 1975b). Dent and co-workers first recognized the importance of this technique in 1937 (von Fredersdorff and Elliott 1963). Hydrogasification of coal has an inherent thermochemical advantage in comparison with the catalytic methanation of synthesis gas produced by gasifying coal with oxygen and steam (von Fredersdorff and Elliott 1963). This is shown in Table 17 by the significantly higher-ideal thermal efficiencies of two variants of the hydrogasification process.

The process is complex, involving pretreatment, slurry preparation, two-stage hydrogasification, fluidized-bed operation, high-pressure shift conversion, and methanation (Huffstetler and Rickert 1977). A diagram of the process is provided in Figure 20.

Coal is crushed to 1/8 in.; if caking coals are used, they are pretreated with air at atmospheric pressure in a fluidized-bed reactor operating at 700 to 800°F. The

Table 17

HEAT BALANCES AND EFFECIENCIES OF IDEAL PROCESSES FOR CONVERSION OF CARBON TO METHANE

	Gasification and Methanation (3 Moles C/Mole CH_4)	Hydrogenation H_2 from Carbon (2½ Moles C/Mole CH_4)	Hydrogenation H_2 from Product CH_4 (2 Moles C/Mole CH_4)
	Btu/lb-mole of Product Methane		
Heat of combustion of reactant carbon	507,879	423,233	338,587
Heat requirements			
Sensible heats	131,380	89,635	84,769
Endothermic heats of reaction	--	--	96,977
Latent heats	37,870	37,870	37,870
Total input	677,129	550,738	558,203
Heat of combustion of product methane	383,040	383,040	383,040
Heat available from sensible heat content of final & intermediate products	127,985	85,334	81,697
Exothermic heats of reaction	166,104	82,364	93,466
Total output	677,129	550,738	558,203
	Thermal Efficiency, %		
Without heat recovery +	56.6	69.6	68.6
With recovery of sensible & latent heat requirements ++	75.4	90.5	87.9*

(Based on enthalpies and standard heats of formation of β-graphite and ideal gases H_2O, O_2, H_2, CO, CO_2, and CH_4 and reference conditions of 25°C, 1 atm & liquid water)

\+ Heat of combustion of product CH_4/(heat of combustion of reactant carbon + total heat).
++ Heat of combustion of product CH_4/(heat of combustion of reactant carbon + net heat).
* Endothermic heat of reaction assumed to be supplied from external source at 1,000°K.

Source: von Fredersdorff and Elliott 1963

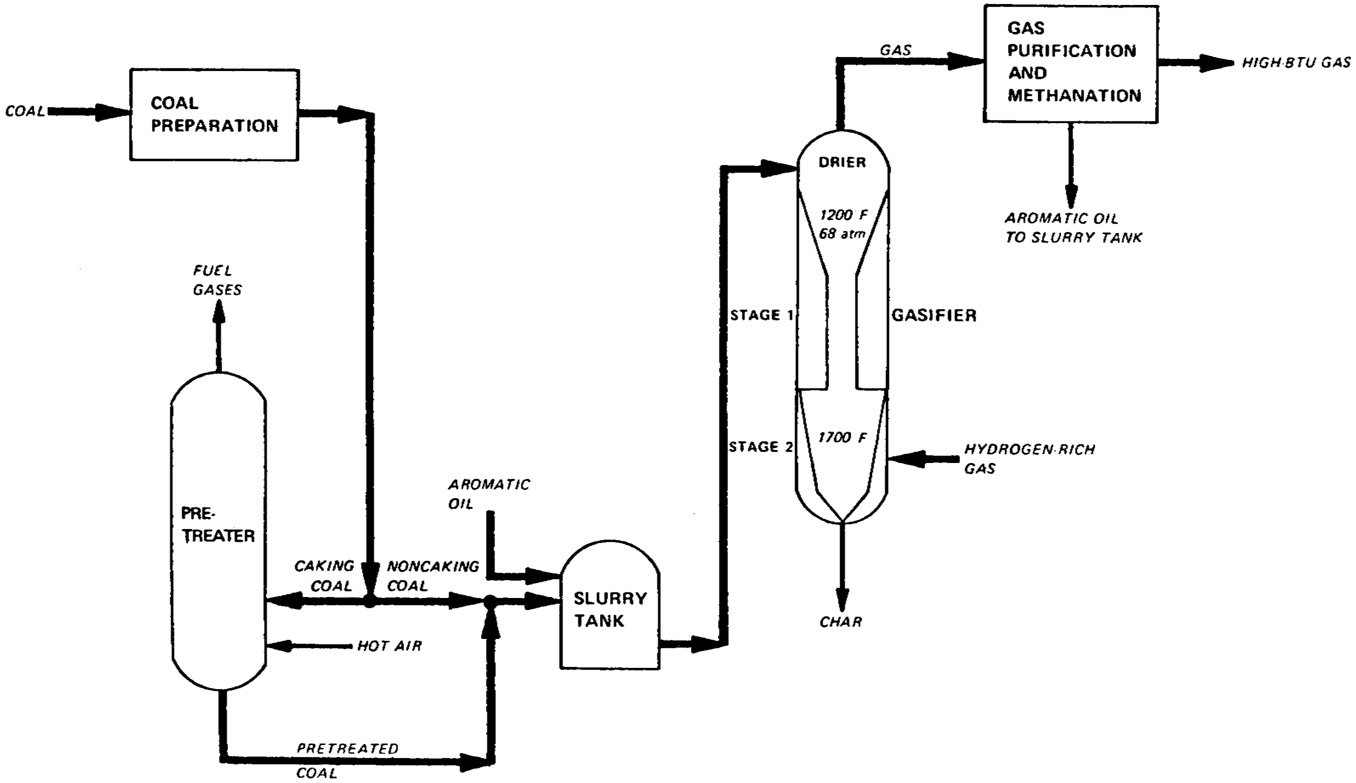


Figure 20

HYGAS PROCESS SCHEMATIC

Source: ERDA 1976b

crushed coal is slurried with a light by-product oil and pumped, under 1,000 to 1,500 psi pressure, into the top of the hydrogasifier (Figure 21) (Huffstetler and Rickert 1977). The oil is driven off to be recycled, and the dried coal particles fall into stage one of the hydrogasifier, where they are flash-heated to the reaction temperature (1,200 to 1,300°F) by rising hot gases. Methane conversion of the volatile matter and the active carbon takes place in a few seconds. The remaining solids fall into the second stage of the hydrogasifier, a fluidized-bed reactor operating at 1,700 to 1,800°F, where the char reacts further with hydrogen-rich gas fed at the bottom of the second stage .(Haynes and Forney 1976). In the present pilot plant, hot gases from the hydrogasifier are methanated, and the liquid aromatics, carbon dioxide, unreacted steam, sulfur, and ammonia removed (Huffstetler and Ricker 1977).

Three different schemes for production of the hydrogen needed by the process have been investigated: electrothermal, steam-oxygen, and steam-iron. The electrothermal scheme has been abandoned because the rise in electricity cost has made it uneconomical. In the steam-oxygen process, hot char from the hydrogasifier is reacted with steam and oxygen in a high-pressure, fluidized bed reactor (Huffstetler and Rickert 1977). In the steam-iron process, hydrogen is produced in a oxidizer by reaction of steam with reduced iron oxide (Huffstetler and Rickert 1977).

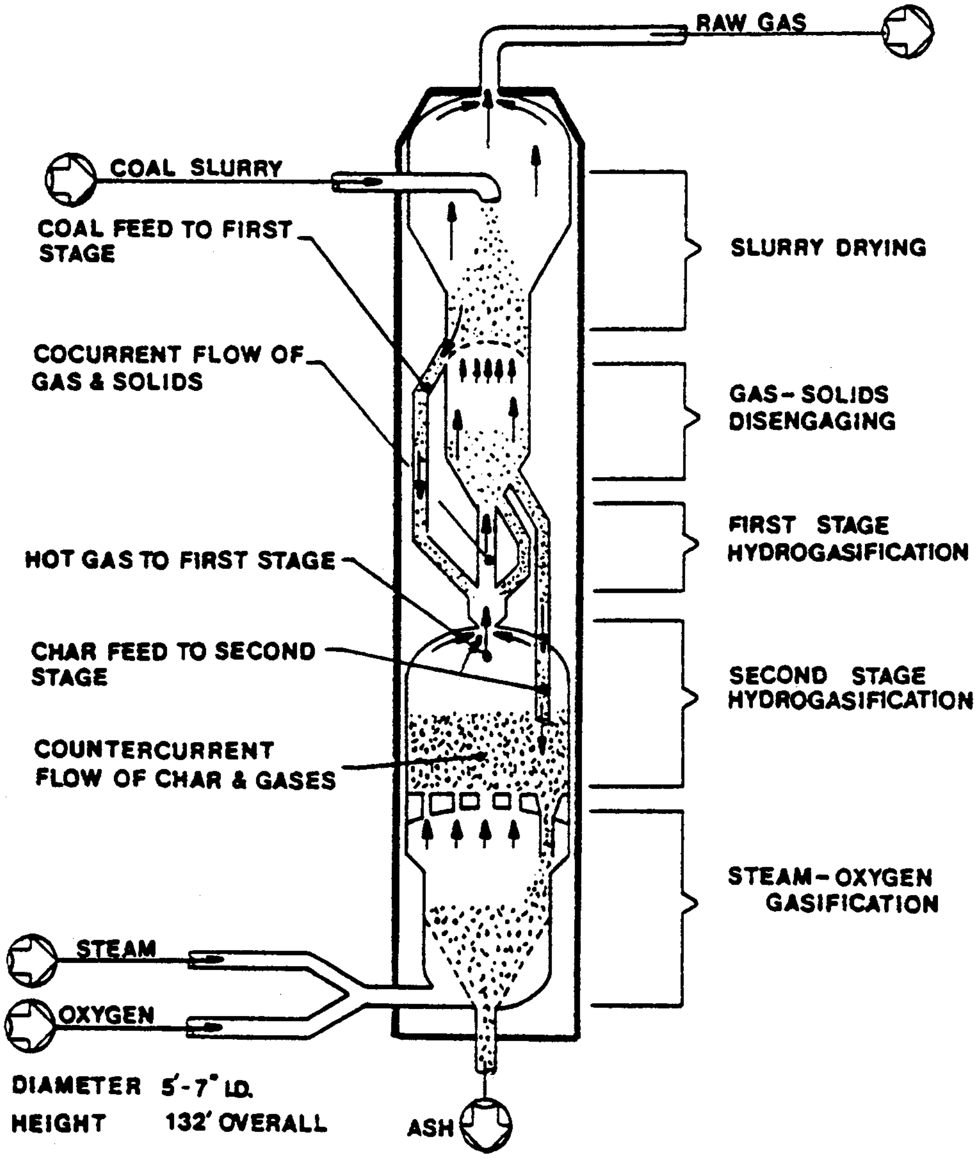


Figure 21

HYGAS GASIFIER

Source: Huffstetler and Rickert 1977

Although the steam-oxygen process is mechanically much simpler, the hydrogen content of its raw synthesis gas is lower than that from the steam-iron process. Presently, a new pilot plant, which will develop the steam-iron process is being completed. The design criteria has been published (Tarman and Punwani 1976). Design work has begun for an 80 million scf per day demonstration plant (Haynes and Forney 1976). It is projected that it can be built by 1980. For a 250 million scf per day commercial plant, coal requirements are expected to be low, about 15,000 tons per day.

5.3 CO_2 ACCEPTOR PROCESS

The carbon dioxide acceptor process is being developed by the Conoco Coal Development Company under the joint sponsorship of DOE and the AGA. DOE is providing two-thirds of the funds and AGA, one-third (ERDA 1976b). The objectives are to show the operability of all features of the carbon dioxide acceptor process through operation of a pilot plant and to obtain enough design data to prepare a design for construction of a commercial plant that will produce 250 million standard cubic feet of high-Btu gas per day (ERDA 1976b).

5.3.1 History of the project

The technology of the process is based on the single-stage high temperature flash carbonization of coal (Lurgi-

Ruhrgas Process) (Theodore 1967). The process was developed by Consolidation Coal Company and carried through the laboratory stage until 1964 when the Office of Coal Research awarded a contract to complete the bench-scale development of the process (Howard-Smith and Werner 1976). This phase was completed successfully in 1968. Construction of a pilot plant in Rapid City, South Dakota, was begun in January, 1970 and completed in November, 1971 by Stearns-Roger who also operated the plant (Howard-Smith and Werner 1976). This facility is designed to use 40 tons of coal and 3 tons of dolomite per day to produce 500,000 standard cubic feet of high-Btu gas (ERDA 1976b). A series of integrated runs which fully demonstrated the feasibility of the process were made in 1974 culminating in a successful 10 day run converting 30 tons/day of coal to 1.37 million standard cubic feet/day of 400 Btu gas (Howard-Smith and Werner 1976). Most of the major mechanical problems have been solved.

5.3.2 Process description

The novel feature of the carbon dioxide acceptor process is the manner in which an acceptor is circulated between the gasifier and regenerator to provide the heat for the gasification process (ERDA 1976b).

A diagram of the process is shown in Figure 22. Lignite or subbituminous coal is ground to 8 x 100 mesh, dried to 5%

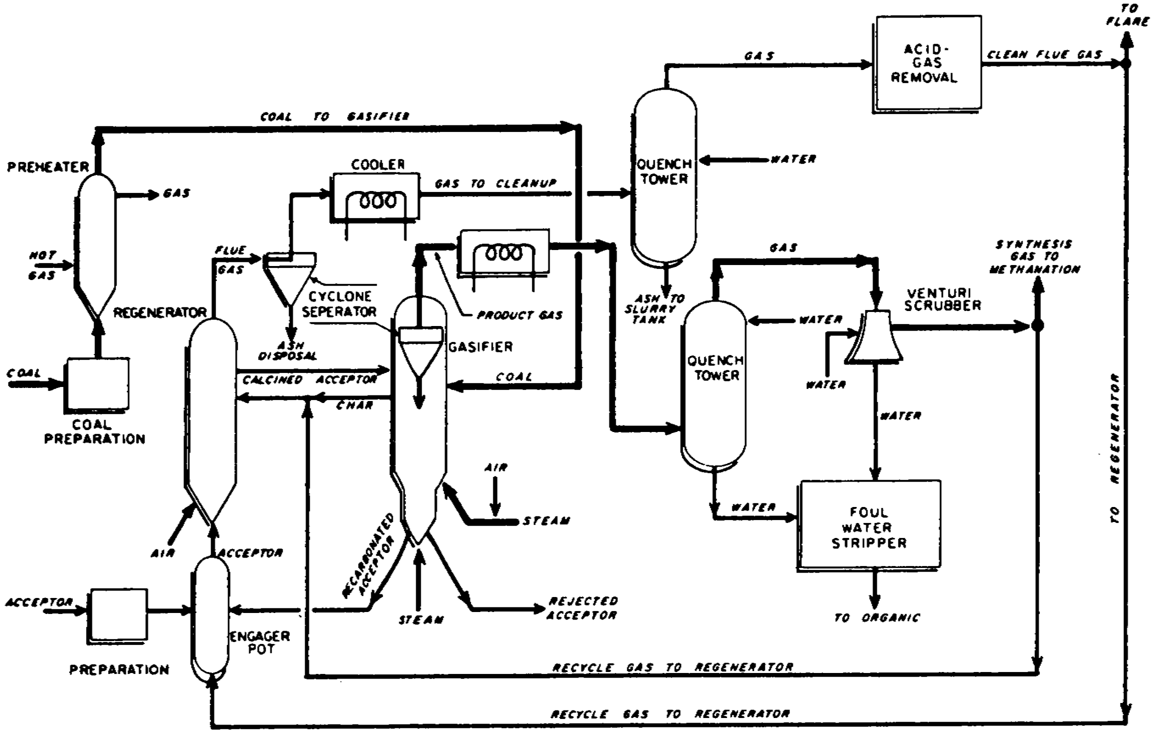


Figure 22

CARBON DIOXIDE ACCEPTOR PROCESS SCHEMATIC

Source: ERDA 1976b

moisture, by weight, and charged to a fluidized-bed preheater (ERDA 1976b). The preheated coal is fed to the bottom of the gasifier where rapid devolatilization occurs, followed by gasification of the carbon. The acceptor, which can be either limestone or dolomite, supplies heat by the exothermic CO_2 acceptor reaction (Fink, Curran, and Sudbury, 1976):

$$CaO + CO_2 \rightarrow CaCO_3$$
$$\Delta H = -76{,}200 \text{ Btu/lb mole } (77^{\circ}F)$$

The partially combusted coal exists as char. Both the char and spent dolomite are then introduced as separate streams into a dolomite regenerator vessel (University of Oklahoma, 1975). In this vessel, the combustion of char with air heats the dolomite and reverses the above reaction. Cyclones separate char, ash, and dolomite fines from the regenerator effluent gas which is used for power generation and steam production.

Raw gas from the gasifier passes through a steam-generating heat exchanger, then goes to the gas cleanup section (ERDA 1976b). Purified gas has an H_2/CO ratio of about 3.2, so that no shift is required before methanation (Bodle and Vyas 1974). Dehydration of the methanated gas produces pipeline gas.

Some of the advantages of this design are:

- No oxygen plant is required.
- The process consumes nearly all of the coal carbon.

- Product gas cleanup requirements are minimized because acceptor reacts with H_2S and CO_2.
- Liquor cleanup is reduced because there are no tars, oil or phenols.

Chapter 6

GENERALIZED UNIT OPERATIONS

> Science makes it possible to predict the future through the ability to reason from known facts and conditions, . . . and thus to reach a rational conclusion in advance of the actual realization of the phenomenon.
>
> William H. Walker, 1923

6.0 INTRODUCTION

Conversion of coal to gaseous fuels can produce high or low Btu gas. High Btu gas has a heating value ranging from 950 to 1,000 Btu per standard cubic foot (SCF) and can be introduced into the natural gas pipelines as substitute natural gas (SNG) (Hittman Associates 1975). Heating values of low Btu gas can range from 150 Btu/SCF to 200 Btu/SCF. Nitrogen from the air used in the process dilutes the gas, making it impossible to achieve the heating values needed for pipeline distribution as SNG (Hittman Associates 1975). Uses for low Btu gas include captive or on-site fuels where clean fuel is needed for direct power generation.

The concept of generating gas from a heated coal particle is simple. Only three ingredients are required--carbon, hydrogen, and oxygen (Braunstein 1977). Coal provides the carbon; steam frequently provides the hydrogen, although elemental hydrogen can be introduced directly; and oxygen is usually supplied as either air or pure oxygen (University of Oklahoma 1975). Heat can be supplied directly by combusting coal and oxygen in the gasifier or indirectly by hot pebbles or ceramic balls (University of Oklahoma 1975).

Unlike the concept, the application is complex requiring nine basic operations. These are shown in Figure 23 and include coal storage, preparation, injection, gasi-

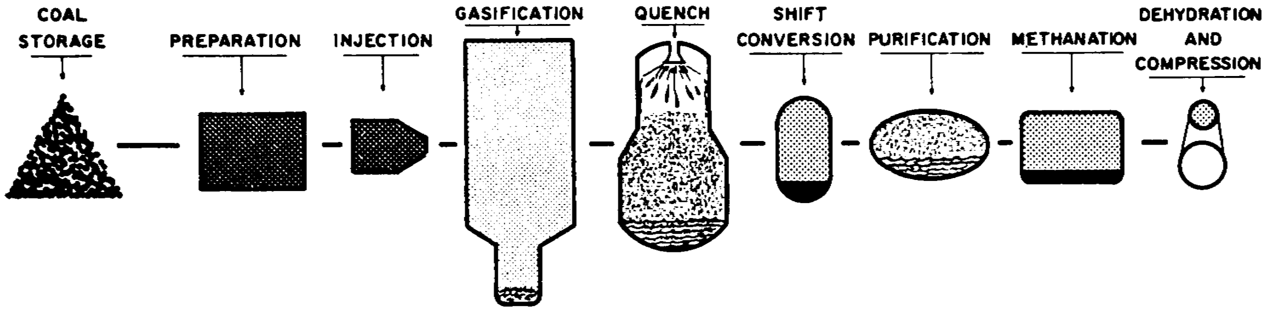


Figure 23

COAL GASIFICATION UNIT OPERATIONS

Source: After Perry 1974a

fication, quench, shift conversion, gas purification, catalytic methanation, and final compression and dehydration of the product into pipeline gas (Macnab 1975 and Braunstein 1977). The large number of named processes arise from an attempt to combine the various alternatives available for each step so that the entire procedure may be optimized (Braunstein 1977). Gasification processes may be classified in a variety of ways as shown in Table 18.

There are at least three basic approaches to determine pollution potential of the coal gasification industry. EPA has addressed each of the major gasification processes individually (Shaw and Magee 1974, Jahnig 1975, and Jahnig and Magee 1974). Another approach is to choose a "typical" process as representative of the industry (Cavanaugh et al. 1975, Hittman Associates 1975). NIOSH used this approach in their occupational safety and health guidelines (NIOSH 1978a). A third approach is to base the analysis on unit operations. As shown in Table 19, most pilot plants have quite similar unit operations (NIOSH 1978a). The commercial coal gasification plant of the future will take advantage of current research and will integrate proven unit operations from different pilot plants.

The unit operations approach was chosen for our evaluation. This approach will provide a thorough understanding of the process flow, permit identification of the major chemical compounds within each unit, and assist in deter-

Table 18

CLASSIFICATION OF GASIFICATION PROCESSES

A. By the method of supplying the required heat

   1. Internal heating

      a. Autothermic
      b. Cyclic
      c. Heat-carrying fluids or solids

   2. External heating

B. Contacting method

   1. Fixed bed

   2. Fluidized bed

   3. Suspension of particles in gasifying medium

C. Flow of reactants

   1. Concurrent

   2. Counter-current

D. Gasifying medium

   1. Steam with oxygen or air or oxygen-enriched air

   2. Hydrogen

E. Removing residue

   1. Dry ash in nonslagging operation

   2. Slag in slagging operation

Source: von Fredersdorff and Elliott 1963

Table 19
UNIT-OPERATIONS SYNOPSIS

Unit Operation	HYGAS	CO_2 Acceptor	MERC Unit	Synthane	Bi-Gas	Agglomerating Burner
Coal stock pile	Yes	Stored offsite	Yes	Stored off site	Yes — compacted	Yes
Coal feed	Payloader-bin-conveyor	Truck-bin-conveyor	Truck-bin-conveyor	Truck or railroad-bin-conveyor	Truck or railroad-bin conveyor	Payloader-bin-screen to -35 mesh
Coal preparation	Williams mill (negative pressure) water scrub	Williams mill (positive pressure) water scrub	Run of mine steam dry	Dryer, Raymond mill, screen	Cage mill wet ball mill	Williams mill
Ground coal storage	Purged bin	Purged bin	Bin	Purged bin	Purged bin	Purged bin
Gasifier feed	Toluene slurry	Simple lockhopper	Simple lockhopper	Petrocarb lockhopper	Water slurry steam-injected	Lockhopper
Pretreatment	Low pressure	No	No	High pressure	No	Low pressure, if required
Gasification	Countercurrent flow through fluid beds	Dolomite plus char fluid beds	Stirred fixed bed	Single fluid bed	Medium-and high-temperature entrained beds	Agglomerated ash supplies gasification heat to fluid bed
Gas quench	Quench towers	Water venturi	Cyclone separator	Water-venturi	Water-venturi	Water-venturi
Gas scrubbing	Water	Water	No	Water, then oil	Water	No
Shift	No	No	No	Fixed bed	Fixed bed	No
Acid gas scrub	Diglycolamine	Hot carbonate	No	Benfield	Selexol	No
Methanation	Ni catalyst cold gas recycle	Packed tube reactor	No	Tube-wall reactor (Raney Ni)	Fluidized bed to fixed bed	No
Gas product disposal	Thermal oxidation	Thermal oxidation	Thermal oxidation	Thermal oxidation	Thermal oxidation	Thermal oxidation
Sulfur	Claus	Thermal oxidation	Thermal oxidation	Stretford	Claus	Thermal oxidation
Water	Filter, city sewage disposal	Hay filter, city sewage disposal	Thermal oxidation	Thermal oxidation	Filter, city sewage disposal	Thermal oxidation
Condensable hydrocarbons	Recycle	None	Thermal oxidation	Thermal oxidation	Tar generation not expected	Thermal oxidation
Ash or Char	Filtered and disposed	Dredged from pond	Disposal	Filtered and disposed	Slag from lower stage is water-quenched	Landfill
Overhead coal or char	Filtered and disposed	Sent to pond to settle for later disposal	Thermal oxidation	Thermal oxidation	Pond for later disposal	Thermal oxidation

Source: NIOSH 1978a

mining possible sources of leaks, vents, or discharges of contaminants to the work environment. The three basic steps involved in this analysis are:

- define the overall chemical process and reaction of basic chemical compounds,
- define the input and output streams of each unit and speculate on chemical compounds formed, and
- define within this unit all sources of possible leaks, vents, or discharges of gases, solids and liquids to the atmosphere (Phillips and Taylor 1977).

6.1 COAL PREPARATION AND STORAGE

Preparatory steps include the normal stockpiling, cleaning, drying, crushing and pulverizing operations that are characteristic of other large coal-using industries such as power plants (Dailey 1977). At coal conversion plants, it is estimated that up to one million tons of coal will be stored in an area of approximately 35 acres (Kornreich 1976). Typically, the raw coal from storage is passed through a presizing crushing operation to eliminate large lumps. The coal is then fed directly to a mill, where it is crushed and dried simultaneously. A mixture of hot flue gas from an auxiliary furnace and recycle gas is piped into the mill at a quantity and velocity such that the ground coal is conveyed pneumatically to a cyclone located at the top of the structure. Coal from the cyclone passes over a vibrating screen which returns over-size material to the mill, while undersize material is conveyed by gravity or screw conveyor to a fine-coal bin (NIOSH 1978a). The capacity of currently available coal grinding equipment is 200 tons/hr. (Detman 1974). A pioneer coal gasification plant will require 20,000 tons of coal per day, requiring multiple grinding units. Caking coals may also require thermal oxidation to prevent agglomeration in the gasifier (Zawadzki 1974).

6.2 INJECTION

A problem common to all the proposed processes is feeding solids into a high-pressure vessel (Hottel and Howard 1971). The injector must be large-scale and capable of steady, controllable operation (Hottel and Howard 1971). Techniques under study include lock hoppers (Detman 1974 and Lewis 1975), slurry pumping (Lee 1975a), and piston displacement (Hottel and Howard 1971). Any presurized gasifier utilizing lock hoppers is plagued with leaking or malfunctioning valves (Palmer 1975). Fine solids adhere to the valve seating surfaces and invariably either the valve surface is abraded, or the valve cannot be closed against the solids (NIOSH 1978a). With slurry feeding, coal is mixed with water or oil, pumped to reactor pressure and injected into the gasifier (Evans 1976). With an oil slurry system, vapor leaks from pump seals are of primary importance (Akhtar, Freidman, and Yavorsky 1976). Oil losses due to pump seal dripping have been estimated to be 84 gallons per day at the 75 T/D HYGAS pilot plant (Lee 1975b). This oil contains 85 percent toluene, 8 percent benzene, and 3 percent C_9 and higher hydrocarbons. The third technique, piston displacement, is relatively new and its performance is yet to be established (Hottel and Howard 1971).

Injection Geometry

Several process variables, e.g., coal heatup rate, product gas residence time, reaction temperature, and gas-contacting, are influenced by coal injection geometry (Nakles et al. 1975). Nakles et al. (1975) have studied the rate of effluent production by varying the injection position. Utilizing the Synthane 4-inch diameter PDU, coal was injected into the gasifier at three different locations:

- The top of the reactor (free-fall)
- Approximately 1 1/3 feet into the fluidized bed (shallow bed-injection)
- Approximately 4½ feet into the fluidized bed (deep bed-injection)

These injection locations are shown in Figure 24. The researchers' conclusions were:

- steady state effluent production rates vary significantly from non-steady state conditions,
- injection geometry has a dramatic impact on steady state effluent production, and
- neither the methane yield or total gas production are affected by injection geometry (Nakles et al. 1975).

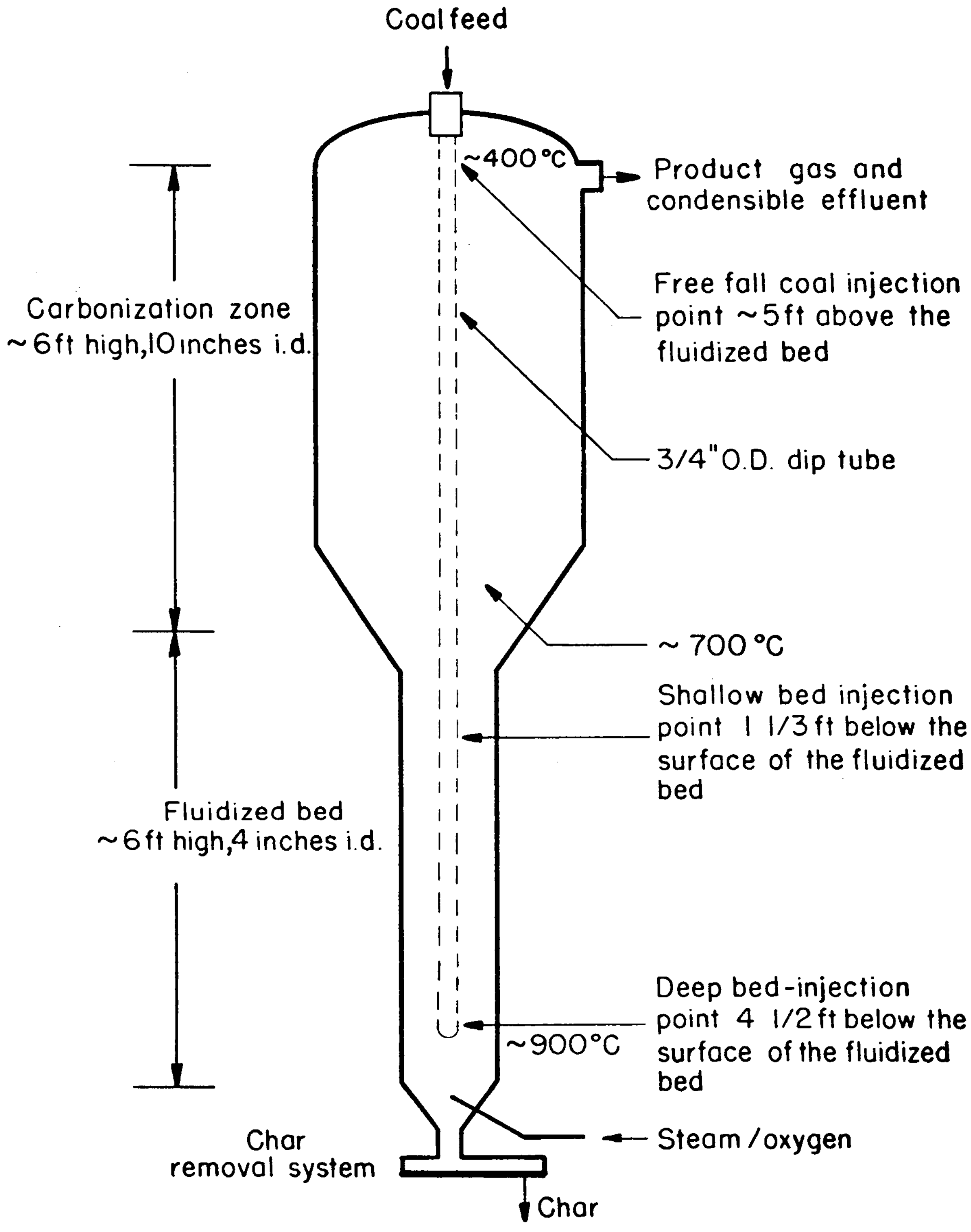


Figure 24

SYNTHANE PDU CONFIGURATION & INJECTION LOCATIONS
Source: Nakles et al. 1975

Of particular occupational health interest is the tar yield of different injection geometries. Tar production rates as a function of time are presented in Figure 25 for the three injection points studied. Steady state tar production levels range from a high of ~ 100 lbs/ton coal at free fall injection to a low of ~ 5 lbs/ton coal at deep bed injection.

6.3 GASIFICATION

Coal is injected into the reactor either above the bed or into it. At the same time, fluidizing gas and/or steam and oxygen, if required, are fed to the bottom of the bed (NIOSH 1978a). Both heat and elevated pressure promote the gasification reactions, which are many and varied (EPA 1978). Three main chemical reactions take place:

$$C + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$C + 2\,H_2 \rightarrow CH_4$$

to achieve the primary overall reaction (Hottel and Howard 1971):

$$2C + 2\,H_2O \rightarrow CO_2 + CH_4$$

If oxygen is introduced directly, one additional reaction occurs (Hottel and Howard 1971):

$$C + \tfrac{1}{2}\,O_2 \rightarrow CO$$

Ash or residual char is removed from the bottom of the bed, and product gas flows upward to the top of the reactor.

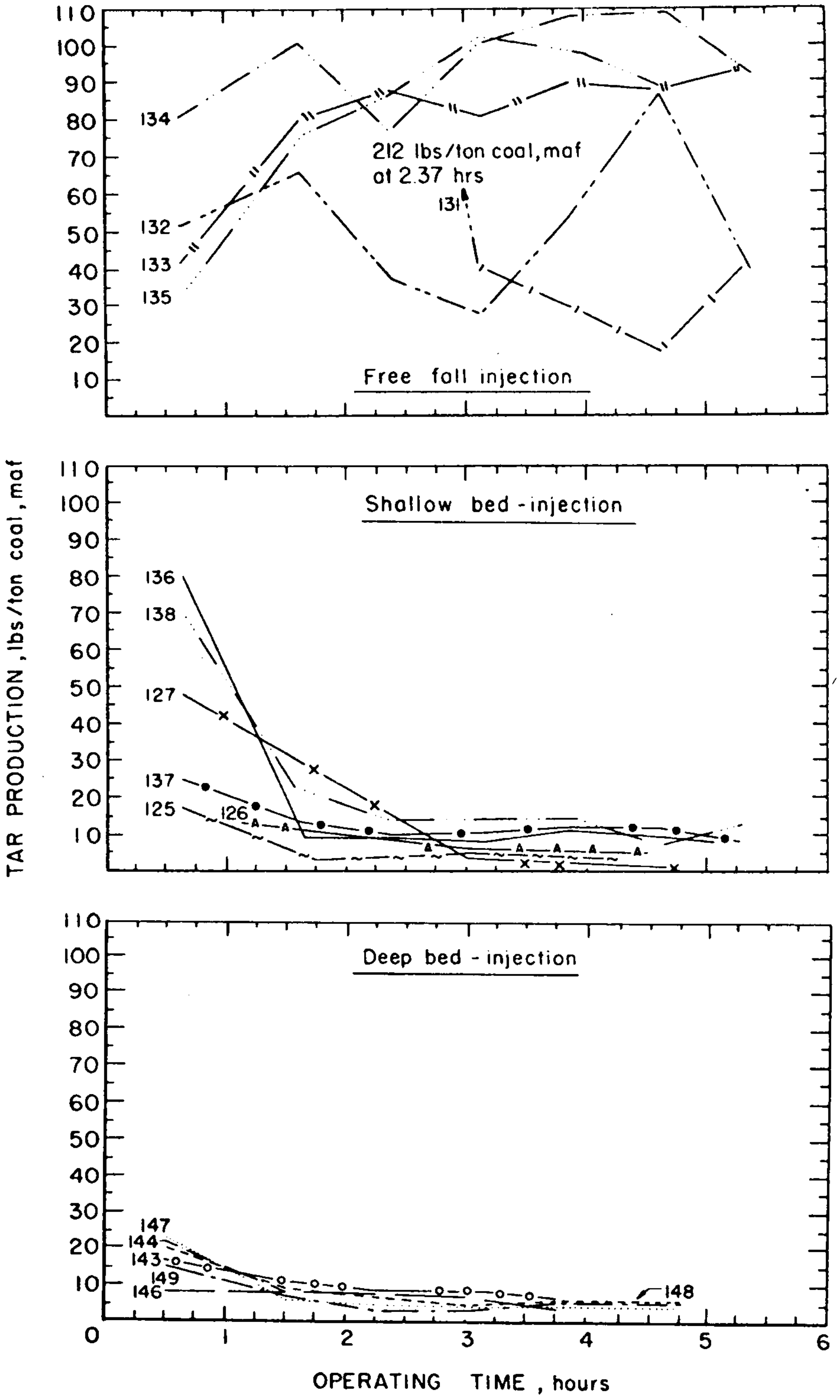


Figure 25

TAR PRODUCTION VERSUS TIME
Source: Nakles et al. 1975

Because the gas is laden with particles elutriated from the bed, it is passed through a cyclone. From the cyclone, the product gas leaves the reactor to be quenched (NIOSH 1978a). In the ash system, the major problems are the probability of leaks in the lockhopper valves and the formation of plugs in the system. If the valves do leak, process gas from the vessel may be vented into the atmosphere.

6.3.1 Operating variables

The following operating variables affect the number and composition of effluent streams (Fleming 1977).

- Number of stages and contacting mode
- Pressure
- Temperature
- Additives

6.3.1.1 Number of States and Contacting Mode

Generally, as the number of stages in the gasifier is increased, the methane concentration in the over-head gas is increased (Fleming 1977). Each stage can be designed to maximize the methane manufacture for each mechanism of coal gasification.

Three types of gas-solid contact have been used (Perry 1974b and Corey 1974). These are:

- Fixed bed

- Fluidized bed
- Entrained-flow

These gasifier types are depicted in Figure 26. These are described individually in the following sections with a discussion of their inherent mechanical characteristics, and advantages and disadvantages. This information is also tabulated in Tables 20, 21, and 22.

Fixed bed

The term fixed-bed is used to signify a fuel bed supported by a grate (Foster-Pegg et al. 1975). In most fixed-bed gasifiers, the blast and reaction gases flow upward through a slowly descending bed of coal. Hence the term gravitating bed is also commonly used. Fixed-bed gasifiers are inherently characterized by a deep fuel bed with a large inventory of carbon, and a fairly well-defined sequence of zones. In the direction of gas flow these are (Foster-Pegg et al. 1975):

- The ash zone.
- The oxidation or combustion zone.
- The reduction or gasification zone.
- The preheating, drying and devolatilization zone.

Thus, although the bed might be considered fixed in space, fuel moves slowly within the bed from the top down through the gasification and oxidation zones, and the residue ash is discharged at the bottom.

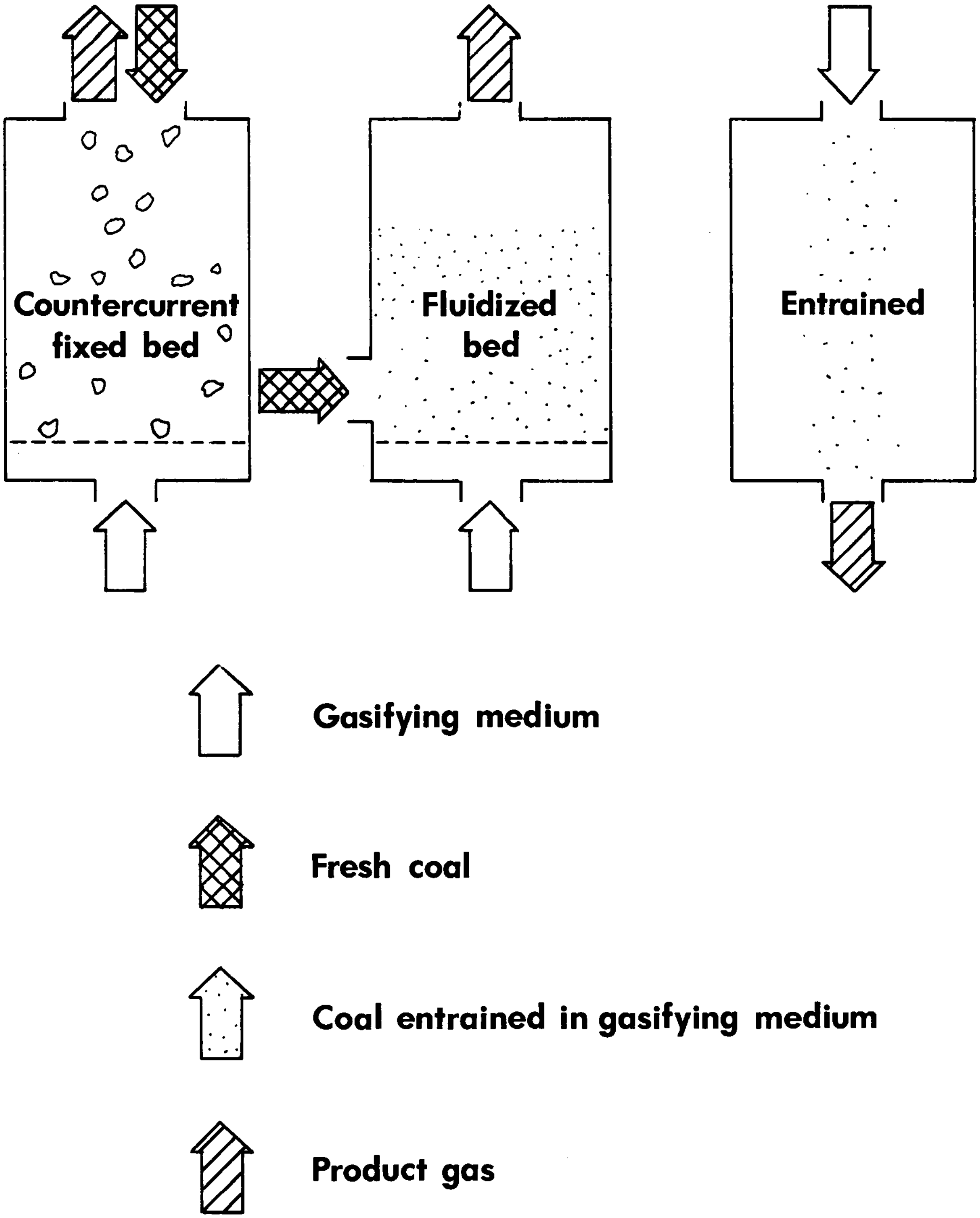


Figure 26

COAL GASIFICATION SYSTEMS

Source: Corey 1974

Table 20

CHARACTERISTICS, ADVANTAGES, AND DISADVANTAGES OF A FIXED-BED GASIFIER

Characteristics	Advantages	Disadvantages
Fixed-bed of coal-char-ash supported by grate	Large fuel inventory	Caking coals cannot be used unless pretreated or the coal bed is constantly agitated
Coal fed through process by gravity	High heat economy due to counter-current flow of gases and coal	Sized coal must be used precluding use of fines unless briquetted
Discrete zones: Ash Combustion Gasification Preheating-drying-devolatilization	Long residence time leads to high-carbon conversion efficiency	Tars are produced and must be washed from gas
Mechanical grate, distributor, agitator	Little solids carry-over	Low capacity per unit ground area due to limitation on gas flow rates

Source: Foster-Pegg et al. 1975

Table 21

CHARACTERISTICS, ADVANTAGES, AND DISADVANTAGES OF A FLUIDIZED-BED GASIFIER

Characteristics	Advantages	Disadvantages
Solid Phase of coal-char-ash supported by gases	Provides superior solids-gas contact	Moderately high loss of sensible heat in product gases
Solids and gases fully mixed	Can tolerate wide variety of fuel quality and particle size	High carry-over loss in char entrained in product gases
	High capacity per unit ground area	Loss due to char in ash residue removed from bed
	Can be operated over a wide range of output, restricted only by the fluidization characteristics of the solids mixture	Fluidization phenomenon sensitive to fuel characteristics. Strongly caking coals require pretreatment
	High degree of process reliability, stability, and safety due to high fuel inventory	
	High degree of process uniformity	
	Product gases are free of tars	

Source: Foster-Pegg et al. 1975

Table 22

CHARACTERISTICS, ADVANTAGES, AND DISADVANTAGES OF AN ENTRAINED-FLOW GASIFIER

Characteristics	Advantages	Disadvantages
Gasifier fed with suspension of pulverized coal-air-steam	Can utilize any grade of coal irrespective of caking characteristic and size distribution	Lowest fuel inventory capacity in reaction vessel
High-temperature, high-rate process	Product gas is tar-free	High carry-over loss in char entrained in product gases
	Highest specific gasification capacity--minimizes ground area requirement	Refractory-lined reaction vessel required
	Can recycle char to improve carbon conversion efficiency	High reaction temperature causes higher heat loss through vessel walls
		High temperature of product gas leads to greater thermal loss in heat-recovery section
		Molten-ash carry-over potentially troublesome in heat recovery section
		Pulverizer adds to energy and maintenance costs

Source: Foster-Pegg et al. 1975

Fluidized-bed

In the fluidized-bed process the solid phase coal-char-ash is supported by a pressure difference created by the flow of gases through the bed (Foster-Pegg et al. 1975). In this fluidized state the solid particles are in random motion within the fluidizing medium, and take on liquid-like characteristics. The main characteristic of a fluidized-bed gasification process is the virtual elimination of temperature zones corresponding to predominantly exothermic and endothermic reactions. The net effect is essentially a mixed temperature dictated by the relative rates of combustion and gasification reactions. This temperature is generally controlled to just below ash softening temperature to avoid ash agglomeration in the bed (Foster-Pegg et al. 1975).

Entrained-flow

Gasification by means of an entrained-flow process entails the suspension of pulverized coal in the gasification medium and the injection of this suspension into a reactor vessel (Foster-Pegg et al. 1975). In this type of process, with very little residence time given to the reactants, the gasification rate must be extremely high. Hence, high conversion efficiency requires high reaction temperatures and has dictated that this gasification process operate under slagging conditions. Refractory lined vessels are also generally indicated (Foster-Pegg et al. 1975).

6.3.1.2 Pressure

Higher pressure operations generally tend to favor the formation of methane within the gasifier and, hence, often improve the overall system efficiency (Fleming 1977). High pressure, of course, magnifies the problems of feed injection.

6.3.1.3 Temperature

The operating temperature of the gasifier will significantly affect the raw gas characteristics and solids discharge (Fleming 1977). The operating temperature will determine whether the ash will be discharged as char or molten slag. High temperatures will result in higher carbon conversion efficiencies, but more of the trace elements in the coal will be volatilized. Also, in a single-stage gasification at extreme temperatures, the off-gases will contain no tars or oils (Fleming 1977).

6.3.1.4 Additives

The agent used to inject the coal into the gasifier will appear in the off-gas (Fleming 1977).

The gasifier design is such that there are no direct discharges of pollutants (Sather et al. 1975). However, contaminants that leave the gasifier in the raw product gas or ash streams may be discharged to the atmosphere in the downstream processing operations (Sather et al. 1975).

6.3.2 Contaminant Generation

The primary problem with the above representation of coal gasification is that coal is not simply carbon, nor does all the carbon in the coal react to fuel-gas species (Fleming 1977). We must consider the product of side reactions, incomplete reactions, and reactions with coal constituents that are not desired in the methane end product (Fleming 1977). Potential contaminants will be considered in detail in the following paragraphs.

6.3.2.1 Trace elements

The processing of 20,000 tons per day of coal that contains 1 ppm of trace element leaves 40 lbs. per day of that element in the plant streams to be accounted for (Magee, Bertand, and Jahnig 1976). Trace elements pathways within a conversion process may include adsorption on particulate matter, inclusion in condensates, deposition on equipment surfaces, inclusion in by-products or final products, and emission as fugitive pollutants (Dailey 1977). The majority of elements are expected to remain in the solid by-products such as ash and chars, although other by-products such as tars may also contain small amounts (Dailey 1977). Arsenic, beryllium, mercury, selenium, cadmium, fluorine, and lead are expected to volatilize during coal conversion, resulting in possible fugitive emissions (Jahnig, Magee, and Kalfadelis 1974 and Hall, Varga, and Magee 1974).

Forney et al. (1975), in a study of the trace element and major component balances around the Synthane PDU gasifier, found that the largest percentages of the 16 elements considered most important ware contained primarily in the chars.

A HYGAS (Bench-Scale) process study of the fate of 11 elements indicates substantial loss of mercury, selenium, arsenic, tellurium, lead and cadmium from the ash (Attair 1973). Trace elements lost (i.e, higher values present in coal than in ash) are expected to be in the raw product gas stream (Dailey 1977).

6.3.2.2 Organometallic compounds

Coal gasification conditions are conductive to the formation of a variety of organometallic compounds consisting of metals bonded to organic groups or ligands (Koppenaal and Manahan 1976). Many metal or metalloid elements that might be expected to form some types of organometallic compounds or stable organic complexes occur at relatively high levels in coal (Koppenaal and Manahan 1976). The major types of organometallic compounds that may be formed include (Koppenaal and Manahan 1976):

Metal-Porphyrin Compounds
Metal Carbonyls
Metallocenes
Arene Carbonyls
Metal Alkyls
Organo Hydrides
Metal Chelates

Of this group of organometallic compounds, most is known about the effects of the metal carbonyls. Thus, these compounds will be dealt with in more detail.

Metal Carbonyls

In 1890, Ludwig Mond et al. announced the discovery of nickel carbonyl (Trout 1937). Berthelot announced the formation of a volatile compound of carbon monoxide and iron in 1891 (Trout 1937). Coke oven gas, furnace gas, and illuminating and heating gases were found to contain iron carbonyls in the same year (Trout 1937, Descham et al. 1963). Mittasch, in 1916, found nearly 500 cc of liquid iron pentacarbonyl in an iron tank containing illuminating gas (Trout 1938).

If gas containing CO comes into contact with the transition series of elements as prescribed temperatures and pressures, metal carbonyls will form (Trout 1937). A generalized equation is:

$$\chi \, \text{Me} + Y \, \text{CO} \rightleftharpoons \text{Me}_{\chi}(\text{CO})y$$

where Me represents the metal (Trout 1937).

Physical properties of several metal carbonyls are tabulated in Table 23. From the viewpoint of volatility,

Table 23

PHYSICAL PROPERTIES OF SELECTED METAL CARBONYLS

Metal Carbonyls	Molecular Weight	Specific Gravity at 20 °C	Melting Point, °C	Boiling Point, °C	Vapor Pressure, mm. Hg.
$Ni(CO)_4$	170.75	1.31	-25	43	390
$CoH(CO)_4$	171.99	...	-26	...	High
$(Co(CO)_4)_2$	341.95	1.73	51	52*	1.5
$(Co(CO)_3)_4$	571.86	...	60*	...	Very low
$Cr(CO)_6$	220.06	1.77	110*	151	0.4
$Fe_2(CO)_9$	363.79	2.08	80*	...	...
$Fe(CO)_5$	195.90	1.46	-21	105	30.5
$Fe(CO)_4$	167.89	2.00	140*	...	...
$Mo(CO)_6$	264.00	1.96	150*	156	0.2
$Ru(CO)_5$	241.12	...	-22	...	...
$W(CO)_6$	351.91	2.65	150*	175	0.1

*Decomposition starts at temperature shown.

Source: Brief et al. 1971

nickel carbonyl, $Ni(CO)_4$, iron pentacarbonyl, $Fe(CO)_5$, and cobalt hydrocarbonyl, $CoH(CO)_4$, have relatively high vapor pressure when compared with other carbonyls (Brief et al. 1971). Thus, these carbonyls warrant careful consideration in terms of potential occupational exposures.

Iron carbonyl can form by reaction of CO at high pressure and low temperature (100-200°C) with carbon steel piping (Strakey et al. 1975). Iron concentrations, indicative of iron carbonyl, as high as 22 percent have been reported in a methanation catalyst (Strakey et al. 1975).

Once formed, metal carbonyls tend to remain as carbonyls only in the presence of CO. They are relatively unstable in air and will dissociate to CO and metal or to other intermediates (Brief et al. 1971). For example the half-lives of $Ni(CO)_4$, $CoH(CO)_4$, and $Fe(CO)_5$ are 675 seconds, 10-15 seconds, and probably on the order of hours, respectively (Brief et al. 1971). Methods for analysis have been published (Brief et al. 1965, Brief et al. 1967, and McDowell 1971).

6.3.2.3 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAH), also known as polynuclear aromatics (PNA) (Manahan 1976), consist of three or more fused benzene rings, and contain only carbon and hydrogen (Blumer 1976). Considering the aromatic nature of coal, the production of PAH is an inevitable consequence of breaking up the coal molecule during gasification (Manahan 1976). The bonds involved in aromatic structures are much stronger than ordinary C-C single or double bonds, so that during the breakdown of the coal molecule, the aromatic molecules are "broken out" of the structure largely intact (Manahan 1976). Twenty-one specific PAH compounds that may be found in coal gasification environs are listed in Table 24. This table includes 12 of the 14 compounds that NIOSH mointored in coke oven operations and aluminum reduction plants (Schulte, Larson, Hornung, and Crable 1974 and Shuler and Bierbaum 1974). Benz(a)anthrone was deleted because it was not detected in any of the samples collected in these two studies. Benz(c)acridine was not included because, strictly speaking, this compound is a heterocyclic ring structure containing nitrogen and not a PAH. Eight additional compounds were added from EPA publications (Kalfadelis et al. 1975 and Cavanaugh et al. 1975). Dibenzo(a,e)pyrene was added because it is an isomer of dibenzo(a,i)pyrene, dibenzo(a,h)pyrene and dibenzo(a,l)-pyrene, all possible by-products of gasification. The structures of these compounds were compiled from Freudenthal, Lutz, and Mitchell 1975, International Agency for Research on Cancer 1973 and National Academy of Sciences 1972.

Table 24

POTENTIAL PAH COMPOUNDS FORMED BY COAL GASIFICATION

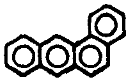
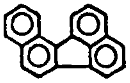
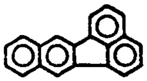
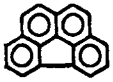
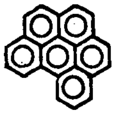
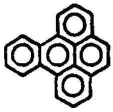
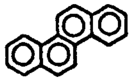
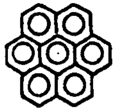
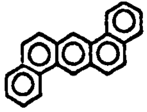
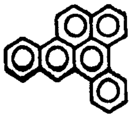
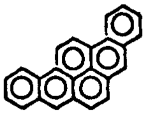
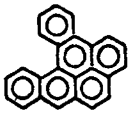
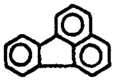
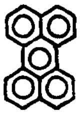
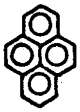
COMPOUND	STRUCTURE	FORMULA	MOL. WT.
anthanthrene		$C_{22}H_{12}$	276.22
benz(a)anthracene		$C_{18}H_{12}$	228.28
benzo(b) fluoranthene		$C_{20}H_{12}$	252.32
benzo(j) fluoranthene		$C_{20}H_{12}$	252.32
benzo(k) fluoranthene		$C_{20}H_{12}$	252.32
benzo(g,h,i)fluoranthene		$C_{18}H_{10}$	226.26
benzo(g,h,i) perylene		$C_{22}H_{12}$	276.22
benzo(a) pyrene		$C_{20}H_{12}$	252.32
benzo(e) pyrene		$C_{20}H_{12}$	252.32
chrysene		$C_{18}H_{12}$	228.28
coronene		$C_{24}H_{12}$	300.34
dibenz(a,h)anthracene		$C_{22}H_{14}$	278.33

Table 24 (Continued)

POTENTIAL PAH COMPOUNDS FORMED BY COAL GASIFICATION

COMPOUND	STRUCTURE	FORMULA	MOL.WT.
dibenzo(a,e)pyrene		$C_{24}H_{14}$	302.28
dibenzo(a,h) pyrene		$C_{24}H_{14}$	302.28
dibenzo(a,i) pyrene		$C_{24}H_{14}$	302.28
dibenzo(a,l) pyrene		$C_{24}H_{14}$	302.28
fluoranthene		$C_{16}H_{10}$	202.24
indeno(1,2,3-cd)pyrene		$C_{22}H_{12}$	276.22
perylene		$C_{20}H_{12}$	252.32
phenanthrene		$C_{14}H_{10}$	178.22
pyrene		$C_{16}H_{10}$	202.24

6.3.2.4 Light oil

Many gasification processes also produce a light oil which is primarily benzene, toluene, and xylene.

6.3.2.5 Sulfur

In the complete combustion of coal, most of the sulfur converts to sulfur dioxide (SO_2). This, of course, is the root of the problem in burning much of our vast eastern coal reserves. Direct burning of these coals in conventional power plants releases excessive quantities of SO_2 that must be scrubbed from boiler stack gases in order to meet emission standards.

During gasification there is not sufficient oxygen to form an appreciable amount of SO_2 (Foster-Pegg et al. 1975). Instead, most of the sulfur is combined with hydrogen to form hydrogen sulfide (H_2S). Figure 27 shows the expected concentrations of H_2S in fuel gases of different heating values for an assumed gasification effiency of 70 percent with coal at 1300 Btu/lb (Ball et al. 1974). Lesser amounts of carbonyl sulfide (COS) and carbon disulfide (CS_2) are formed (Glaser, Hershaft, and Shaw 1974). Sulfur compounds must be removed from the gas stream prior to methanation to prevent fouling of the methanation catalysts (Glaser, Hershaft, and Shaw 1974).

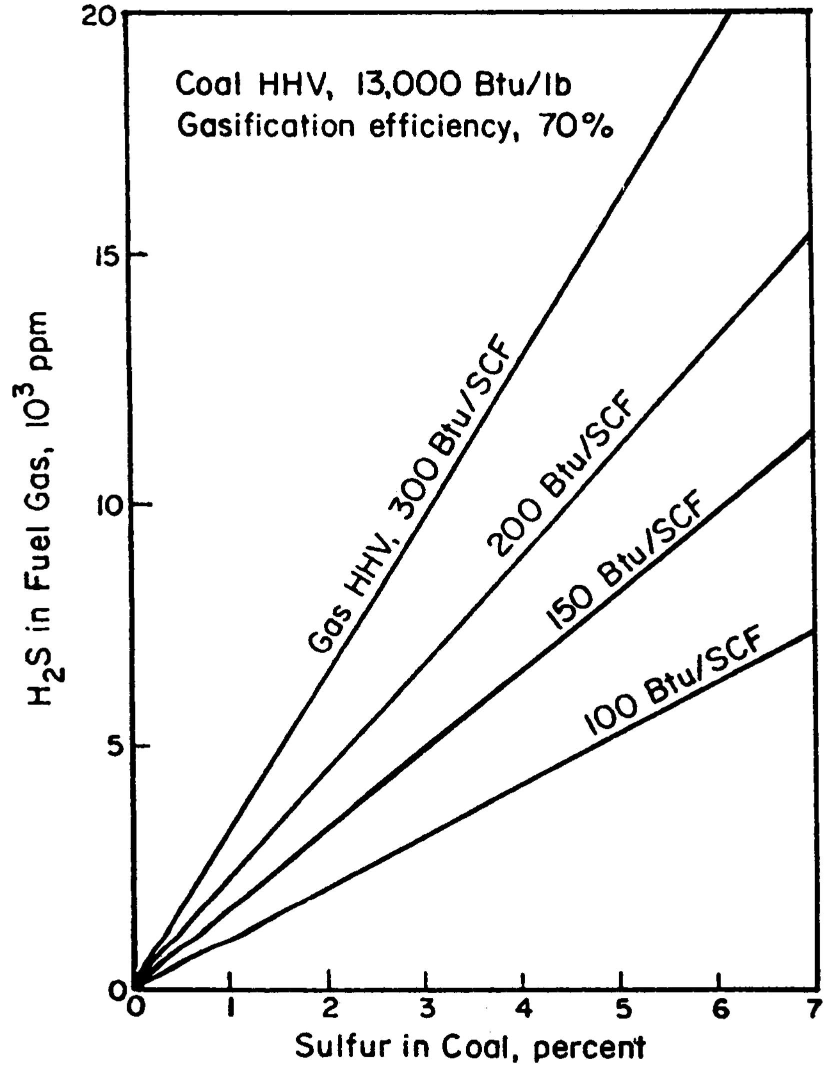


Figure 27

H_2S IN FUEL GAS VERSUS PERCENT
SULFUR IN COAL FOR DIFFERENT
GAS HIGH HEATING VALUES (HHV)

Source: Ball et al. 1974

6.3.2.6 Nitrogen

Under gasifier conditions, organic nitrogen is released and reacts to form primarily ammonia (about 60 percent) and lesser amounts of hydrogen cyanide, amines, and heterocyclic nitrogen compounds (Hittman Associates 1975 and Manahan 1976). Nitrogen from the air stream also takes part in compound formation (Hittman Associates 1975). Table 25 lists seven polyheterocyclic nitrogen compounds that could be formed during gasification.

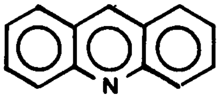
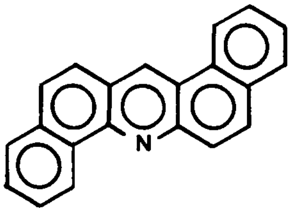
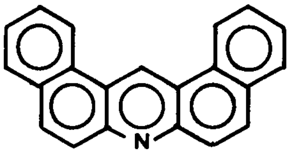
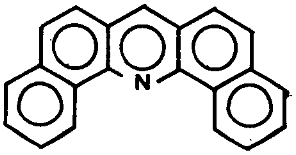
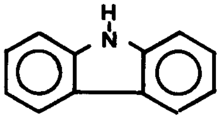
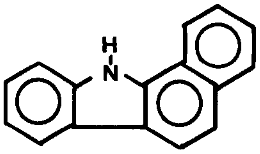
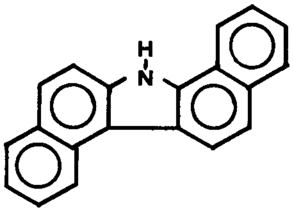
6.4 GAS COOLING AND FINE SOLIDS REMOVAL

The function of this section of the process is twofold: (1) to remove solids, tars, and oils that would foul the processing elements downstream, and (2) to cool the gas sufficiently for further processing (Fleming 1977). The gases must be cooled before further clean-up because conventional gas purification systems operate at lower temperatures than those of the gasifier (Zawadzki 1974). New technology is being developed to permit hot gas clean-up and thereby improve the thermal efficiency of the gasification process (Zawadzki 1974).

The gas cooling and washing may be achieved by two approaches--direct and indirect (Fleming 1977). Indirect cooling, perhaps in waste heat boilers, is perhaps more thermally efficient because of the higher temperature of heat recovery. This approach, however, offers problems

Table 25

POLYHETEROCYCLIC NITROGEN COMPOUNDS

COMPOUND	STRUCTURE	FORMULA
Acridine		$C_{13}H_9N$
Dibenz(a,h)acridine		$C_{21}H_{13}N$
Dibenz(a,j)acridine		$C_{21}H_{13}N$
Dibenz(c,h)acridine		$C_{21}H_{13}N$
Carbazole		$C_{12}H_9N$
Benzo(a)carbazole		$C_{16}H_{11}N$
Dibenzo(a,g)carbazole		$C_{20}H_{13}N$

with fouling of the heat exchange surfaces. Direct contact of the gas with liquid is required for effective solids removal; this may be accomplished through contact with condensate from the waste heat boiler or direct quenching with either oil or water.

Several different methods of initial gas washing have been proposed, depending primarily upon the constituents in the raw overhead gas (Fleming 1977).

- With extremely high-temperature gasifiers that generate no tars or oils, significant heat can be recovered in indirect waste heat boilers. The over-all process thermal efficiency is improved, but because that heat had been developed initially by burning some of the coal char with oxygen within the gasifier, the net process efficiency is low. Fine solids are removed by direct contact with either oil or water.
- In systems that generate tars and oils, a staged condensation is employed. In the first stage, heavy tars and solids are condensed and these will settle from the water. In the second stage, lighter oils that will float on the water are condensed.
- In systems that produce only light oils, a preliminary wash with light oil, without condensation of water, has been suggested for removal of fines without three-phase (water, floating oil, sinking solids) problems.

The disposition of various impurities into the solid, liquid, and gaseous streams will be a function of the processing used (Fleming 1977). Most trace elements that were volatilized during gasification would have reacted to chemical species that have low vapor pressure, and these species would have condensed upon the fine solids. Many other volatile metals will be condensed during the washing stage and also withdrawn with the solids.

Organic liquids will be separated from the aqueous streams and recovered for by-product value. Some water-soluble organics, such as phenols and cresylic acids, may extract into the aqueous phase.

The water will have washed-out ammonia, cyanides, and hydrogen chloride to varying degrees, depending upon the contacting mode employed. Also, the ammonia in the water will tend to wash some sulfur (as hydrosulfide) and carbon dioxide (as bicarbonate) from the raw gas stream. Sulfur can also react with cyanide to form thiocyanates. The relative removal of sulfur and carbon dioxide will be a function of the gas-water contacting mode and the complex NH_3 - H_2S - CO_2 equilibrium (Fleming 1977).

Cavanaugh et al. (1975) concluded that the quenching operation is one of the most important potential sources of toxic material emissions in a gasification plant.

At this point in the gasification process, a medium-- or low--Btu gas has been produced. All particles and heavy tars have been removed from the gas, and the quantities of water and light oil have been reduced (NIOSH 1978a). If a high-Btu gas of pipeline quality (900 to 1,000 Btu/scf) is desired, steps must be taken to increase the methane content of the gas (Huffstetler and Rickert 1977).

These steps are shift conversion and catalytic methanation.

6.5 SHIFT CONVERSION

In the downstream methanation reaction, hydrogen is reacted with residual carbon monoxide to form methane according to the reaction (Fleming 1977):

$$3\,H_2 + CO \rightarrow CH_4 + H_2O$$

Therefore, the ratio of hydrogen to carbon monoxide in the gas feeding the methanation reactor should be approximately 3:1. This ratio is significantly less than 3:1 in most gasifier types; therefore, some of the carbon monoxide is catalytically reacted with steam in a water gas shift reaction (Fleming 1977):

$$CO + H_2O \rightarrow H_2 + CO_2$$

Generally, a portion of the gas is reacted to high ratios of hydrogen to carbon monoxide and the remainder of the gas is bypassed so that the final mixed gas has been converted to the average 3:1 ratio (Fleming 1977). An iron chromium oxide compound is the catalyst in general use (University of Oklahoma 1975).

6.6 GAS PURIFICATION

The purpose of this step is to remove the acid gases, including hydrogen sulfide and carbon dioxide, which are produced in the gasification and shift conversion steps. Usually, ammonia is removed from the gas stream by water scrubbing before the gas stream enters the acid gas removal step (Evans 1976). Desulfurization processes can be divided, according to their principle of operation, as follows (Colton, Dandavati and May 1976):

- Chemical solvent
- Physical solvent
- Direct conversion
- Dry bed

Examples of each category are shown in Table 26 along with additional process information. All of these cleanup techniques operate at low temperature (250°F or less). Several high temperature (up to 2,000°F) methods are under development. Table 27 lists some of these processes. These systems are not commercially available and have yet to prove their effectiveness and reliability (Colton, Dandavati, and May 1976).

The acid gas removed in the purification step is processed further to recover the sulfur as dilute sulfuric acid or elemental sulfur (Dailey 1977).

6.7 SULFUR RECOVERY

The conventional technique for disposal of the hydrogen sulfide stream from the acid-gas treatment is the Claus process (Glaser, Hershaft, and Shaw 1974 and Dailey 1977). In the presence of bauxite, hydrogen sulfide burns directly to sulfur and water (Nelson 1958). However this reaction

Table 26

COMMERCIAL LOW TEMPERATURE CLEAN-UP PROCESS

Process	Absorbent	Temp. (°F)	Pressure	Effluent H_2S (ppm)	Selectivity	Make-up Rate	Form of Sulfur Recovery
Chemical solvent							
MEA	Monoethanolamine	80 to 120	Insensitive to variation in pressure	$\sim$100	Forms non-regen, comp. with COS, CS_2	50 to 100%	H_2S
DEA	Diethanolamine	100 to 130	Insensitive to variation in pressure	$\sim$100	Absorbs CO_2, does not absorb COS, CS_2	<5%	H_2S
TEA	Triethanolamine	100 to 150	Insensitive to variation in pressure	$\sim$100	H_2S	<5%	H_2S
Alkazid	Potassium dimethylamino acetate	70 to 120	Insensitive to variation in pressure 1 - 80 atm	$\sim$100	H_2S		H_2S
Benfield	Activated potassium carbonate solution	150 to 250		$\sim$100 (H_2S + COS)	H_2S is high		H_2S

Table 26 (Continued)

COMMERCIAL LOW TEMPERATURE CLEAN-UP PROCESS

Process	Absorbent	Temp. (°F)	Pressure	Effluent H_2S (ppm)	Selectivity	Make-up Rate	Form of Sulfur Recovery
Catacarb	Activated potassium carbonate solution	150 to 250	Insensitive to variation in pressure generally >300 psi	~ 100 (H_2S + COS)	H_2S - partial; also absorbs COS, CS_2	$<5\%$	H_2S
Physical solvent							
Sulfinol	Sulfolane + Dilsopropanoamine	80 to 120	High pressure preferred	~ 100 (H_2S + COS)	H_2S, also absorbs COS		H_2S
Rectisol	Methanol	<0		~ 100	H_2S		H_2S
Direct conversion							
Stretford	Na_2CO_3 + anthraquinone sulfonic acid			~ 10	H_2S	50 to 100%	Elemental sulfur

Table 26 (Continued)

COMMERCIAL LOW TEMPERATURE CLEAN-UP PROCESS

Process	Absorbent	Temp. (°F)	Pressure	Effluent H_2S (ppm)	Selectivity	Make-up Rate	Form of Sulfur Recovery
Townsend	Triethylene glycol	150 to 250		~10	H_2S		Elemental sulfur
Drybed							
Iron sponge	Hydrated Fe_2O_3	70 to 100		~100 (H_2S + COS)	H_2S, also towards COS, CS_2 and mercaptans		Elemental sulfur

Basis: 8400 tons/day Illinois No. 6 Coal Fed to BCR Gasifier, or 6700 ppm of influent H_2S

Source: Modified from Colton et al. 1976

Table 27

HIGH TEMPERATURE CLEAN-UP PROCESSES

Process	Absorbent	Type of Bed	Temp. °F	Pressure	Efficiency of S Removal		Absorbent Characteristics				Form of Sulfur Recovery	Status
					%H_2S Influent	Effluent H_2S ppm	Life	Regeneration	Selectivity toward	Make up rate		
Bureau of Mines	Sintered pellets of Fe_2O_3 (25%) and fly ash	Fixed bed	1000 to 1500	Insensitive to variation in pressure	~95	~350	>174 cycles Wt loss < 5%	With air	H_2S, COS	<5%	As SO_2 gas	Pilot
Babcock and Wilcox	Fe_2O_3	Fixed bed	800 to 1200	Insensitive to variation in pressure	~99	~75					As 12-15% SO_2 gas	Experimental
Consolid. Coal	Half calcined dolomite	Fluidized bed	1500 to 1800	~200 psia H_2S removal is high at low pressure	~95	~350		10-13% with steam and CO_2	H_2S, COS	1% of circulation rate	As H_2S gas to Claus process	Pilot
Battelle Northwest	Molten carbonates (15% $CaCO_3$)	Solution	1100 to 1700	Atmospheric H_2S removal is high at low pressure, 5-6 psig	~95	~350		With steam and CO_2	H_2S, COS, fly ash		As H_2S gas to Claus process	Pilot
IST - Meissner	Molten metal (proprietary)	Splashing contact	900		~98	~150		Electrolytic	H_2S, COS			Conceptual

Basis: 8400 tons/day Illinois No. 6 Coal Fed to BCR Gasifier, or 6700 ppm of influent H_2S

Source: Modified from Colton et al. 1976 is so highly exothermic that sulfur is usually produced in two steps as follows (Nelson 1958). The acid-free gas is combined with stoichiometric air sufficient to burn 1/3 of the total H_2S and SO_2 (NIOSH 1978a). Alternatively, one-third of the total acid-free gas is burned, then recombined with the unburned gas.

In the reactor, the SO_2 and H_2S react to form sulfur:

$$2\ H_2S + SO_2 \xrightleftharpoons[\text{catalyst}]{\text{bauxite}} 1.5\ S_2 + 2\ H_2O$$

From the reactor, the hot gases flow into the condenser, where they are cooled and the liquid sulfur is removed (NIOSH 1978a).

A number of modifications of the basic process have been developed to cope with special conditions (National Academy of Engineering 1974). If the H_2S content of the gas is low, the split-stream method operates best. When the H_2S content is below 20 percent, it may be necessary to use oxygen instead of air to preheat the feed for the combustion of the H_2S.

Hydrocarbon in the feed to the Claus unit causes an increase in undesirable side reaction products. The following are some of the possible reactions (NIOSH 1978a):

$$CH_4 + SO_2 \rightarrow COS + H_2O + H_2$$

$$CO + S \rightarrow COS$$

$$CO_2 + H_2S \rightarrow COS + H_2O$$

$$CH_4 + 2\ S_2 \rightarrow CS_2 + 2\ H_2S$$
$$2\ CO + S_2 \rightarrow CO_2 + CS_2$$

6.8 METHANATION

The purified gas contains a large quantity of carbon monoxide and hydrogen, which must be removed to bring the gas up to pipeline quality. This can be accomplished by methanation--the hydrogenation of carbon oxides to methane. When the hydrogen to carbon monoxide ratio in synthesis gas is equal to or greater then 3, the conversion of carbon monoxide and hydrogen to methane can be described by the reaction (Mills and Steffgen 1974):

$$3\ H_2 + CO \rightarrow CH_4 + H_2O$$

This reaction is relatively slow and a catalyst is needed to accelerate the reaction (Mills and Steffgen 1974). Early in 1920's, Fischer, Tropsch, and Dilthey compared the methanation properties of various metals (Mills and Steffgen 1974). The order of activity was found to be:

$$Ru > Ir > Rh > Ni > Co > Os > Pt > Fe > Mo > Pd > Ag$$

of which only Ru, Ni, Co, Fe and Mo can be considered commercially important (Mills and Steffgen 1974).

Almost all methanation catalysts are nickel-based, since nickel is cheap, vary active, and very selective for methane (Strakey, Forney, and Haynes 1975 and Mills and Steffgen 1974). These catalysts contain 25 to 77 percent Ni on a high surface area, refractory support, such as alumina or Kieselguhr (Mills and Steffgen 1974).

Catalyst inactivation by sulfur compounds or carbon deposition is a problem. Other problems arise from the highly exothermic nature of methanation (Mills and Steffgen 1974). With nickel catlysts, it is usual to limit sulfur in the gas to less than 1 ppm (Mills and Steffgen 1974 and Strakey, Forney, and Haynes 1975). Carbon deposition can be avoided by maintaining a sufficiently high H_2/CO mole ratio. Excessive temperatures in methanation are avoided by either limiting the carbon monoxide content of reactant gases or providing apparatus for rapid heat removal (Mills and Steffgen 1974).

Nickel carbonyl can form from reaction of nickel with carbon monoxide (Kornreich 1976). The reaction is favored at temperatures below 275°C (Strakey et al. 1975).

Since water is formed during the conversion of carbon monoxide to methane, a drying step is required after methanation (Evans 1976).

6.9 DEHYDRATION AND COMPRESSION

The final step is to compress the methanated gas from about 140 psig to pipeline pressure of 1,000 psig, and dry it. Compression normally involves inter-coolers and after-coolers from which condensed water will be removed. The gas then passes through a clean-up dryer, such as one using glycol, alumina, or molecular sieves (Jahnig and

Magee 1974).

To be interchangeable with natural gas, the synthetic gas should meet the following specifications (Strakey, Forney, and Haynes 1975):

Heating value $>$ 900 Btu/SCF
CO $< 0.1\%$
$H_2S < 0.25$ gr/100 SCF
Total S < 10 gr/100 SCF
Inerts $< 5\%$
$CO_2 < 3\%$
Water < 7 lb/million SCF
Specific gravity 0.59 to 0.62
Hydrocarbon dewpoint $< -40^{\circ}$ at 1,000 psig
No poisonous compounds or gum formers

Chapter 7

POTENTIAL HEALTH HAZARDS

> The same new method or new product which improves our lives can also be the source of unpleasantness and pain. For man's capacity to innovate is not always matched by his ability to understand his innovations fully, to use them properly, or to protect himself against unforseen consequences of the changes he creates.
>
> Richard Nixon, 1969

7.0 INTRODUCTION

Since exposure to occupational hazards is dependent upon the worker's environment, it is helpful to approach the problem of identifying these potential health hazards by returning to the unit operations described in the preceding chapter. Although the environment surrounding a unit operation is not isolated from the rest of the industrial plant, workers involved in this unit operation will be most heavily exposed to whatever hazard is contained in the process stream as it is processed at their work site. Thus it may be a useful approximation to consider each unit operation site as a micro environment with fluctuating exposures dependent upon operating conditions, meteorological conditions (many of the gasification operation will be exposed to open air) and the nature of the gasification technology.

7.1 COAL PREPARATION AND STORAGE

Most second generation technologies (HYGAS, CO_2 Acceptor, Synthane, Bigas, Agglomerating Burner) require that coal be dried and pulverized prior to gasification (NIOSH 1978a). The major hazards associated with these operations will be exposure to noise and coal dust. Noise levels from similar equipment used in milling operations are shown in Table 28. The amount of coal dust produced during the grinding and screening operation will be

Table 28

TYPICAL NOISE LEVELS PRODUCED BY EQUIPMENT USED IN COAL CLEANING

Equipment	Typical Sound Level At Worker Position dbA
Car shakeout	110-120
Screens	95-105
Blowers, dryers, air pumps, fans, crushers	90-105

Source: Adapted from Patterson et al. 1975 dependent upon the amount and condition of coal processed. The pulmonary hazard should be of a lesser magnitude than that experienced by underground coal miners, but the potential of development of coal workers pneumoconiosis will be present to some degree.

7.2 COAL INJECTION

Injection of solid material into the high pressure gasification chamber may be done via lockhopper or via pressurized slurry. The potential health hazards associated with this operation may come from leakage of gasifier product around malfunctioning injector valves or from materials (oil or gas) used to convey the coal particles into the gasification chamber.

Hazards that arise when an oil slurry is used to convey coal to the gasifier result from leakage around pump seals. As mentioned previously, oil losses at the HYGAS pilot plant have been estimated to be 84 gallons/day (Lee 1975b). When the oil is toluene, as it currently is at HYGAS, the route of exposure may be through vapor or condensed liquid. Absorption of toluene is accomplished readily through skin and vapor inhalation. Short high dose exposures produce non-specific central nervous system signs including muscular weakness, incoordination, gait difficulties, paresthesias, coma. Skin and mucous membranes (such as conjunctiva) are readily irritated by toluene.

Repeated skin contact with toluene may produce extremely dry skin and dermatitis (Tabershaw et al. 1977). The frequent presence of benzene contamination in toluene may predispose workers exposed to toluene to develop the same hematopoietic problems which result from benzene exposure (Infante et al. 1977).

If light oil condensed from the gasifier off gas is recycled for use in the slurry, the hazards will be potentiated by the inclusion of other compounds including benzene and other aromatic hydrocarbons present in this oil (Anastasia and Bair 1976).

Another hazard posed by the injection operation involves the addition of finely ground silica to the water-coal slurry in the Bigas pilot plant to alter the slagging properties of coal (NIOSH 1978a). This would expose workers involved in silica grinding and silica mixing to levels of respirable silica which might cause silicosis.

7.3 GASIFICATION

Once the properly sized coal particle is injected into the gasification chamber it may undergo many reactions depending upon temperature, pressure and transit time. The main constituents of gasifier off gas will be elemental hydrogen, carbon monoxide, carbon dioxide, methane and ethane (Forney et al. 1974). Other constituents are legion but may include light oils (benzene, toluene, xylene), organic sulfur containing compounds (carbonyl sulfide, thiophene, carbon disulfide, mercaptans), phenols, polynuclear aromatic hydrocarbons (anthracene, benz(a)pyrene), azaheterocyclic hydrocarbons, volatized trace elements (arsenic, lead, cadmium, nickel, beryllium, mercury, selenium), hydrogen sulfide and ammonia (Kornreich 1976, Forney et al. 1974, and Attari 1973).

Exposure to this meagerie of chemical hazards will probably only occur during maintenance procedures such as correction of plugged process lines and during leaks from the gasifier chamber. The chemical state of the hazardous materials will be either vapor or liquid depending upon the boiling point of the compound being considered. Potential health effects resulting from exposure to gasifier products are numerous but some of the more important ones are listed in Table 29.

Hazards associated with the gasification process may also be found during char and ash disposal. Ash and char may carry adsorbed polynuclear aromatic hydrocarbons, and the majority of trace elements found in coal (Kornreich 1976 and Forney et al. 1975). Thus health effects due to ash disposal may include those reported from polynuclear aromatic hydrocarbon exposure (lung cancer, skin cancer, bladder cancer, renal cancer) and those reported from exposure to various trace metals. The major trace elements contained in ash/char along with possible health effects

Table 29

POTENTIAL HEALTH EFFECTS RESULTING FROM EXPOSURE TO GASIFIER PRODUCTS

Organ System	Effect	Etiologic Agent
Central Nervous System	Death	H_2S[1], CS_2[1], Phenol[2]
	Encephalopathy	CS_2[1]
	Demethia	CS_2[1]
	Anxiety Neurosis	Hg[3]
	Ataxia	Hg[3]
Peripheral Nervous System	Motor Paralysis	Pb[3], As[4]
	Dysaesthesia	Hg[3], CS_2[1], As[4]
Skin	Burns	NH_3[1], Phenol[5], SeH_2[3]
	Ulceration	Be[6], Phenol[7]
	Dermatitis	As[8], Ni[9], Be[6]
	Cancer	PAH[10-12]
Eyes	Conjunctivitis	SeH_2[3], Toluene[13]
Respiratory	Upper Airway Irritation	NH_3[1], H_2S[2]
	Nasal Sinus Cancer	Ni[14-16]
	Bronchoconstriction	Ni[17]
	Chemical Pneumonia	Be[18,19]
	Pulmonary Edema	Cd[20,21], Phenol[22,23] Cd[24-27]
	Emphysema	Cd[24-27]
	Imparied Alveolar Capillary Diffusion of Oxygen	Be[28-30]
	Lung Cancer	Ni[14-16,31,32] PAH[33-35], As[36,37]

Table 29 (Continued)

POTENTIAL HEALTH EFFECTS RESULTING FROM EXPOSURE TO GASIFIER PRODUCTS

Organ System	Effect	Etiologic Agent
Gastrointestinal	Colic	Pb[3]
	Nausea/vomiting	Phenol[2]
Liver	Liver Damage	Phenol[23]
Urinary System	Renal Transport Abnormalities	Cd[25,38], Phenol[23]
	Bladder Cancer	B-Naphthylamine[39]
	Prostate Cancer	Cd[40,41]
Blood and Blood Forming Organs	Leukemia	Benzene[42-46]
	Maturation Defects	Pb[3]
	Bone Marrow Depression	Benzene[47], Pb[3], As[48]
	Inference with O_2 Carring Capacity of Hemoglobin	CO[49]
General	Weakness	Toluene[13]
	Asphyxia	CH_4, C_2H_6
	Co-Carcinogen	Phenol[50]
	Explosion Hazard	CH_4, H_2

Table 29 (Continued)

References:

1 Hunter 1975
2 Lucas and Lane 1895
3 Browning 1969
4 McCutchen and Utterback 1966
5 Cronin and Brauer 1949
6 Van Ordstrand et al. 1945
7 Hubler 1943
8 Birmingham et al. 1965
9 Calnan 1956
10 Bryan and Shimkin 1943
11 Weil and Condra 1960
12 Sexton 1960
13 Thienes and Haley 1972
14 Morgan 1958
15 Doll 1958
16 Pederson et al. 1973
17 McConnell et al. 1973
18 Denardi et al. 1949
19 Aub and Grier 1949
20 Zavon & Meadows 1970
21 Townshend 1968
22 Miller 1942
23 Issaces 1922
24 Lane and Campbell 1954
25 Kazantzis et al. 1963
26 Fribery 1959
27 Chowdhury and Louria 1976
28 Austrian et al. 1951
29 Cugell et al. 1956
30 Marker et al. 1957
31 Mastromatteo 1967
32 Williams 1958
33 Menek et al. 1974
34 Doll et al. 1965
35 Redmond et al. 1972
36 Blot and Fraumeni 1975
37 Lee and Fraumeni 1969
38 Potts 1965
39 Mancuso and El-Attar 1967
40 Kipling and Waterhouse 1967
41 Lemen et al. 1976
42 Infante et al. 1977a
43 Infante et al. 1977b
44 Bigliani 1976
45 Aksoy et al. 1974
46 Ishimaru et al. 1971
47 Cronkite 1961
48 Kyle and Pease 1965
49 NIOSH 1972
50 Boutwell and Bosch 1959

are shown in Table 30.

7.4 GAS COOLING AND SOLIDS REMOVAL

Quenching the hot gas cools it and removed particles and some constituents in the process stream. Worker exposure to hazardous substances during this unit operation may arise from fugitive emissions from the process stream (constituents and potential health hazards similar to those described under the gasification discussion), maintenance procedures due to tar occluded lines or sludge accumulation in vessels, and waste liquid disposal.

Since the products produced by gasification depend upon temperature, pressure and transit time, each gasification process will produce a characteristic group of chemical substances. Health hazards of workers in the same unit operation will accordingly vary widely between different gasification processes.

Assuming that the reactor off gas composition will be the same as that discussed in the section on potential health hazards of gasification (this composition in fact does conform to that seen in Synthane gasification), the following potential hazards may exist. Water quenching will cool the reactor off gas and will remove water, solids, and tars by condensation; some gases by solubilization and particles by contact. The waste water will be comprised of aqueous organic and solid phases which will

Table 30

CONCENTRATIONS OF VARIOUS TRACE ELEMENTS IN CHARS AND REPORTED HEALTH EFFECTS

Trace Element	Conc., ppm	Reported Health Effects
Al	3200	pulmonary fibrosis (Morgan & Seaton 1975a)
As	2.9	See Table 30
Be	5.7	See Table 30
Cr	220	dermatitis, ulcers, lung cancer (NIOSH 1975a
Mg	2700	conjunctivititis rhinitis (Browning 1969)
Ni	25	See Table 30
Pb	5.7	See Table 30
Ti	1100	pneumoconiosis (TiO_2) (Morgan & Seaton 1975)
V	47	asthma (NIOSH 1977a) rhinorrhea (NIOSH 1977a) lacrimation (NIOSH 1977a) bronchitis (Morgan & Seaton 1975)
U	4.7	lung cancer (Lundin et al. 1971)

Source: Young et al. 1978

separate upon standing. The particles removed from the reactor off gas may contain adsorbed polynuclear aromatic hydrocarbons and trace elements. The Synthane process will recycle the aqueous portion of waste liquid for use during the water quenching and separate and solids, tars and oils by settling or decanting with subsequent removal and disposal.

The trace element composition of the fine solids removed from the reactor off gas and potential hazards due to exposure to these solids (during disposal or later reentry into the atmosphere) are shown in Table 31.

The amount of polynuclear aromatic hydrocarbons adsorbed on the fine particles will determine whether the hazards reported to be associated with polynuclear aromatic hydrocarbon exposure will exist for those exposed to these particulates.

The organic compounds condensed during cooling of the reactor off gas by water quenching are a complex mixture of aromatic hydrocarbons and heterocyclic compounds. Some of the compounds isolated by Forney et al. in the organic phase of Synthane condensate include benzene, toluene, zylene, phenol, naphthalene and derivatives, 3 ring aromatics, and N heterocyclics (Forney et al. 1974). Thus the health hazards involved with disposal of the organic phase of the waste liquid could include renal cancer, bladder cancer, skin cancer and possibly lung cancer.

Table 31

TRACE ELEMENTS FOUND WITH FINE PARTICLES REMOVED FROM REACTOR OFF GAS AND REPORTED HEALTH EFFECTS

Element	Conc. (ppm)	Health Effect
Al	330	pulmonary fibrosis (Morgan & Seaton 1975)
As	6.1	See Table 30
F	690	osteosclerosis (NIOSH 1975b)
Ti	1100	pneumoconiosis (TiO_2) (Morgan & Seaton 1975)
U	5	lung cancer (Lundin et al. 1971)
V	50	asthma (NIOSH 1977a) rhinorrhea (NIOSH 1977a) lacrimation (NIOSH 1977a)

7.5 SHIFT CONVERSION

This shift reaction requires an iron-chromium oxide or cobalt-molybdenum catalyst. The possibility of hazard arising from catalyst decomposition (molybdenum reacting to form molybdenum trioxide) or carbonyl formation (iron, cobalt) is slight. The major hazards to workers involved in this area should arise from the flammability of hydrogen and the possibility of fugitive emissions of the raw gas. A minor hazard could result from changing a spent catalyst or otherwise handling the catalyst during maintenance procedures. Some potential health effects associated with raw gas components are shown in Table 32.

7.6 GAS PURIFICATION AND SULFUR RECOVERY

When removal of sulfur compounds is accomplished by the Claus process, the reaction is catalyzed by bauxite. Hazards associated with this process include possible inhalation of bauxite dust which may produce pulmonary fibrosis (Theines and Haley 1972 and Morgan and Seaton 1975). This association has been debated since silica has been found to be present in the dust (Browning 1969).

7.7 METHANATION

For several reasons nickel is the most probable metal catalyst for methanation (Mills and Steffgen 1974 and Strakey et al. 1975). This gives rise to the possibility

Table 32

RAW GAS CONSTITUENTS AND POSSIBLE HEALTH EFFECTS

Constituent	Potential Hazard
H_2	explosion
CO	asphyxia
CO_2	asphyxia
CH_4, C_2H_6	flammable, asphyxia
H_2S	CNS depression death, upper airway irritation

Source: Young et al. 1978

of nickel carbonyl formation during catalyst deactivation. The hazard may be prevented by maintaining the temperature inside the methanation chamber at 260°C or greater. All the potential catalysts can form carbonyls under the proper conditions but the health hazard to workers is greatest with nickel carbonyl. Exposure potential exists during maintenance procedures and possibly from fugitive emissions from the methanation chamber. Health effects of nickel carbonyl exposure include lung cancer, nasal cancer and pulmonary edema (Tabershaw et al. 1977).

7.8 DEHYDRATION AND COMPRESSION

In the product gas compression and dehydration process, the primary hazard, leaks of highly combustible gases, should be protected against by routine maintenance and inspection of pumps and flange connections. The possibility of a gas fire should be recognized and easy access to the area by fire fighting equipment should be provided (NIOSH 1978b).

7.9 CONCLUSION

The foregoing description of potential health hazards in coal gasification is not intended to be complete. Much of the information about process stream composition is data obtained from process stream analysis of bench scale units and cannot be extrapolated to pilot plants or commercial gasification plants. The gasification of coal produces an incredible array of organic and inorganic compounds. A 1963 Bureau of Mines listing of organic coal carbonization compounds numbered 832 (Anderson and Wu 1963). Our lack of knowledge about potential health effects in gasification is compounded further by the paucity of data on toxicologic, teratogenic and carcinogenic properties of many of the products.

Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

"Each master . . . has in great measure the health and happiness of his workpeople in his power . . . let benevolence be directed to the prevention, rather than to the relief of the evils, which our civic state so widely and deeply produces."

Charles Thackrah (1795-1833)

Coal is the most abundant fossil fuel in the United States and in that respect is a logical choice for achieving energy independence. However, the use of coal is limited by its lack of versatility in use, its high cost of transportation, and the high sulfur content of many of the more readily available coals. Aside from its industrial use as a metallurgical and reductant fuel, coal in solid form is use principally for steam and electricity generation, whereas energy markets demand considerable quantities of fuel in liquid form (mainly for transportation, including railroads, and for household heating) and in gaseous form (mainly for household, commercial and industrial users). There is considerable activity in the United States to develop processes to convert coal to other liquid, gaseous or solid forms (Reber et al. 1976).

8.1 CONCLUSIONS

The following are the major conclusions that have been reached:

- Coal differences are rooted in the physical processes by which the coal was created. As prehistoric plants died, accumulated, and were gradually buried, subterranean heat and compression combined to drive off volatile fragments from the basically carbon molecular skeletons. The varying degree of this devolatilization produced variations from anthracite (the lowest in volatile content) through bituminous and subbituminous coal, lignite, and peat. Accordingly, these are broad classifications which represent approximations of the differences in coals (ORNL 1976).

- The extremely complicated and variable nature of coal has made impossible any efforts to describe accurately its structure and composition. However, most workers believe that coal is an essentially aromatic material (Ensminger 1977).
- On a moisture and ash-free basis, a typical organic matter composition of coal would be 70 to 90 percent carbon, 2 to 6 percent hydrogen, 1 to 2 percent nitrogen, 0.5 to 6 percent sulfur and 2 to 20 percent oxygen by weight.
- Nearly all trace elements show an enrichment in coal relative to their abundance in the earth's crust.
- In general, a strategy for process development evolves through the stages of bench, process development unit, pilot plant, and demonstration plant.
- The history of coal gasification can be traced back to 1691 when Clayton produced an inflammable vapor by distilling coal.
- The production of gas from coal was practical as

far back as the early part of the 19th century when coal was destructively distilled in retorts to produce a gas suitable for burning in fish-tail burners for lighting purposes. The early gasifiers were simple machines, consisting basically of a retort, burners, and air and steam blast devices. Gas cleaning consisted of water sprays for tar removal and iron boxes for H_2S removal.

- The unit operations approach provides a understanding of the process, permits identification of the major chemical compounds within each unit, and assists in determining possible sources of emissions.
- Coal gasification requires nine basic operations: coal storage, preparation, injection, gasification, quench, shift conversion, gas purification, catalytic methanation, and final compression and dehydration.
- Gasifier design drastically affects production of undesirable "by-products". This is dramatically shown by the work of Nakles et al. (1975) who studied the rate of effluent production by varying the injection position.
- Processes attainable in ten to fifteen years are referred to as second-generation. These processes are currently at the PDU or pilot plant stage, and

include HYGAS, CO_2 Acceptor, Synthane, Bigas, and Agglomerating Burner.

- The potential hazards associated with each coal gasification unit operation have been listed in Table 33. The highest potential for exposure to toxic contaminants exists in the initial operations through the quenching step. The equipment used in the processing steps down-stream from the quenching operation is convential apparatus similiar to that found in the petro-chemical industry. Thus, potential hazardous exposures in this part of a coal gasification plant should be of a lesser magnitude, except for potential carbonyl formation.
- The range of toxicants and possible health effects is extremely wide, from simple chemicals like carbon monoxide to complex mixtures of organic carcinogens. This complexity is further complicated by the special problems associated with carcinogens: long latent period, doubt about "safe" levels, and unpredictable multi-agent interactions. Another problem is the issue of undetermined mutagenicity and teratogenicity of such compounds. Existence of such effects raises the question of possible reproductive effects in workers exposed to them as yet another health hazard.

Table 33

POTENTIAL HEALTH HAZARDS IN COAL GASIFICATION

Unit Operation	Potential Pollutants	Pressure	Temperature	Corrosiveness	General Housekeeping	Potential for Hazardous Exposure
Coal preparation and storage	noise coal dust	L	L	L	Fair	H
Injection						
via lockhopper	pressurization gas	H	L	H	Good	H
via slurry pumping	vapor leaks	H	L	H	M	H
Gasification	reactor off-gas char	H	H	M-H	M	M-H
Quench	PNA's H_2S COS NH_3 sulfides mercaptans thiophenes trace elements heterocyclic compounds	L	M-H	H	M	H

Table 33 (Continued)

POTENTIAL HEALTH HAZARDS IN COAL GASIFICATION

Unit Operation	Potential Pollutants	Pressure	Temperature	Corrosiveness	General Housekeeping	Potential for Hazardous Exposure
Shift conversion	carbon monoxide carbon dioxide sulfur species CH_4	H	H	L	Good	L-M
Gas Purification	H_2S CO_2	L	L	L	M	M
Sulfur Recovery	H_2S SO_2 CS_2 COS Trace elements	L	L	L	M	L-M
Methanation	metal carbonyls CO CH_4	H	H	L	Good	L-M
Dehydration and Compression	CH_4	H	L	L	Good	L

Source: After Cavanaugh et al. 1975

L-Low, M-Medium, H-High

8.2 RECOMMENDATIONS

In discussing chemical carcinogens, Dr. J.R. Heller, the former director of the National Cancer Institute, stated (Heller 1950):

> "In view of the lack of knowledge of where the danger lies, or the extent of it, no one is in a position to say today just what remedial action is needed. But in view of what we do know, we have to consider precautionary action now to protect the workers involved.."

With coal gasification, we are in this same situation. Thus, on the basis of this study and review we recommend the following:

8.2.1 Control Technology

Research and development work on methods for engineering control is required to ensure that adequate systems of control are available for application to coal gasification technologies in a cost effective manner (i.e., to prevent the necessity of extensive retrofit application of control devices, but rather be able to integrate the technologies and control systems prior to commercial plant installation).

8.2.2 Prospective Mortality Study

Attempts should be made to keep track of those who are or have been employed in coal gasification technology and accumulate epidemiological information about them. Among other things, this program would have the goal of detecting any delayed or late effects such as the appearance of tumors, lung disorders, etc. A central depository for records from terminated projects should be established.

8.2.3 Medical Surveillance

Present limitations in our knowledge of human response to environmental factors found in coal gasification facilities, require that periodic medical examinations of exposed workers be performed. NIOSH is currently in the process of developing a detailed medical protocol under contract. The nine specific tasks are as follows (NIOSH 1977b):

Task 1: Potential Health Hazards

Utilizing available information, identify all known and potential hazards associated with coal gasification.

Task 2: Present Medical Surveillance Procedures

Review and report on the existing medical facilities, surveillance procedures and existing systems for recording worker exposure to hazardous substances.

Task 3: Minimum Health Facilities

Recommend minimum facilities required to handle an acute unforseen occurrence, such as accident, fire or massive discharge of process streams.

Task 4: Standard Medical Forms

Develop a standard form for medical and occupational history. The form will include a section on family history with emphasis placed on inheritable conditions that might predispose the worker to develop cancer or chronic disease.

Task 5: Form for Recording Worker Exposure

A method for recording worker exposure to hazardous substances occurring during the performance of his or her job within the conversion plant will be developed. The form will ensure that each exposure to a hazard is documented with regard to time and date of occurrence, duration of exposure, the exact nature of the worker's duties that provided opportunity for hazardous materials contact, the place of contact, possible hazardous materials present, protective measures instituted, nature of the worker's complaints, if any, following cessation on the job, proposed course of action, and follow-up of the worker's problem.

Task 6: Preventive Screening

The contractor shall review the pertinent literature on the association between aryl hydrocarbon hydroxylase (AHH) activity and polynuclear aromatic hydrocarbon carcinogensis. A review of the literature on the assay technique for AHH activity in human leukocytes will be performed and the feasibility of including a measurement of AHH activity in widespread screening of coal conversion employees should be determined.

Task 7: Medical Surveillance Program

Develop a surveillance protocol specifically designed to detect acute, chronic and carcinogenic effects of exposures within a work area.

Task 8: Monitoring for Teratogenicity

The contractor shall describe the screening tests for the detection of occupationally induced germ cell alterations that are now feasible, now being developed or now being researched. The contractor shall recommend a program of surveillance for occupational teratogenicity which is feasible now and gives due consideration to the practical problems of gathering data in sensitive personal areas.

Task 9: Follow Up

The contractor shall develop a mechanism for compilation and review of all abnormal findings detected by implementation of the medical surveillance protocol within the coal gasification industry. The contractor shall also recommend a mechanism for maintaining acess to the population of former workers.

8.2.4 Methanator Work Practices

The following procedures should be followed to minimize the possibility of metal carbonyl exposure (Allen and Yen 1973):

Temporary Shutdown

If a short duration shutdown is expected, and the temperature in the methanator will not fall below 400°F, the methanator may be blocked in under an atmosphere of process gas.

Long-term Shutdown

If the methanator is not going to be opened during the shutdown, the following steps are sufficient:

- Discontinue to flow of process gas and depressure the methanator.
- Purge the methanator with H_2 or N_2 that is free of CO, CO_2, and O_2. Temperature should be above 500°F when the purge gas is admitted.
- When the purge gas effluent indicates no CO or CO_2 is present, the reactor may be blocked in under an atmosphere of purge gas. Provisions should be made to maintain a positive pressure in the system to prevent a vacuum forming as the reactor cools.
- The methanator should be blocked in using a double block and bleed valve system or blinds to insure the CO containing gas cannot enter the methanator.

Shutdown for Catalyst Removal

If the catalyst is to be removed, the following procedure can be used:

- Discontinue the flow of process gas and depressurize the system while purging with steam. The steam purge should be started before the catalyst temperature drops below 500°F.

- Maintaining the steam purge, cool the methanator to the temperature of the available steam supply.
- Establish and maintain a N_2 purge and cool to 300°F or lower.
- If it is desired to inspect the top of the bed before dumping, the top manway may be opened. After inspecting, the manway should be closed before opening the bottom manway for catalyst unloading. This will prevent a chimney effect and help insure that air will not enter the reactor
- Open the bottom manway and unload the catalyst into steel drums or a steel bodied dump truck. A water hose with a spray head should be available to spray the catalyst as it is discharged.

The properties of nickel carbonyl are such that it is possible for liquid carbonyl to be trapped in a methanator and not be detected by air monitoring (Allen and Yen 1973). If it is necessary for personnel to enter a methanator where nickel carbonyl may be present, they should be equipped with self-contained breathing apparatus and skin protection.

8.2.5 Analytical/biological Rapid Screening Technique

There is considerable evidence that with few exceptions carcinogens are mutagens (Ames, McCann and Yamasaki 1975 and McCann and Ames 1976). The Ames test system is a highly sensitive yet simple bacterial assay for chemical mutagens. Compounds (or mixtures) are tested with a group of well-characterized mutants of Salmonella typhimurium requiring histidine for growth. Simple stated, the assay detects genetic damage induced by chemicals by the reversion of these specific strains to the wild-type (the ability to grow without histidine supplement). Additionally, the particular type of gentic dammage--base alterations, frame shifts (addition or deletions)--can be detected with the appropriate strain.

Liquid chromatographic techniques have been developed that will separate a complex sample into eight fractions by compound class (Jones et al. 1976). These overlapping fractions are shown in Figure 28. Estimated minimum detection limits by infrared spectroscopy are listed in Table 34. A combined analytical/biological rapid screening technique for process streams is thus feasible. Guerin and Epler (1976) from the Oak Ridge National Laboratory have experimented in this area.

8.2.6 Employee Health Education Program

Concerning worker education, Eckardt (1959) states:

> "It seems axiomatic that if a man is to protect himself from a hazard, he must be informed of the nature of the hazard from which he is protecting himself."

A meeting of all employees should be held to describe all potential health hazards, as well as the features of the medical surveillance program (NIOSH 1978a). Although exposures to carcinogenic materials will necessarily

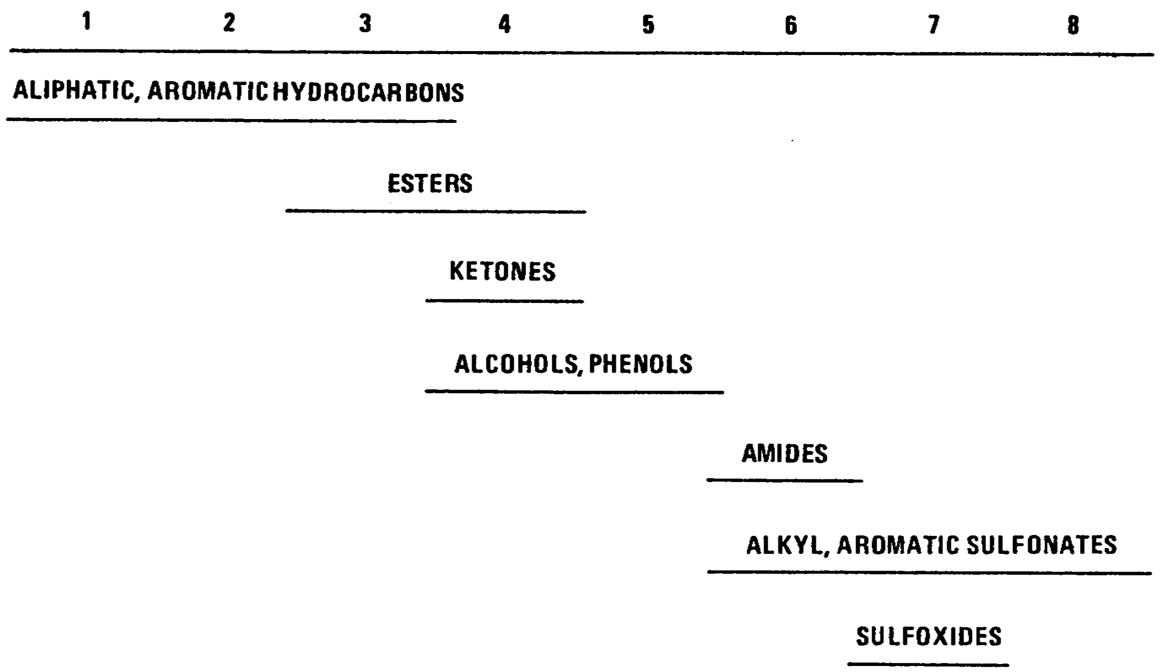


Figure 28

LIQUID CHROMATOGRAPHIC FRACTIONS VS. CLASS TYPES

Source: Lochmüller 1976

Table 34

CLASSES OF ORGANIC COMPOUNDS ELUTING IN EACH LIQUID CHROMATOGRAPHY FRACTION AND THEIR APPROXIMATE IR DETECTION LIMITS

Fraction	Compound Type	Approximate IR Sensitivity*
1	Aliphatic hydrocarbons	1-10 ug
2	Aromatic hydrocarbons POM PCB Halides	1-10 ug
3	Esters Ethers Nitro compounds Epoxides	0.1-1 ug
4	Phenols Esters Ketones Aldehydes Phthalates	0.1-1 ug
5	Phenols Alcohols Phthalates Amines	0.1-1 ug
6	Amides Sulfonates Aliphatic acids Carboxylic acid salts	0.1-1 ug
7	Sulfonates Sulfoxides Sulfonic acids	0.1-1 ug
8	Sulfonic acids	0.1-1 ug

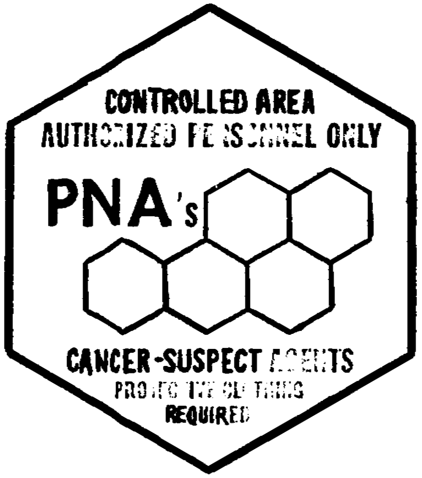
* Using Perkin Elmer 521 (or equivalent) when used by a professional IR Spectroscopist.

Source: Jones et al. 1976

receive the greatest attention, exposure to other potential toxicants or irritants such as CO, H_2S, and coal dust, as well as harmful physical stresses such as noise and heat, should be discussed. Techniques used at Oak Ridge National Laboratory have been published (Bolton et al. 1977). Figure 29 and 30 show their employee health brochure.

8.2.7 Exposure Monitoring

Exposure monitoring evaluates the effectiveness of the installation of engineering and work practice controls and informs the employer whether additional controls need be instituted. NIOSH (1978a) has recommended continuous monitoring of carbon monoxide concentrations as an indicator of potential hazard from process stream leakage.



The above symbol was developed for identifying areas where polynuclear aromatic's (PNA's) were being produced and/or handled in significant quantities to represent a potential health hazard.

INTRODUCTION

The Health Division believes that all persons involved in the Coal Technology Program should be made aware of the potential hazards connected with this work and informed as to what measures of protection and surveillance will be implemented. Each phase of the experimental work will be evaluated separately, recommendations made, and pertinent information disseminated. Our basic philosophy will be to protect all personnel fully.

BACKGROUND INFORMATION

Conversion of coal to liquid products or gas by any of the methods currently in use subjects the employees involved to several chemical and physical stresses. At the present time these problems include exposure to: (1) polynuclear aromatic hydrocarbons (PNA's); (2) an assortment of organic compounds (phenols, cresols, etc.); (3) sulfur compounds (H_2S, SO_x, organic sulfur); (4) toxic trace elements present in coal (mercury, arsenic, selenium, cadmium, etc.); (5) coal dust; and (6) noise and heat stress. Most of these problems are already familiar to industrial hygienists, and no unusual difficulty is anticipated in their control. The personnel exposure to the PNA's is expected to generate the most concern and is the reason for issuing this brochure. Some of the PNA's are known to be carcinogenic and are expected to be found in most of the process streams. These compounds may be handled safely if all workers in the program follow prescribed guidelines for personal protection.

MEDICAL ACTIVITIES

The Health Division of ORNL is proceeding with the following health surveillance plan:

1. Physical examinations will be performed on all individuals involved in the Coal Technology Program with emphasis on evaluating existing skin lesions. Thereafter, periodic skin examinations will be scheduled.
2. Photographs of the face, neck, hands, and arms will be taken to provide "baseline" data to assist in monitoring and determining the significance of skin changes.
3. A consultant in dermatology will be retained as an advisor to the skin examination program.
4. All coal technology personnel will be required to participate in the Sputum Cytology Program. Results will be evaluated individually and appropriate action taken. Re-examinations will be performed at intervals that depend on the individual's potential for exposure to PNA's.
5. A periodic review of the results of the medical studies and the industrial hygiene program will be presented as a seminar to coal technology personnel.

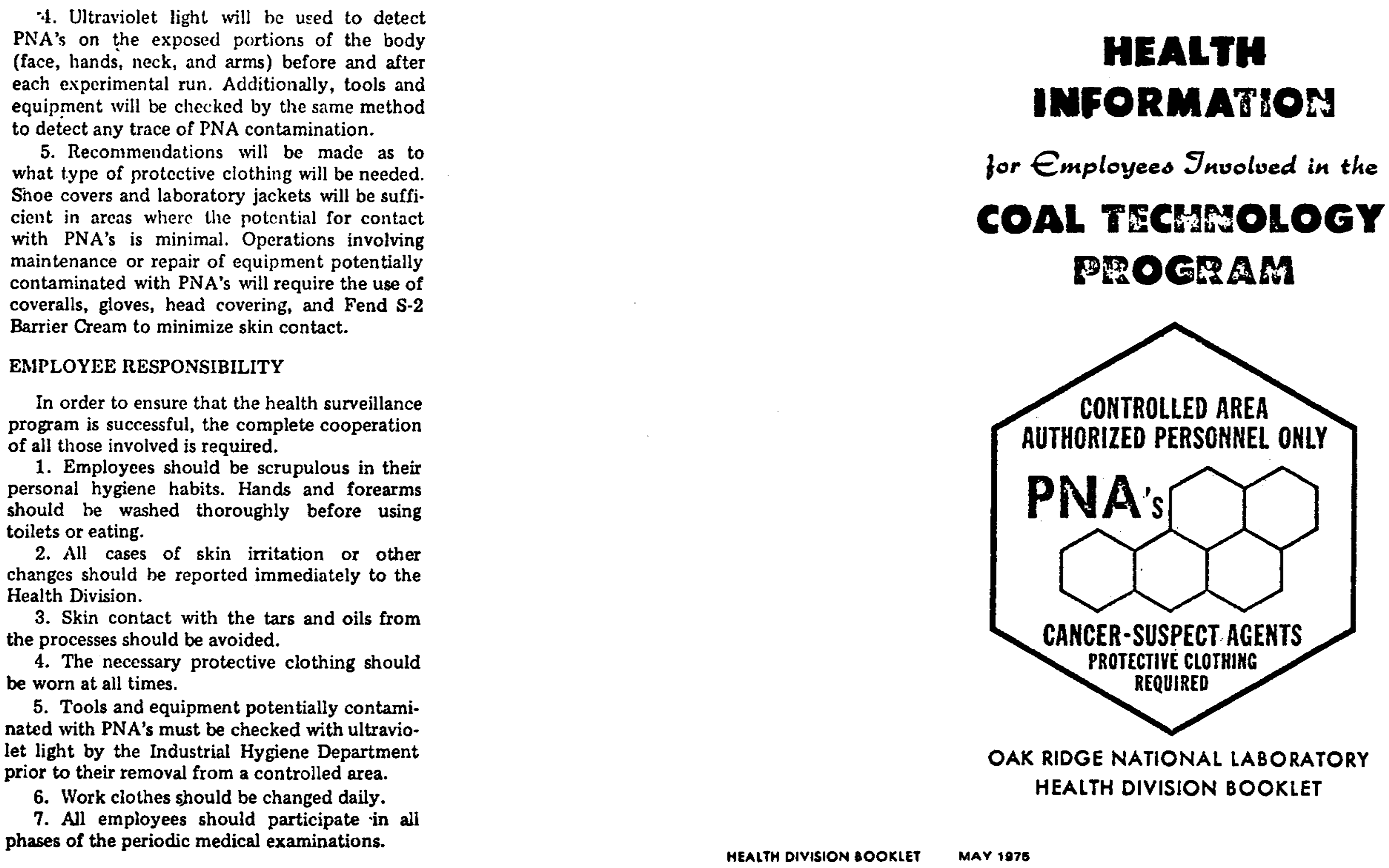
INDUSTRIAL HYGIENE ACTIVITIES

The Industrial Hygiene Department, as part of its ongoing program in occupational health and environmental control, is instituting the following as part of its initial plan for employee protection. As the program develops, modifications may be necessary.

1. Periodic talks with the technicians, craftsmen, engineers, etc. will be held to inform them of the health hazards, our program, and their responsibilities.
2. A routine air sampling program for contaminants will be initiated in those areas where experimental work is in progress.
3. Respirators will be provided for use in the coal technology facilities. All individuals working in these areas will be trained, fitted, and tested by the Industrial Hygiene Department before they attempt to wear a respirator.

Figure 29

ORNL'S HEALTH INFORMATION BROCHURE (front)



4. Ultraviolet light will be used to detect PNA's on the exposed portions of the body (face, hands, neck, and arms) before and after each experimental run. Additionally, tools and equipment will be checked by the same method to detect any trace of PNA contamination.

5. Recommendations will be made as to what type of protective clothing will be needed. Shoe covers and laboratory jackets will be sufficient in areas where the potential for contact with PNA's is minimal. Operations involving maintenance or repair of equipment potentially contaminated with PNA's will require the use of coveralls, gloves, head covering, and Fend S-2 Barrier Cream to minimize skin contact.

EMPLOYEE RESPONSIBILITY

In order to ensure that the health surveillance program is successful, the complete cooperation of all those involved is required.

1. Employees should be scrupulous in their personal hygiene habits. Hands and forearms should be washed thoroughly before using toilets or eating.
2. All cases of skin irritation or other changes should be reported immediately to the Health Division.
3. Skin contact with the tars and oils from the processes should be avoided.
4. The necessary protective clothing should be worn at all times.
5. Tools and equipment potentially contaminated with PNA's must be checked with ultraviolet light by the Industrial Hygiene Department prior to their removal from a controlled area.
6. Work clothes should be changed daily.
7. All employees should participate in all phases of the periodic medical examinations.

HEALTH INFORMATION

for Employees Involved in the

COAL TECHNOLOGY PROGRAM

OAK RIDGE NATIONAL LABORATORY
HEALTH DIVISION BOOKLET

HEALTH DIVISION BOOKLET MAY 1975

Figure 30

ORNL'S HEALTH INFORMATION BROCHURE (back)

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