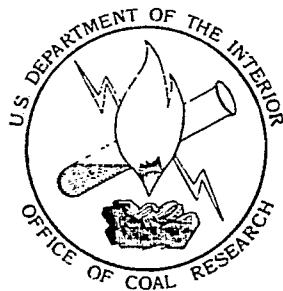ENVIRONMENTAL FACTORS

IN

COAL LIQUEFACTION PLANT DESIGN

R&D REPORT NO. 82 - INTERIM REPORT NO. 3

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ENVIRONMENTAL FACTORS IN COAL LIQUEFACTION PLANT DESIGN

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B. I. Loran, and W. J. Mindheim

ABSTRACT

Environmental factors will play an important role in design and operation of coal liquefaction plants. Such plants are a major national goal and the first large units could be built during this decade. Proposed treatment methods are discussed for solid, liquid, and gaseous effluents based on a preliminary liquefaction plant design developed for the Office of Coal Research by The Ralph M. Parsons Company. An approach to noise control procedures designed to satisfy requirements of the Occupational Health and Safety Act is also described.

Further research during the course of future development efforts to develop additional data and information on environmental factors is recommended. Such data will further improve effectiveness and economy of plant environmental control and monitoring systems.

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ENVIRONMENTAL FACTORS IN COAL LIQUEFACTION PLANT DESIGN

J. B. O'Hara, S. N. Rippee,
B. I. Loran, and W. J. Mindheim*

INTRODUCTION

Environmental factors were an extremely important influence on the study recently completed by The Ralph M. Parsons Company for the Office of Coal Research (OCR) of preliminary design and estimated cost for a demonstration-scale plant to produce clean boiler fuels from coal.

The importance of proper environmental safeguards was considered twofold. First, the design of a demonstration-scale plant is expected to be a forerunner of many large plants producing clean fuels from coal; therefore, the advantages of good environmental protection elements in the design could be magnified many times nationwide. Second, a large body of opinion maintains today that environmental protection and efficient energy production are natural enemies. Since both environmental protection and coal conversion are major national goals, the validity of this widely held opinion would pose a substantial problem to both national programs.

In Parsons role as Technical Evaluation Contractor to the Office of Coal Research, we found that the environmental protection objectives, as presently known or anticipated by pending legislation, can probably be achieved with appropriate expenditure of money and effort.

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Our approach to a discussion and current assessment of environmental factors in coal liquefaction centers on a brief description of the preliminary design for a complex to liquefy 10,000 tons/day of coal. This paper discusses its expected effluent streams and the probable methods of treating them in order to create an environmentally acceptable facility.

The discussion also includes best judgment estimates of quantities and compositions of certain effluent streams, and our recommendation that coal liquefaction pilot plants emphasize further environmental research and development to ensure use of the most effective treatment methods when commercial plants are built.

The design basis of our presentation uses Illinois No. 6 coal to produce two grades of boiler fuels plus lesser quantities of naphtha and by-product sulfur. The design was developed as a part of our assignment from the OCR. Reports describing the results have been published by the OCR (ref. 1). Therefore, the process description presented here is brief, and is chiefly intended to show principal sections of the coal conversion complex pertinent to the discussion of environmental factors.

PROCESS DESCRIPTION

The process configuration is depicted in the block process flow diagram shown in figure 1. This clean boiler-fuel facility consists of (1) a coal preparation section, (2) a coal liquefaction section, and (3) a gasification section. This complex is designed to produce two low-sulfur liquid fuels, sufficient to supply a 600-megawatt power plant. Some naphtha and by-product sulfur are also produced. The light hydrocarbons formed are burned as plant fuels.

COAL PREPARATION, DRYING, AND GRINDING

Run-of-the-mine coal is stockpiled and prepared for plant feed. Preparation of coal feed consists of a washing plant where a series of jigs, screens, centrifuges, cyclones, and a roll crusher produces washed minus 1-1/4 inch coal. Refuse from this operation is returned to the mine area for burial. Fine refuse is pumped to settling ponds for further treatment. The crushed coal is then dried in a flow dryer and reduced to minus 1/8 inch in pulverizers for dissolver feed.

LIQUEFACTION PROCESS

Feed to the liquefaction section consists of minus 1/8-inch coal as a 50%-by-weight slurry in a recycle solvent, which is fed to reactors where it is contacted with reducing gases at about 850°F and 1,000 psig. The gas phase of the reactor discharge is largely recycled while the solid phase is separated from the liquid phase by filtration. The resulting filter cake serves as feed to the gasification section for syngas production.

The liquid-phase filtrate produced in the filtration operation is further separated by fractionation into an overhead naphtha stream, a distillate light boiler fuel, and a residual fuel oil. Further hydrogenation of the distillate fuel produces acceptable low-sulfur fuels for boiler firing.

Gases produced in the various units are combined and fed to the acid-gas-removal plant, where carbon dioxide and hydrogen sulfide are removed by scrubbing. The hydrogen sulfide is converted to sulfur in sulfur recovery plants. Carbon dioxide is vented to the atmosphere.

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GASIFIER PLANT

Wet filter cake from the liquefaction process is fed to a slagging, suspension-type gasifier where it reacts with steam and oxygen at 3,000°F and 200 psig pressure. The carbonaceous material is gasified and produces primarily synthesis gas (carbon monoxide and hydrogen). An on-site oxygen plant supplies the required oxygen for this operation.

Most of the cooled syngas is treated for hydrogen sulfide removal and fed directly to the coal liquefaction section of the plant. Syngas not sent directly to the liquefaction section undergoes shift conversion, carbon dioxide removal, and methanation to produce a high-purity, hydrogen-gas stream, which is used in hydrogenation of the light distillate and naphtha product streams produced in the liquefaction section.

An overall material balance is shown in figure 2. The 10,000 tons of coal feed are converted into five products. Salable products are 1,440 tons/ day of 0.2% sulfur liquid fuel oil, 2,920 tons/day of heavy liquid fuel at 0.5% sulfur, 270 tons/day of naphtha with 1 ppm of sulfur, and 320 tons/ day of sulfur. The 2,140 tons/day of plant-produced fuel gas and a small amount of heavy liquid fuel oil are burned for plant operation. The remaining feed streams consist of 1,980 tons/day of oxygen and 21,760 tons/day of water.

Major process waste streams shown consist of (1) 19,430 tons/day of waste gases, (2) 6,390 tons/day of waste water, and (3) a solids waste stream consisting primarily of 710 tons/day of gasifier slag. Each of these categories is discussed in the following sections.

GASEOUS EFFLUENT

Gaseous process waste streams exhausted to the atmosphere are generated in various sections of the plant. These streams are shown in figure 3, which again depicts the plant process with highlights of gaseous emission streams. Principal gas streams leaving the complex are from the oxygen plant, CO_2 removal unit, sulfur plant stack gas, and the combustion gases resulting from fired heaters in the liquefaction and steam generation sections. Off-gases from the gas turbines utilized for power generation are also present.

Figure 4 summarizes the exhaust gas streams and their thermal contents that are expelled from the plant complex. Combustion gases amount to about 90% by volume of the total plant gas emission. A total of 990 million cubic feet/day of combustion exhaust gas containing about 15 billion Btu/day is exhausted to the atmosphere. Contaminants will consist of sulfur dioxide and nitrogen oxides. When firing with the low-Btu gas produced in the plant, contaminant concentrations will range from about 4 to 15 ppm of sulfur dioxide and 50 to 100 ppm of nitrogen oxides. The small amount of fuel oil required to supplement the low-Btu gas firing for plant power needs contributes about 2.2 million cubic feet/hour of combusion gases containing about 80-100 ppm of sulfur dioxide and 100-150 ppm of nitrogen oxides.

Other waste gases exhausted to the atmosphere consist of the oxygen plant exhaust, sulfur recovery plant tail gas, and the carbon dioxide waste stream from the CO_2 removal unit. It would be possible to recover an additional 2,260 tons/day of nitrogen and rare gases from the oxygen facilities if area sales justify costs for their recovery. The same is true for the carbon

dioxide waste stream from the CO_2 removal unit, which amounts to about 14.3 million cubic feet/day of gas containing about 99% carbon dioxide.

Waste gas effluent from the sulfur recovery plant would be about 32.4 million cubic feet/day at 93°F. Hydrogen sulfide content of this stream during normal operation is expected to be less than 5 ppm. The main constituent of the gas stream is 72% nitrogen. The remainder is primarily carbon dioxide.

In summary, approximately 1 billion cubic feet/day of various gas streams from the complex are exhausted to the atmosphere. All gaseous waste effluent streams meet applicable standards. Fuel combustion gases exhausted will meet ambient air quality standards for nitric oxide (NO_x) and sulfur dioxide (SO_2); this is also true for particulate (fly ash) entrained in the gases since primarily gaseous fuels are used. When fuel oil is used to supplement gaseous fuel, particulates are estimated at about 39 ppm, which meets ambient air quality standards. The rate of NO_x production by various plant fuel sections is a function of maximum flame temperature and retention time. Furnace designs shall be such that exit combustion gases shall meet the nitrogen dioxide (NO_2) standards. The gas waste effluent stream from the sulfur recovery unit is designed to operate normally at about 5 ppm of hydrogen sulfide, well within standards.

LIQUID EFFLUENT

Figure 5 is a flow diagram showing the major aqueous waste water streams leaving the plant complex. Approximately 532,000 pounds/hour of waste water are discharged from the complex, or about 1,060 gallons/minute. Cooling tower blowdown is slightly more than one-half of the total, or about 600 gallons/minute.

Sanitary waste water, boiler blowdown, treated oily water, and stripped plant sour water make up the remainder of the plant complex waste water stream.

Process means have been provided for stripping nonphenolic process water, and this stripped water is returned to process for reuse. Also, stripped waste phenolic water effluent, which contains the greatest number of pollutants, will average about 40 gallons/minute. This stream joins the sanitary waste, treated oily water, cooling tower and boiler blowdown streams along with backwash water from demineralizers and sand filters. This combined stream undergoes final treatment in the aerated lagoon and bio-pond before leaving the complex.

Cooling tower and boiler blowdown streams are expected to contain not greater than 15 ppm of phosphate, 10 ppm of chromate, and 5 ppm of zinc.

Table 1 summarizes the estimated waste water treatment data and contaminants in the effluent stream leaving the complex.

The total oil in the process waste stream is expected to consist of 80% by weight of naphtha and 20% acid oil, which amounts to about 5 ppm TOC feed. The COD feed is estimated at a level of about 150 ppm with a BOD level of about 40 ppm.

The aerated lagoon operation is expected to provide reduction of 96% of the inlet sulfide concentration; also 94% of ammonia, 88% of acid oil, 75% of BOD, 75% of suspended solids, 95% of phenols, 69% of COD, and 99% of phosphates. The aerated lagoon is expected to handle most of the impurities in the waste streams of the coal-conversion complex based on a flow of water from the phenolic sour water stripper of 40 gallons/minute into the aerated lagoon. However, it

is possible that phenol and heavy metals may still exceed local or state standards. In this case, they will be further reduced by adding an activated sludge plant prior to final bio-pond treatment or extending the retention time and providing more aeration to the bio-pond. The final design decision will be based upon data obtained from the pilot plants.

Dissolved impurities from the cooling tower and boiler blowdown streams are stable and will not be destroyed by either impounding or aeration. However, it is possible to eliminate chromates by utilizing organic and biodegradable cooling water inhibitors. These inhibitors are normally not as economical or effective as chromates. Provision has been made for pretreatment of these streams in the neutralization pit should it be necessary to precipitate impurities prior to pumping to the aerated lagoon.

SOLID WASTES

The block flow diagram of figure 6 shows the types of waste solids generated by the complex. Major solid wastes are produced during (1) pretreatment of the run-of-mine coal and (2) gasification of the liquefaction filter cake to produce syngas. Additional solids of lesser quantity also requiring disposal are various spent catalysts generated in the hydrogenation, shift reaction, methanation, and tail gas sections. After being rendered inert, these spent catalysts, which have a lifetime of 2 to 3 years, will be disposed of by backhaul and fill in the mined-out coal areas.

In the coal preparation plant, reject material from the primary coal breaker amounts to about 450 tons/hour. This material is combined with the double-deck screen reject, about 88 tons/hour, and conveyed to a truck loading bin. Trucks transport the waste material to the coal mine for burial in mined-out areas.

This solid consists mainly of low-grade coal and shale and is about minus 3 inches in size. The thickener underflow, which is a fine reject material of minus 1/16 inch in size, is pumped to a tailings pond for solids recovery and recycle of the decanted water to the coal preparation plant. These solids also consist primarily of low-grade coal and shale.

Gasifier slag produced is approximately 710 tons/day. This material will be dewatered and conveyed to a truck loading bin for transport to the mined-out areas of the coal mine for burial. The material will probably be utilized later as an inert additive in the manufacture of cinder blocks.

NOISE POLLUTION

Figure 7 shows possible plant and equipment areas suspected of noise pollution. The Occupational Safety and Health Act of 1970 regulates the amount of "weighted" noise to which a worker can be exposed, in order to protect him from ear damage. Local code usually regulates the amount of noise, in decibels, that an industrial plant can generate above the normal ambient background level of the community, measured at the property line. Noise control is an integral part of the layout and design of coal conversion plants. Special attention during equipment design and engineering layout will be given to fans and compressors, gasifiers, fired heaters, and gas turbine areas to minimize noise-source levels and any excessive noise radiation effect on plant personnel.

Equipment vendors will be requested to show evidence that installed equipment will meet noise level requirements. However, noise from equipment components may not represent the total sound level, including all equipment items, motor drives, piping or ductwork, and other associated equipment. Added to

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these factors are reverberations from adjacent equipment, buildings, and sound interferences from different sound sources. Consequently, total engineering plant and equipment layout design will play an important part in lessening plant noise level.

DEVELOPMENT PROGRAM RECOMMENDATIONS

Past experience and judgment superimposed on the preceding brief summary and analysis led us to recommend that further coal liquefaction and gasification research determine the presence or absence of the constituents shown in Table 2. If present, they are expected to occur in minor concentrations, but will require proper treatment facilities. Availability of this added information will further improve reliability of the plant's environmental control and monitoring systems.

REFERENCE

1. Demonstration Plant - Clean Boiler Fuels From Coal - Preliminary Design/ Capital Cost Estimate, R&D Report No. 82, Interim Report No. 1, Vols. I and II, prepared by The Ralph M. Parsons Company for the United States Department of the Interior, Office of Coal Research.
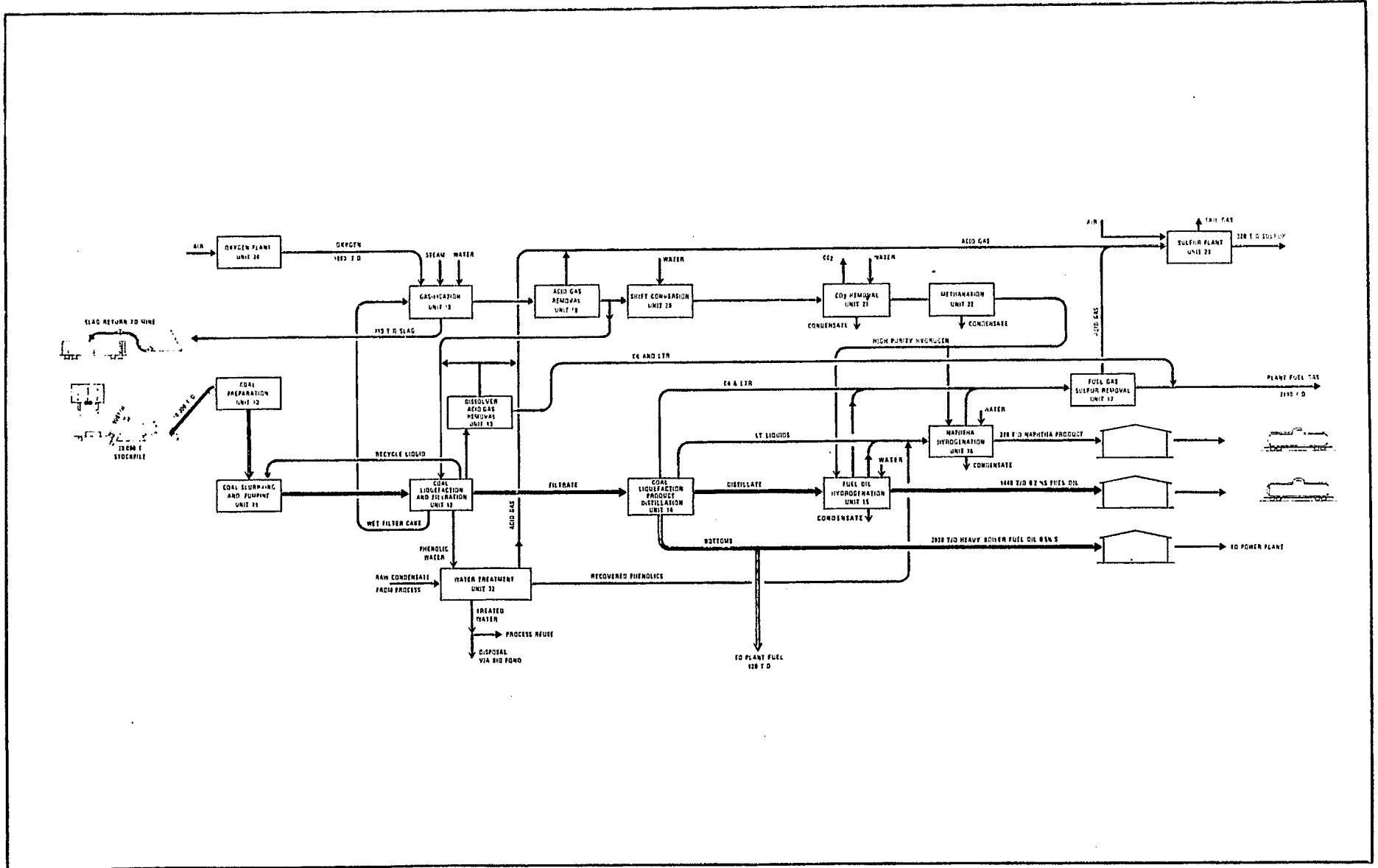
Figure 1 - Demonstration Plant
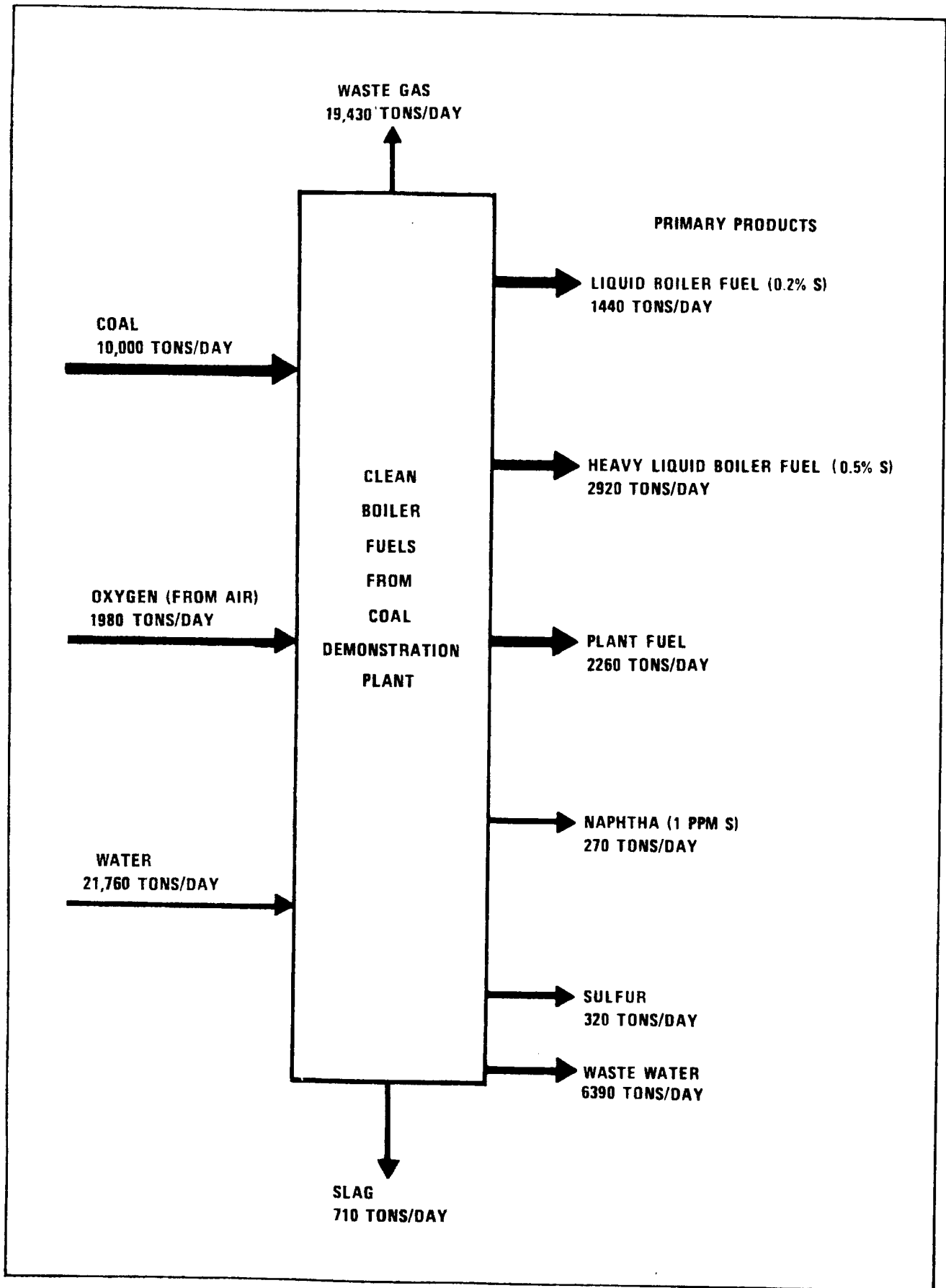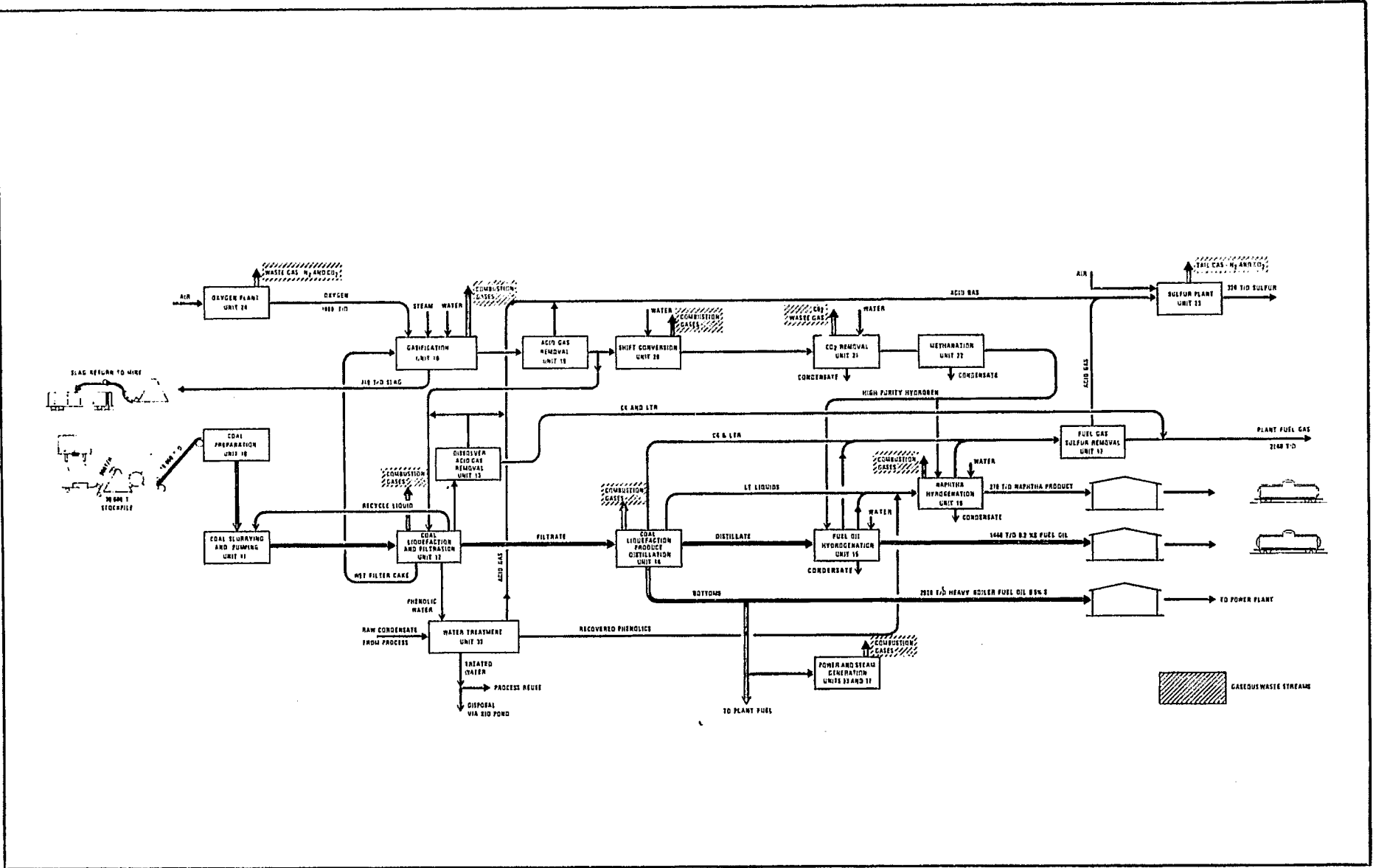Clean Boiler Fuels From Coal
Process Block Flow Diagram

WASTE GAS
19,430 TONS/DAY

PRIMARY PRODUCTS

LIQUID BOILER FUEL (0.2% S)
1440 TONS/DAY

COAL
10,000 TONS/DAY

HEAVY LIQUID BOILER FUEL (0.5% S)
2920 TONS/DAY

CLEAN
BOILER
FUELS
FROM
OXYGEN (FROM AIR)   COAL
1980 TONS/DAY   DEMONSTRATION   PLANT FUEL
PLANT   2260 TONS/DAY

NAPHTHA (1 PPM S)
270 TONS/DAY

WATER
21,760 TONS/DAY

SULFUR
320 TONS/DAY

WASTE WATER
6390 TONS/DAY

SLAG
710 TONS/DAY

Figure 2 - Overall Material Balance

Figure 3 - Demonstration Plant
Clean Boiler Fuels From Coal
Gaseous Process Waste Streams

Inputs:
- COAL — 10,000 TONS/DAY
- OXYGEN (FROM AIR) — 1,980 TONS/DAY
- WATER — 21,700 TONS/DAY

CLEAN BOILER FUELS FROM COAL DEMONSTRATION PLANT

Outputs:
- COMBUSTION GASES
- OXYGEN PLANT UNIT 24 WASTE GAS
- SULFUR RECOVERY PLANT TAIL GAS
- CO_2 REMOVAL, UNIT 21 WASTE GAS
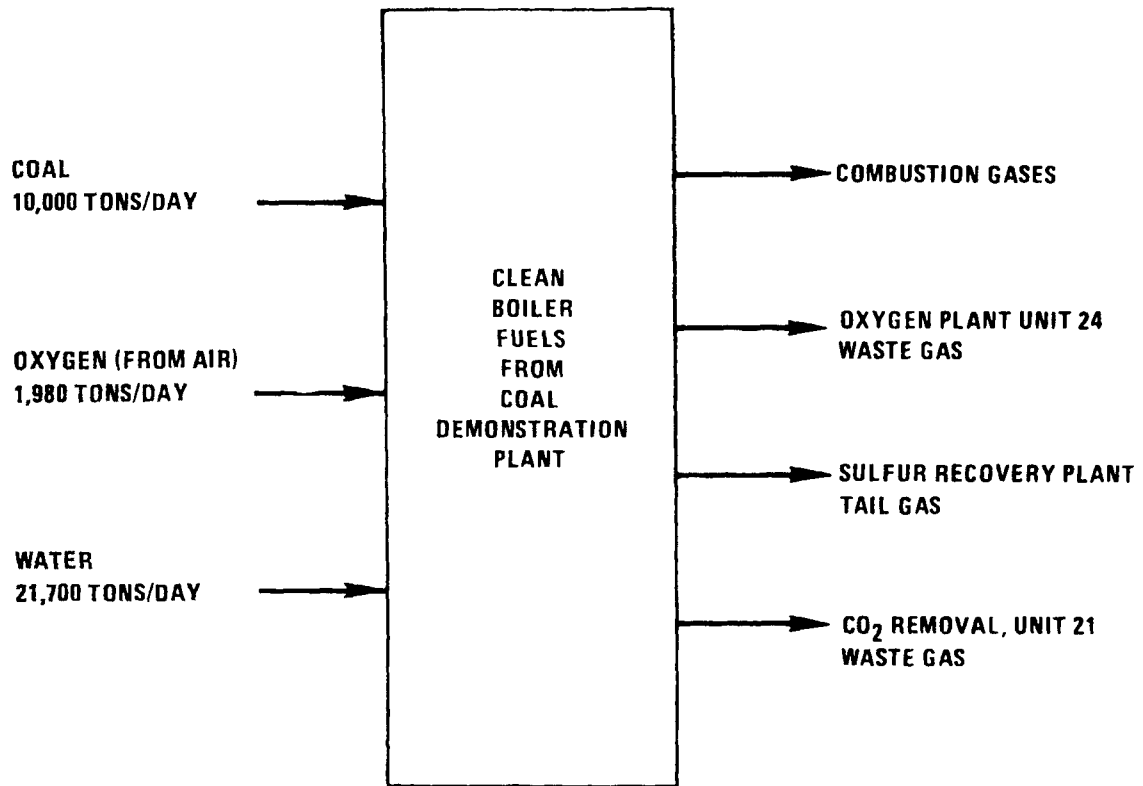
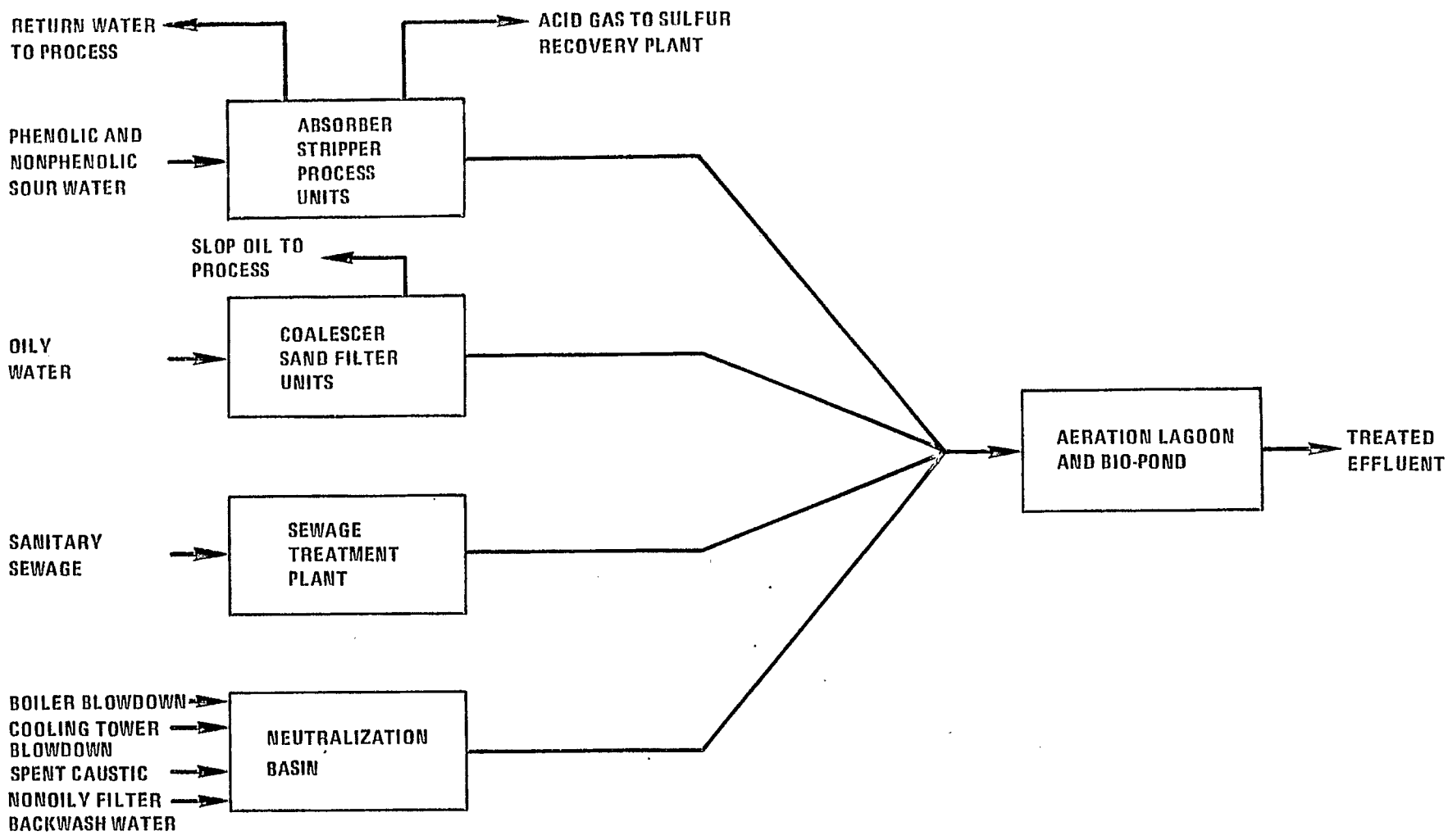| WASTE GAS STREAM	COMPOSITION	OUTPUT, CUBIC FEET/DAY (MILLIONS)	CONTENT, BTU/DAY (MILLIONS)	MAJOR CONTAMINANT
COMBUSTION GASES 1. FUEL GAS	32% O_2, 9.4% CO_2, 15.6% H_2O, 71.3% N_2	935	14,150	4-15 ppm SO_2 50-100 ppm NO_x
2. FUEL OIL	3.3% O_2, 10.8% CO_2, 12.7% H_2O, 73.2% N_2	54	850	80-100 ppm SO_2 100-150 ppm NO_x 35 ppm PARTICULATES
OXYGEN PLANT UNIT 24	N_2 AND RARE GASES	64	NIL; AMBIENT CONDITIONS	NONE
SULFUR REMOVAL PLANT TAIL GAS	72% N_2; REMAINDER CO_2	32.4	NIL; AMBIENT CONDITIONS	10 ppm max H_2S
CO_2 REMOVAL UNIT 21	99% CO_2	14.3	NIL; AMBIENT CONDITIONS	NONE

Figure 4 - Gaseous Waste Process Streams

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Figure 5 - Demonstration Plant - Clean Boiler Fuels From Coal
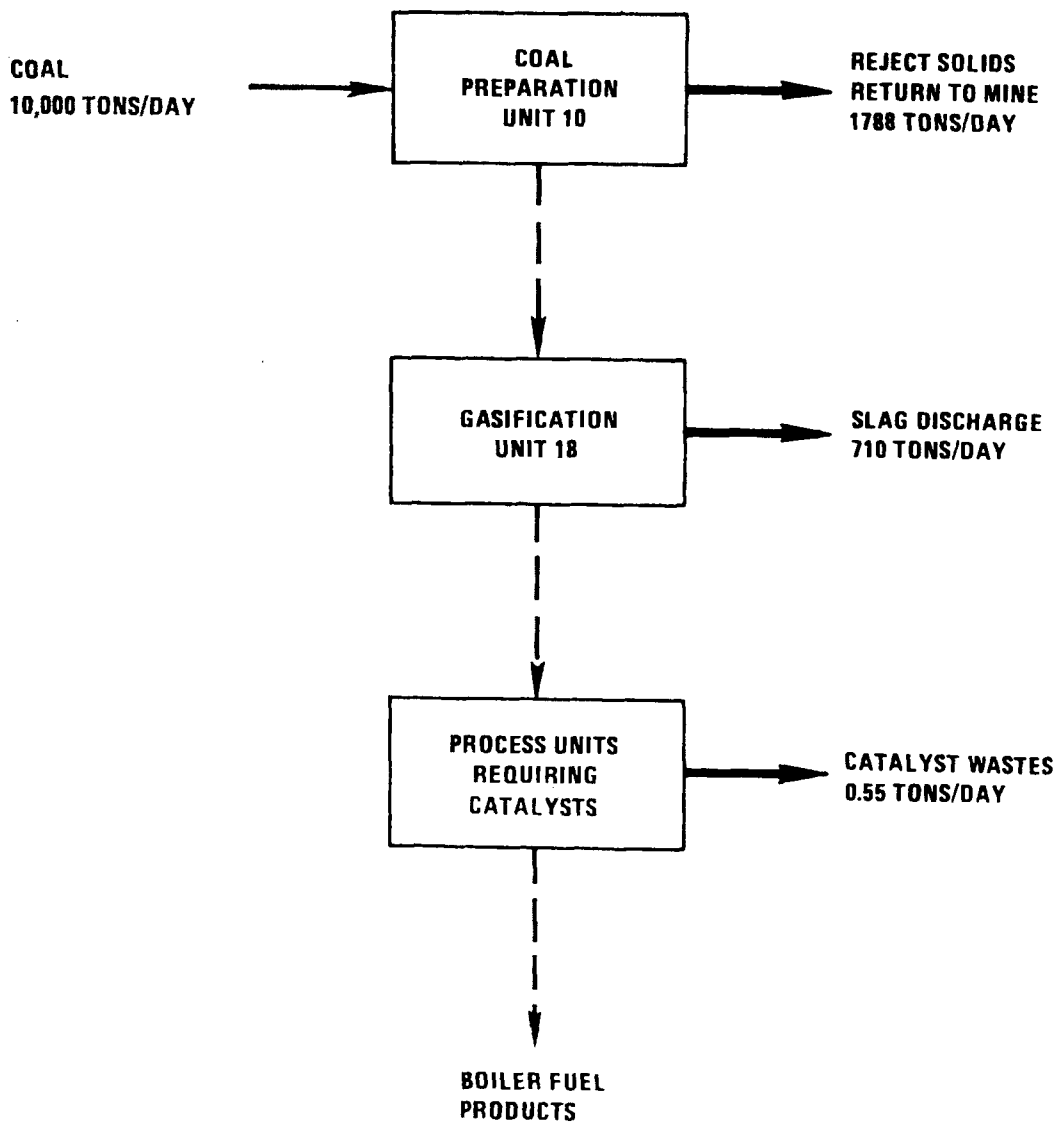Major Aqueous Waste Water Streams

COAL
10,000 TONS/DAY → **COAL PREPARATION UNIT 10** → REJECT SOLIDS
RETURN TO MINE
1788 TONS/DAY

GASIFICATION UNIT 18 → SLAG DISCHARGE
710 TONS/DAY

PROCESS UNITS REQUIRING CATALYSTS → CATALYST WASTES
0.55 TONS/DAY

BOILER FUEL
PRODUCTS

Figure 6 - Demonstration Plant - Clean Boiler Fuels From Coal
Major Solid Waste Streams
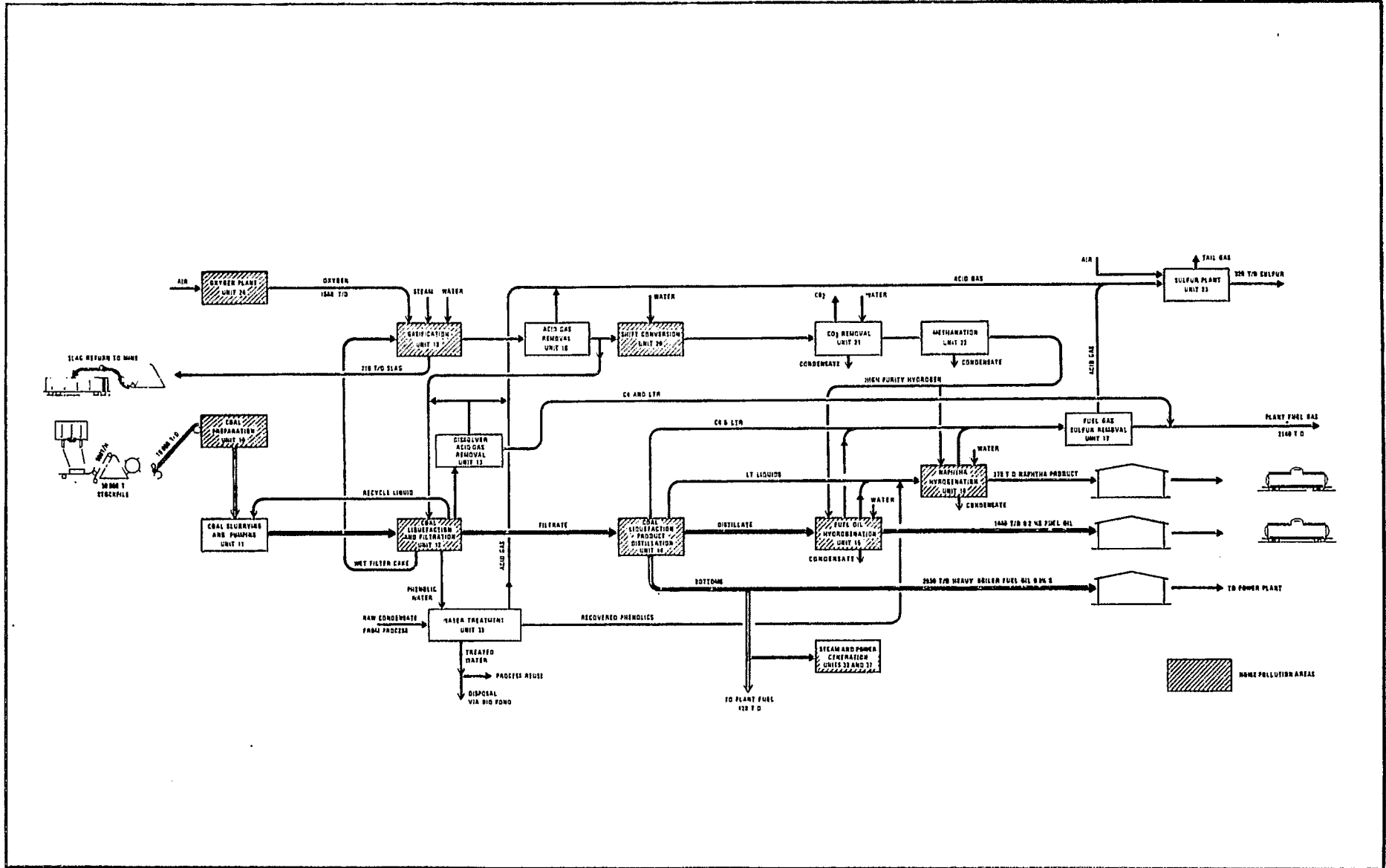
Figure 7 - Demonstration Plant
Clean Boiler Fuels From Coal
Unit Areas Possible Noise Pollution

Table 1 - Estimated Waste Bio-Pond Effluent Concentrations
for Demonstration Plant

| CONSTITUENTS | BIOLOGICAL CHARGE | | BIOLOGICAL EFFLUENT | | STATE REQUIREMENT |
	LB/DAY	PPM	LB/DAY	PPM	PPM
SULFIDE	1.48	0.12	0.06	0	—
AMMONIA	24	1.88	1.45	0.11	2.5
OIL	72	5.63	8.64	0.68	1.0
TOC	60	4.69	—	—	—
BODs	538	42	134.5	10.5	20
SS	660	51.6	165	12.9	25
PHENOL	96	7.5	4.8	0.38	0.3
COD	1,920	150	576	45	—
PHOSPHATE	145	11.3	1.45	0.11	1.0 as P
PH	6-9	6-9	6-9	6-9	5-10
CHROMATE	91	7.1	91	7.1	0.05 as CrO_4
ZINC	45	3.5	45	3.5	1.0
COLIFORM ORGANISM		15/100 ml		15/100 ml	400/100 ml

TOTAL ESTIMATED FLOW TO BIO-POND
1060 GAL/MIN $\approx$ 12.8 MILLION LB/DAY

Table 2 - Recommended Additional Contaminant Research Program
for Coal Liquefaction Plants

COMPOUND	EXPECTED TO OCCUR IN	REMARKS
AMMONIA (NH_3)	BOTH GASIFICATION AND LIQUEFACTION	ASSUME PRESENT; QUANTITY NEEDS VERIFICATION
HYDROGEN CYANIDE	BOTH GASIFICATION AND LIQUEFACTION	ASSUME PRESENT; QUANTITY NEEDS VERIFICATION
THIOCYANATES	BOTH GASIFICATION AND LIQUEFACTION	PRESENCE SUSPECTED; NEED DATA
PHENOLS	LIQUEFACTION	PRESENT; QUANTITY NEEDS VERIFICATION
ORGANIC ACIDS ALDEHYDES AND KETONES	LIQUEFACTION	PRESENT; QUANTITY NEEDS VERIFICATION
METAL SULFIDES	LIQUEFACTION	PRESENCE SUSPECTED; NEED DATA
MERCAPTANS	LIQUEFACTION	PRESENCE SUSPECTED; NEED DATA
CARBON DISULFIDE CARBONYL SULFIDE	BOTH GASIFICATION AND LIQUEFACTION	PRESENT; REMOVED IN GAS PURIFICATION STEPS; QUANTITY NEEDS VERIFICATION
COAL-TRACE ELEMENTS (Be, F, As, Hg, AND Pb)	BOTH GASIFICATION AND LIQUEFACTION	GASIFICATION DATA AVAILABLE INDICATES PRESENCE; LIMITED DATA AVAILABLE ON LIQUEFACTION PROCESS

Gaseous Environmental Factors in Coal Pyrolysis Plant Design

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The gaseous environmental factors of a conceptual commercial COED coal pyrolysis plant
are discussed. The COED process, which converts coal into synthetic crude oil and, in
addition, produces gaseous fuel which can be utilized for electric power generation and
elemental sulfur, is briefly reviewed. The removal of sulfur and particulates from the fuel
streams generated, the sulfur balance of the conversion process, and the quantity and types
of gases or aerosols projected to be vented to the air are described. Estimated emissions are
compared with applicable standards and found capable of meeting the present and
projected regulations. Possible effects from carbon dioxide emissions are briefly considered.

Gaseous Environmental Factors in Coal Pyrolysis Plant Design

B. I. LORAN   **J. B. O'HARA**   **N. E. JENTZ**   **H. F. HINCKS**

INTRODUCTION

Coal is an abundant resource in the United States. Greater coal use will provide a major contribution to a future indigenous U.S. energy supply.

However, coal cannot directly replace all other fuels such as vehicle fuels. Coal movement from mine to the place of utilization is expensive because of its physical nature as well as the weight of its ash and moisture content. Coal combustion can also produce more nitrogen oxides because many of the combustion modification techniques used for liquid and gaseous fuels are not applicable to coal. Furthermore, when burning high-sulfur coals, such as many Eastern coals, amounts of sulfur dioxide are released which can be deleterious to human health and injurious to plants and materials.

These disadvantages can be largely eliminated by converting coal to liquid and gaseous forms. One means of doing this is by the COED pyrolysis process developed under sponsorship of the Fossil Energy Department of the Energy Research and Development Administration (ERDA-FE). A COED pilot plant operated by the FMC Corporation has now been functioning for more than 5 years. The Ralph M. Parsons Company, active in assisting ERDA-FE in its program to speed the development of viable, commercial coal-conversion technology, has completed work on a conceptual design for a commercial plant based on the COED pyrolysis process. This plant will produce synthetic crude oil and, in addition, gaseous fuel utilized for electric power generation and elemental sulfur. We gratefully acknowledge the support and guidance of ERDA-FE in our work.

OBJECTIVES

It is the purpose of this paper to describe the gaseous environmental factors of a commercial COED plant and the processes and operating procedures required to assure environmental acceptability of the plant.

Outline of the Process

While complete conceptual design of a commercial COED plant is described in a separate report, some process description is necessary for orientation purposes.

As conceived, the plant will be located adjacent to a coal mine in the Eastern Region of the Interior (coal) Province of the United States. The design is based on use of high volatile C bituminous coal, with the typical properties shown in Table 1.

The block flow diagram in Fig. 1 depicts the conceptual design. The plant includes facilities to crush and wash the coal to minus 1/6-in. size, then dry it with hot process gas. Coal is subsequently pyrolyzed in a series of three fluidized beds, with heat for the pyrolysis process provided by gasification with oxygen and steam of the residual char. Oil condensed from the pyroly-

Table 1 Typical Properties of Design Coal (Data in Weight Percent Average)

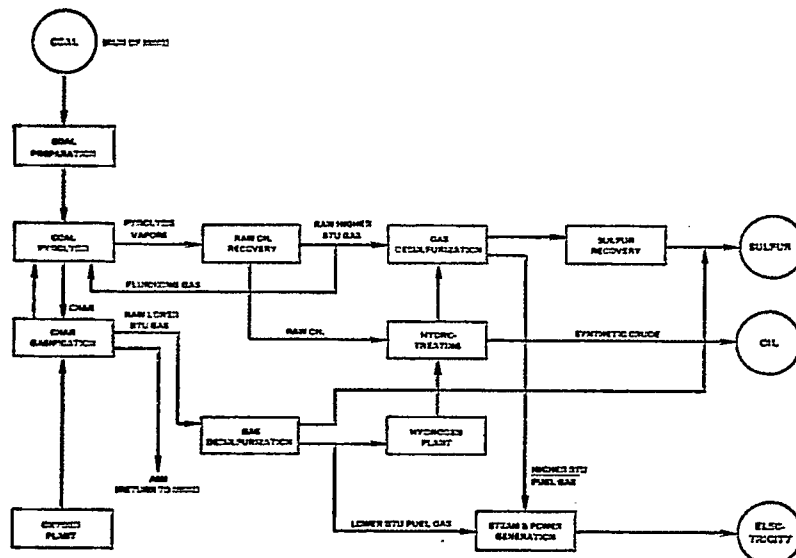| Average Proximate Analysis (Plant Feed)		
Fixed Carbon	53.6	(MAF Basis)*
Volatile Matter	46.4	(MAF Basis)
Moisture	10.5	(Wet Basis)
Ash	12.2	(Dry Basis)
Ultimate Analysis (MAF Basis)		
Carbon	78.6	
Hydrogen	5.4	
Nitrogen	1.5	
Sulfur	4.3	
Oxygen	10.2	
	100.0	
*MAF = Moisture and Ash Free		

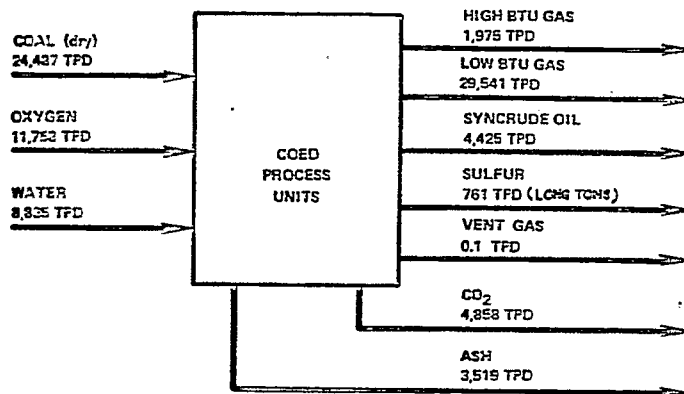Fig. 1 Block flow diagram, conceptual design, commercial COED plant

Fig. 2 Typical overall material balance (TPD = tons per day; 1 ton = 0.907 metric ton)

sis vapors is filtered to remove suspended solids, then hydrotreated to remove sulfur, nitrogen, oxygen, and hydrocarbon unsaturation. Higher Btu pyrolysis gas is desulfurized and utilized for steam and power generation. Lower Btu gas obtained from gasification of the residual char is also desulfurized, then used in the manufacture of hydrogen and for steam and power generation.

The overall material balance, based on a typical specific feed coal analysis, is shown in Fig. 2. In terms of input and output products for this sample coal feed, the plant converts 25,000 tons (22,675 metric tons) of coal per day into 28,000 bbl (4.4 mm liters) of low-sulfur synthetic crude oil, 850 MW of electric power, 760 tons (689 metric tons) of sulfur. An

artist's concept of the combined clean fuel/power facility is shown in Fig. 3.

Air Pollution Abatement

One of the major benefits of the COED pyrolysis process is that high sulfur coals are converted to ecologically acceptable fuels with negligible sulfur and ash contents. The fuels produced are also more adaptable than solid coal to combustion modification techniques used to decrease the production of nitrogen oxides.

Air pollution control is, therefore, achieved by cleaning the COED-produced fuel before combustion. This involves handling a relatively small volume of gas and dealing mainly with a sulfur species, hydrogen sulfide, which can be readily removed and converted to elemental sulfur by
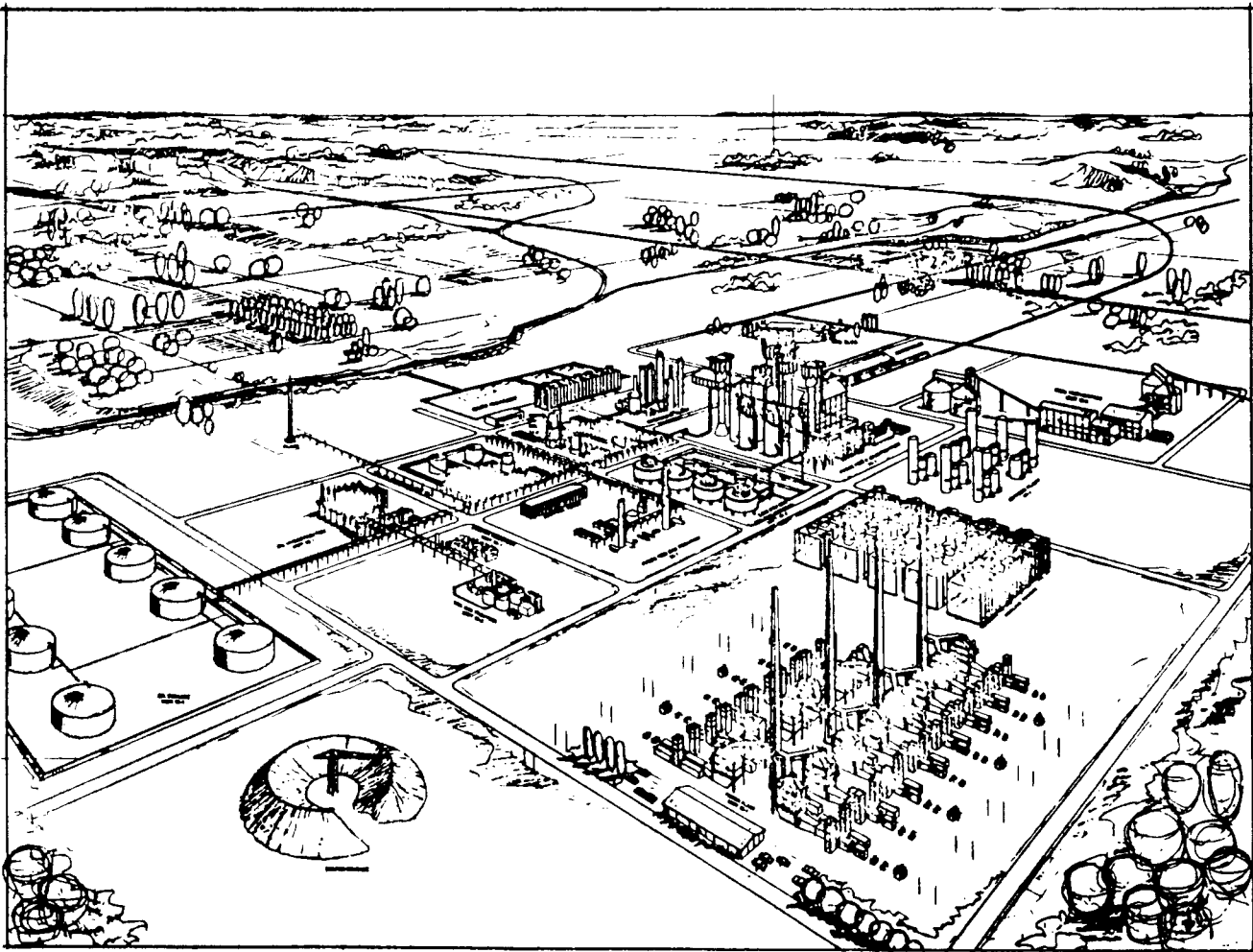
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Fig. 3 Artist's concept of combined clean fuel/
power facility COED process

proven means.

Most gases generated during the coal con-
version process are the desired fuel gases. For
the most part, inert gases (nitrogen and carbon
dioxide) are vented to the air. The major air
pollution abatement effort is aimed at desulfur-
izing the fuel streams to make them environmental-
ly acceptable.

Fugitive particulate emissions from coal
sizing and handling and from residual ash disposal
(char gasifier unit) are prevented from becoming
airborne by maintaining a wet condition when not
in a closed system.

The COED commercial plant as conceived
produces three fuel streams from coal: a liquid
stream (the pyrolysis oil) and two gaseous streams.
Of these two gaseous streams, the pyrolysis gas
stream has a higher Btu content (approximately
890 Btu/scf, or 7920 kcal/cu m HHV). The char
gasifier gas stream has a lower Btu content (ap-

proximately 250 Btu/scf or 2224 kcal/cu m HHV).
The desulfurization of the gaseous fuel streams
is outlined in Fig. 4, which also shows the na-
ture and amount of all streams vented to the air.

Raw COED oil is generated as a vapor in the
pyrolyzers along with gaseous products. The mix-
ture leaves each of the pyrolyzers through a cy-
clone separator which removes entrained dust down
to a particle size of about 10 microns. Gas and
oil vapor from the three pyrolyzers are conducted
to a condensation tower where they are cooled by
heat transfer down to 130 F (54 C).

Condensed oil is pressure-filtered, then
treated with hydrogen at 700 F (370 C) and 2400
psig (163 atm) to reduce sulfur content by 95 per-
cent (from 2.0 to 0.1 percent), nitrogen content
by 94 percent, the oxygen content by 90 percent
(approximate values). At the same time, API
gravity of the oil is raised from -5 to +25 dg.
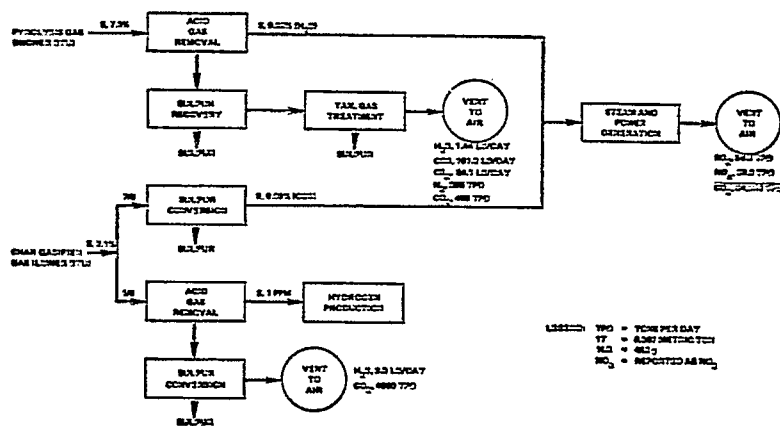The nitrogen content of the pyrolysis oil from the

Fig. 4 Block flow diagram, air pollution abatement

design coal is sufficiently high so that the hydrogen sulfide released in hydrotreating is tied up as ammonium hydrosulfide. The latter is dissolved in injected water and removed from the hydrotreater condensing train as an aqueous solution that can be separated into salable ammonia and hydrogen sulfide directed to the sulfur conversion unit. The hydrotreater off-gas is sufficiently low in sulfur to be used as fuel and is combined with the higher Btu fuel gas.

The pyrolysis gas separated from the oil vapor in the condensation tower is washed countercurrently with an amine to remove carbon dioxide and more than 99 percent of the hydrogen sulfide present. The heated amine solution releases hydrogen sulfide and carbon dioxide as an acid gas stream which is conveyed to the sulfur recovery unit. Effluent gases from the sulfur recovery unit are further desulfurized in a tail gas treatment unit. When the effluent gases are finally vented to the air, contain approximately 1 ppm of hydrogen sulfide, 40 ppm of carbon oxysulfide, and 20 ppm of carbon disulfide. The desulfurized pyrolysis gas is used as fuel for power and steam generation.

The lower Btu gas stream from the char gasifier is purified from entrained dust down to a particle size of approximately 10 microns by a series of cyclone separators. A water scrubber removes the residual solids, then the gas is divided into two streams.

The major stream (seven-eighths) of the char gasifier gas is contacted with an alkaline solution is a sulfur conversion unit where approximately 96 percent of the sulfur present is removed, residual sulfur appearing mainly as carbon sulfide. The absorbed hydrogen sulfide is subsequently oxidized to high purity (99.9 percent)

sulfur. The desulfurized gas is used for power and steam generation (approximately 97 percent)and directly in plant utilities.

The minor stream (one-eighth) of the char gasifier gas is used for hydrogen production. This stream is desulfurized in an intermediate step between shift conversion and methanation; only a trace (1 ppm) of sulfur is left in the stream. The acid gas stream generated as a result of desulfurization is led to a sulfur conversion unit similar to the one used for the major char gasifier gas stream. This sulfur conversion unit vents to the air large amounts (4860 tpd, 4408 metric tons/day) of carbon dioxide, containing a trace (approximately 1 ppm) of residual hydrogen sulfide.

The various desulfurizing units perform the dual function of sulfur removal and wet scrubbing of streams to eliminate residual particulates which evaded the previous control devices.

The desulfurized higher and lower Btu gas streams are used as fuel for gas turbines. Each turbine is directly connected to an electric generator, and the hot exhaust gases are used for steam production in heat recovery boilers. Electric power generated is exported and used for process unit and coal mine requirements. All steam produced by the heat recovery boilers is used for process and power plant requirements.

Prior removal from the gaseous fuel streams of most particulates and sulfur assures that the power generating plant emissions are below applicable standards, as discussed later. Nitrogen oxide production is controlled by water injection to decrease the combustion temperature.

Sulfur Balance

The sulfur balance for the conceptual de-

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Table 2 Sulfur Balance (TPD)

Total Input from the Typical Feed Coal	905.0
Outputs: In the COED oil	1.7
As Elemental Sulfur from Pyrolysis Gas	177.0
As Elemental Sulfur from Char Gasifier Gas	679.0
As Sulfur Dioxide Emissions	28.4
As Reduced Sulfur Emissions	0.1
In the Ash	18.8
	905.0

Table 3 Comparison of Emissions with Standards,
Coal Gasification Plant

Pollutant	New Mexico Standards	Emissions, COED Coal Gasification Plant
Total Reduced Sulfur $(H_2S+COS+CS_2)$	100 ppm	62 ppm
Hydrogen Sulfide	10 ppm	2 ppm
Hydrogen Cyanide	10 ppm	Nil
Hydrogen Chloride/ Hydrocloric Acid	5 ppm	Nil
Particulate Matter	0.03 gr/ft^3	Nil
Ammonia	25 ppm	Nil
Gas Burning Process Boilers, Particulate Matter	0.03 lb/MM Btu, LHV	NA*
Gas Burning Process Boilers, Sulfur Dioxide	0.16 lb/MM Btu, LHV	NA*
Total Sulfur	0.008 lb/MM Btu of feed (coal) heat input, HHV	0.003 lb/MM Btu
*Not Applicable (none included in the design)		

sign of a commercial COED plant is detailed in Table 2. A total of 95 percent of the coal sulfur content is recovered as elemental sulfur. An additional 2 percent remains in the ash from the char gasifier unit.

Compliance With Source Emission Standards

Standards of Performance for New Stationary Sources for coal gasification plants have not been issued by the Federal Government. Standards somewhat related to a coal gasification process are those issued for petroleum refineries and for fossil-fuel-fired steam generators. Among the states, only New Mexico has issued specific regulations covering coal gasification plants. The standards

are more strict than either petroleum-refinery or fossil-fuel-fired steam generator Federal standards.

The New Mexico standards are compared in Table 3 with the emissions from the Parsons conceptual design of a commercial COED coal gasification plant. This comparison is shown for illustrative purposes only because, as mentioned in the foregoing, the plant, as conceived, would be located in the U.S. Eastern Interior (coal) Region. As shown in the table, all standards are met.

Projected emissions from the COED power generating plant are compared in Table 4 with Federal standards for gaseous fossil-fuel-fired steam generators (existing New Mexico standards

Table 4 Comparison of Emissions with Standards,
Power Generating Plant

Pollutant	Federal Standard	Emissions, COED Power Generating Plant
Particulate Matter	0.1 lb/MM Btu	Nil
Sulfur Dioxide	0.8 lb/MM Btu	0.332 lb/MM Btu
Nitrogen Oxides	0.2 lb/MM Btu	0.182 lb/MM Btu

do not differ from the Federal ones). It can be seen that estimated plant emissions are significantly below the standard for sulfur dioxide and meet the nitrogen oxide standard.

Carbon Dioxide Emissions

It is estimated that significant carbon dioxide emissions (on the order of 29,000 tpd, or 26,500 metric tons/day) would be generated by the COED commercial plant. It appeared desirable to investigate possible effects of these emissions. Carbon dioxide is not toxic, and the natural background concentration in the atmosphere has been estimated at 300 to 500 ppm.

Global weather modification effects have been attributed to increased carbon dioxide generation by fossil-fuel combustion. A gradual warming trend has been predicted, on the order of 0.5 C in 25 years. However, actual temperature trends have shown a cooling of 0.3 C from 1945 to the present.

On a localized scale, no micrometeorological effects due to increased carbon dioxide have been reported. Emissions from the COED facility could approximately double the average atmospheric carbon dioxide concentrations to 600 to 1,000 ppm in the vicinity of the plant. The lowest concentration at which some physiological effects (dyspnea and headache) have been observed is 30,000 ppm; therefore, no effects are expected at the levels mentioned. However, vegetable life has been reported to benefit from increased atmospheric concentrations of carbon dioxide.

CONCLUSIONS

The COED commercial plant concept increases U.S. energy resources by enabling use of a fossil-fuel, high sulfur coal, which is otherwise environmentally unacceptable. At the same time, coal is converted into liquid and gaseous physical forms, which can be used in a greater variety of applications. Desulfurization of the fuel yields sulfur at the elemental state, the most suitable for utilization and storage.

Coal conversion and removal of sulfur and particulates from product streams can be accomplished with emission of negligible amounts of air contaminants within existing and projected standards.

ENVIRONMENTAL FACTORS FOR

OIL/GAS COAL CONVERSION TECHNOLOGY

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ABSTRACT

The environmental factors of a conceptual commercial Oil/Gas
coal conversion plant are discussed. The Oil/Gas process,
which converts coal into fuel oil and substitute natural gas,
is briefly reviewed. The removal of sulfur and particulates
from the fuel streams generated, the sulfur balance of the
conversion process, and the quantity and types of effluent
streams projected to be released are described. Estimated
air emissions and aqueous effluents are compared with appli-
cable standards and found capable of meeting the present and
projected regulations. The fate of trace elements present
in the coal and occupational safety aspects are also briefly
considered.

INTRODUCTION

Development of viable coal conversion technology is a national priority. A prime responsibility for development of this technology rests with the Energy Research and Development Administration - Fossil Energy (ERDA-FE). The Ralph M. Parsons Company is assisting ERDA-FE in reaching this objective by developing preliminary designs and economic evaluations for commercial coal conversion facilities. Integral to this effort is definition of facilities and procedures to assure that environmentally acceptable plants can be designed and operated. The many coal conversion process development units and pilot plants being operated in the United States plus experience gained from related industries such as petroleum processing provide the basis for establishing environmental control facilities and operating procedures.

A conceptual design of a commercial-scale Oil/Gas plant to convert coal to both liquid and gaseous fuels has been developed under ERDA sponsorship. The gaseous fuel produced is to be pipeline gas quality, and the liquid fuels are to be of quality adequate to meet environmental protection standards at the time of their use.

The control of any contaminants released to the environment had a high priority in plant and process design. Applicable standards were used in design and engineering of the process and equipment.

OBJECTIVES

The purpose of this paper is to describe the environmental factors of a commercial Oil/Gas plant, and also the processes and operating procedures required to assure environmental acceptability of the plant.

OUTLINE OF THE PROCESS

The design criteria for a commercial Oil/Gas plant have been published; the details of the design and an economic evaluation will be described in a separate report.[1] A brief process description is presented here for orientation purposes.

As conceived, the plant will be located adjacent to a coal mine in the Eastern Region of the Interior (coal) Province of the United States. The design is based on use of high volatile C bituminous coal, containing 1.5% nitrogen and 4.5% sulfur. The simplified block flow diagram in Figure 1 depicts the conceptual design. The plant includes facilities to wash the coal, crush it to 20-200 mesh, and then dry it indirectly with steam. The Oil/Gas plant is designed for production of clean boiler fuel plus significant quantities of substitute natural gas (SNG); it therefore includes both coal liquefaction and coal gasification process steps.

Coal liquefaction will be based on data developed by the Pittsburg and Midway Coal Mining Company in their solvent refined coal (SRC) program. The SRC II mode of operation was adopted; this mode uses recycle of dissolver effluent slurry as part of the coal slurry solvent, permitting a high hydrogen uptake. The major product obtained is a low sulfur fuel oil.

High pressure steam-oxygen gasification of feed coal will be used to produce methane and a hydrogen-rich synthesis gas (syngas) product. The raw gasifier product stream will be treated to produce the hydrogen required as feed for the dissolvers and for naphtha hydrogenation. The methane will be recovered as part of the product SNG. The gasifier will be an entrained, slagging, two-stage design. It will take advantage of data published by the Bituminous Coal Research Company during the ERDA-sponsored Bi-Gas development program. The fuel gas required for process heaters and power plant boilers will be generated in a low pressure, air-blown, two-stage, slagging gasifier.

The complex will further contain units to remove acid gases consisting primarily of H_2S and convert them to elemental sulfur and environmental acceptable tail gases. Process steps will be included to separate the gas streams

into SNG, liquefied petroleum gases (LPG), and hydrogen. Liquid product
treatment will be provided to produce 0.5 wt% sulfur fuel oil and commercially
salable naphtha.

The overall material balance, based on a typical specific feed coal analysis,
is shown in Figure 2. In terms of input and output products for this sample
coal feed, the plant converts 34,700 tons of coal per day into 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.

Approximately 600 acres would be allocated for the complex site exclusive of
the coal mine. Over a 20-year project life, about 60 square miles would be
mined. An artist's concept of the Oil/Gas complex is shown in Figure 3.

AIR POLLUTION ABATEMENT

The major air pollution abatement effort is aimed at desulfurizing the gases
generated during the coal conversion process to make the fuels produced
environmentally acceptable. The desulfurization process extends to the
gaseous fuels produced for in-plant consumption, so that overall plant opera-
tions generate negligible sulfur emissions.

The air pollution abatement procedure is outlined in Figure 4, which shows the
nature and amount of all streams vented to the air; these streams consist, for
the major part, of inert gases (nitrogen and carbon dioxide). The effluent
gases as shown are vented separately to the air to identify the contribution
of specific process units. In reality, however, most streams, with the excep-
tion of the particulates from the coal drying plant and the effluents from the
process boilers, are combined into a single stack before venting to the air.

Fugitive particulate emissions from coal sizing, handling, and residual ash
disposal are prevented from becoming airborne by maintaining a wet condition
when not in a closed system. The coal grinding and drying unit is the only
source of particulate emissions. A cyclone system removes the coarse particles
from the vent streams; a subsequent baghouse system removes most of the fines.
Ground, dry coal is fed to three reactors: the process gasifier, the dis-
solver, and the fuel gas gasifier.

The process gasifier receives recycle char, steam, and oxygen in the lower
slagging section and ground coal and steam in the upper section, which con-
verts to hydrogen, carbon monoxide, carbon dioxide, methane, hydrogen sulfide,
and lesser amounts of ammonia, carbon oxysulfide, cyanides, and sulfur dioxide.
At the elevated reactor temperature, any oils or tars formed are expected to
crack to gaseous products. The gas stream produced contains entrained char
and is cooled from 1700 to 945°F through a series of heat exchangers heating
the incoming gases and producing steam. The char is then separated by a
cyclone system and returned to the gasifier. The remaining fine particles
which escaped the cyclone are removed by two dust filters capable of operating
at high temperature and pressure.

The gaseous stream is then conveyed to a shift conversion unit where the stream is enriched in hydrogen by reaction of carbon monoxide with water. The metal catalyst employed operates in a sulfided condition reached by initial reaction with the hydrogen sulfide present. Each of the three shift reactors operates at progressively lower temperature, gas cooling being provided by water spray in quench pots. Final cooling of the gas down to 100°F occurs in a series of heat exchangers and condensate separators. The quench pot/condensate separator system acts as a water scrubbing system, removing practically all traces of particulates from the gas stream. The ammonia and part of the hydrogen sulfide and hydrogen cyanide present are also removed.

The next treatment step concerns the removal of acid gases. A physical solvent process removes these gases from the main stream; then, on selective regeneration, releases a stream of hydrogen sulfide containing part of the carbon dioxide, and a stream of nearly pure carbon dioxide. The hydrogen sulfide stream is sent to the sulfur recovery plant where it is oxidized to elemental sulfur; any hydrogen cyanide present is oxidized concurrently. The carbon dioxide stream, containing some carbon monoxide (833 ppm) and hydrogen sulfide (up to 10 ppm) is vented to the air through the main plant stack, where overall concentrations of contaminants decrease on combination with other effluents. The purified gas stream, consisting mainly of hydrogen but with sizable amounts of carbon monoxide and methane present, is conveyed to the coal dissolver.

The dissolver unit receives a preheated, pressurized slurry of ground coal in coal-derived solvent and hydrogen, and generates two product phases: a gas phase and a slurry phase.

The gas phase is cooled and depressurized (recovering heat and power) and then conveyed to an acid gas removal unit where hydrogen sulfide is removed by reaction with an amine; and the traces of carbon dioxide present are removed by reaction with caustic. The acid gas stream obtained on regeneration of the amine is led to the sulfur recovery plant. The purified gas stream undergoes drying by molecular sieves and cryogenic separation, with hydrogen returned to the dissolver and hydrocarbon products fractionated to a methane-rich stream, LPG, and naphtha. Naphtha and LPG are treated to reduce the sulfur level to 1 ppm or less, while the methane-rich stream is upgraded to SNG. The SNG produced is essentially sulfur-free because a zinc oxide guard reactor removes sulfur traces prior to methanation.

The liquid slurry phase consists of liquefied coal, unreacted coal, and ash. After cooling by heat exchange and depressurization by power recovery (hydraulic turbines), the slurry is fractionated (with recovery of solvent for return to the dissolver), and then filtered to separate solid materials from liquid hydrocarbons. The solids (filter cake) are fed to the fuel gas gasifier. The liquids (fuel oil) represent the largest single product stream in the plant. This fuel stream contains 0.5% sulfur and 1 to 1.5% nitrogen: the amount of sulfur is environmentally acceptable; the amount of nitrogen present, however, may lead to increased production of nitrogen oxides on combustion with respect to crude oil-derived fuels.

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The fuel gas gasifier receives char, filter cake, air, and steam in the lower (slagging) section; coal and some additional air in the upper section; and produces primarily synthesis gas (carbon monoxide and hydrogen), plus nitrogen, carbon dioxide, hydrogen sulfide, and lesser amounts of ammonia, carbon oxysulfide, and sulfur dioxide. At the elevated reactor temperature, any oils or tars formed are expected to crack to gaseous products. The gas stream produced, leaving the gasifier at 1800°F, is separated from most of the entrained char in a cyclone system and the char is returned to the gasifier after using its heat content for filter cake drying. The gas is then cooled to 100°F through a series of heat exchangers heating the gasifier input gases and producing steam; the condensate formed contains all of the ammonia and part of the sulfides and cyanides, and is treated as described below. The cooled gas stream passes through an electrostatic precipitator, where most of the fine particulates suspended are removed, and is then conveyed to a sulfur removal unit where a redox solution converts all but 1 ppm of the hydrogen sulfide and sulfur dioxide present to elemental sulfur. At the same time, practically quantitative removal of any remaining particulates is achieved.

The cleaned low Btu (145 Btu/cu ft) fuel gas is used to satisfy in-plant energy requirements for steam generation (4/5) and process heaters (1/5). On combustion a negligible amount of SO_2 (141 lb/day) is generated by oxidation of the trace of hydrogen sulfide present. The amount of nitrogen oxides generated is also moderate, due to the flame-cooling effect of the large amount of inert gases (carbon dioxide and nitrogen) present. Combustion experiments with low Btu gas[2] show that a maximum NO_x concentration in the effluent gases of 50 ppm (as NO_2) can be expected.

The sulfur recovery plant receives three hydrogen sulfide streams, originating from the acid gas removal unit on the process gasifier train, from a similar unit on the dissolver train, and from the sour water stripping unit; 95% of the sulfur present is converted to high purity elemental sulfur, with the remaining 5% converted in a subsequent unit, the tail gas unit. The tail gas treatment involves reduction of all sulfur species to hydrogen sulfide, absorption by an alkaline solution, and oxidation to give high purity sulfur. The final vent gas contains carbon dioxide, plus traces of carbon oxysulfide (80 ppm), hydrogen sulfide (1 ppm), and carbon monoxide (412 ppm). The carbon monoxide and carbon oxysulfide concentrations decrease on mixing with the other vent gases.

In conclusion, air effluents are emitted into the atmosphere from four outlets: the coal drying plant (particulates), two process heaters (one-fifth of fuel combustion gases), and the main plant stack (all other effluents combined). The composition of the effluents emitted to the air from the outlets specified is detailed in Table 1.

Source emission standards for coal conversion plants have not been issued by the Federal Government. Among the states, only New Mexico has issued specific regulations covering coal gasification plants; these regulations can be considered for illustration purpose only. The State of Illinois, a likely candidate for a plant site, has issued standards for petrochemical process; this process is related to the Oil/Gas plant operation. The standards are as strict or stricter than the Federal standards for petroleum refining.

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Table 1. Effluents Emitted to the Air

Outlet	Gaseous Effluent	Amount	Concentration
Main Stack	Carbon Dioxide	31,024 TPD	-
	Carbon Monoxide	11.7 TPD	166 ppm
	Carbon Oxysulfide	0.5 TPD	3 ppm
	Hydrogen Sulfide	316 lb/day	2 ppm
	Sulfur Dioxide	113 lb/day	0.3 ppm
	Nitrogen Oxides	4.5 TPD	39 ppm
Process Heater 1	Carbon Dioxide	1,528 TPD	-
	Sulfur Dioxide	14 lb/day	0.4 ppm
	Nitrogen Oxides	0.6 TPD	50 ppm
Process Heater 2	Carbon Dioxide	1,528 TPD	-
	Sulfur Dioxide	14 lb/day	0.4 ppm
	Nitrogen Oxides	0.6 TPD	50 ppm
Coal Drying Plant	Particulates	0.95 TPD	-

The Illinois and the New Mexico source emission standards are compared for illustration purpose in Table 2 with the emissions from the Parsons conceptual design of an Oil/Gas coal conversion plant. As shown in the table, all estimated emissions are lower than the ones mentioned in the standards.

SULFUR BALANCE

The sulfur balance for the conceptual design of a commercial Oil/Gas plant is detailed in Table 3. A total of 95% of the coal sulfur content is recovered as elemental sulfur, with most of the remainder present in the fuel oil product. The amount adsorbed by the catalyst beds (mainly in the shift reactors) would be emitted every six months as sulfur dioxide on regeneration of the catalyst. At the temperature conditions prevailing in the gasifiers it was assumed that negligible amounts of sulfur would remain with the ash.

Table 2. Comparison of Gaseous Emissions with Illinois and New Mexico
Source Emission Standards

Pollutant	Illinois Standards, Petrochemical Plant	New Mexico Standards, Coal Gasification Plant	Gaseous Effluents, Oil/Gas Plant
Particulate Matter	81 lb/hr	0.03 gr/ft^3	79 lb/hr,[a] 0.023 gr/ft
Sulfur Dioxide	1.2 lb/MM Btu	-	1 ppm[b]
Carbon Monoxide	200 ppm, 50% excess air	-	147 ppm[c]
Nitrogen Oxides	0.2 lb/MM Btu[d]	-	0.1 lb/MM Btu
Organics (methane excluded)	100 ppm (CH$_4$ equivalent)	-	Nil
Total Reduced Sulfur (H$_2$S+COS+CS$_2$)	-	100 ppm	5 ppm
Hydrogen Sulfide	-	10 ppm	2 ppm
Hydrogen Cyanide	-	10 ppm	Nil
Hydrogen Chloride/ Hydrochloric Acid	-	5 ppm	Nil
Ammonia	-	25 ppm	Nil
Gas Burning Process Boilers, Particulate Matter	-	0.03 lb/MM Btu, LHV	Nil
Gas Burning Process Boilers, Sulfur Dioxide	-	0.16 lb/MM Btu, LHV	0.001 lb/MM Btu
Total Sulfur	-	0.008 lb/MM Btu of feed (coal) heat input, HHV	0.002 lb/MM Btu[e]

[a]From coal drying plant.

[b]66.4 tons of sulfur dioxide emitted twice a year, over 24-48 hours, on regeneration of the catalyst of each shift reactor (three reactors total). The sulfur dioxide generated on combustion of the plan fuel gas amounts to 26 tons per year. If these combined amounts were averaged out over the year, they would correspond to 0.003 lb/MM Btu/day.

[c]Value obtained on application of the 50% excess air correction to the effluent from the steam generating unit.

[d]Applies to firing of gaseous fossil fuel.

[e]Includes the sulfur dioxide emitted occasionally on regeneration of the shift reactor catalyst (see Note b above)

Table 3. Sulfur Balance (TPD)

Total Input from the Typical Feed Coal		1312.7
Outputs: As Elemental Sulfur		1252.3
In the Fuel Oil		59.9
As Carbon Oxysulfide Emissions	·	0.2
Adsorbed on Catalyst Beds		0.3
		1312.7

AQUEOUS EFFLUENTS

As conceived, the geographic area where the Oil/Gas plant would be located is the U.S. Eastern Interior (coal) Province, where an abundant supply of water is available. Most likely, one of the major rivers in this area would provide the water supply for the plant.

Based on adequate availability of water, the wastewater treatment is a combination of recycling and discharge of aqueous effluents. The most heavily contaminated streams undergo steam distillation; the organic contaminants separated are fed with steam to the process gasifier to achieve their thermal destruction. Medium contaminated streams are purified physically and biologically, then are reused for slag quenching. The lightly polluted streams are treated to make them acceptable to the environment and are then discharged to the river.

The generation and treatment of aqueous contaminants is outlined in Figure 5. Wastewater sources are listed on the left hand side of the figure, with the degree of pollution of the wastewater streams decreasing from top to bottom. The progressive treatment and disposition of the streams is also shown and approximate flow values for streams withdrawn and returned to the river are reported.

The most highly contaminated stream is the combined sour water generated as, aqueous condensates by the process gasifier, fuel gas gasifier, and coal dissolver. Major contaminants present are hydrogen sulfide, ammonium sulfide, phenols, cresols, xylenols, thiocyanates; cyanides and solids (ash and char particles) may also be present. The gaseous contaminants (hydrogen sulfide and ammonia) are removed by steam stripping. Ammonia is separated by contact with an ammonium phosphate/phosphoric acid solution, regenerated on heating, and purified to anhydrous ammonia. Hydrogen sulfide is conveyed to the sulfur plant for conversion to elemental sulfur. Under the acidic conditions of the

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sour water, any cyanides present would be volatile (hydrogen cyanide), and therefore be stripped with the hydrogen sulfide and conveyed to the sulfur plant to be destroyed by thermal oxidation. The stripped aqueous stream is conveyed to a high temperature steam drum in the process gasifier unit, where the organic contaminants volatilize and are fed with the steam to the gasifier to undergo thermal oxidation. The blowdown from the steam drum is vaporized on cooling the product gas prior to shift conversion; any solids present are removed by filters on the condensate return lines.

Oily water streams produced during plant operation or collected as contaminated runoff from process areas are conveyed to a gravity separator. The water phase is further purified in an oily water pond, with the effluent used for slag quench. The combined oil fractions are led to a separator, with the oil phase returned to the fractionation unit for product recovery. The aqueous phase is combined with the effluents from the slag settling basin and the sewage treatment plant and treated in a bio-oxidation pond, which also provides firewater; the effluent from the biopond is also used for slag quench.

The cooling tower blowdown stream is the largest in volume and is only lightly contaminated by corrosion inhibitors (zinc salts and inorganic phosphates). This stream is combined with deionizer wastes (containing mainly inorganic salts) and boiler blowdown, also lightly contaminated by corrosion inhibitors. After neutralization, it is treated with lime in a settler-clarifier. The lime sludge, containing most of the zinc and phosphates, is disposed of in a landfill, while the treated stream is returned to the river, together with any runoff collected from clean areas. If required by specific site conditions, a final polishing pond may be added for removal of suspended solids from the runoff collected.

No aqueous effluent standards specifically addressed to coal conversion plants have been issued by the Federal government or by state legislatures. Federal standards issued for petroleum refining are somewhat related to an Oil/Gas process. Average attainable concentrations which were the base for such standards[3] are reported in Table 4, together with the corresponding values for the aqueous effluents estimated for the Oil/Gas plant. As shown in the table, these values are either the same or lower than the Federal parameters.

The State of Illinois has issued aqueous effluent standards applicable to all sources discharging to the natural waters of the state. These standards are reported for illustration purpose in Table 5. All Oil/Gas plant effluents estimated are either meeting or lower than such standards.

SOLID WASTES

The Oil/Gas plant generates two main types of solid waste materials: ash and slag from the gasifiers and sludge from various wastewater treatment units. Present plans call for burial of the slag with the mine spoils and landfill disposal of the ash and sludge.

Table 4. Comparison of Aqueous Effluents with
Federal Petroleum Refinery Standards*

Parameter	Federal Standards Petroleum Refinery	Aqueous Effluents, Oil/Gas Plant (mg/1)
BOD-5	15	10
COD	100	100
Total Organic Carbon	33	33
Suspended Solids	10	10
Oil and Grease	5	5
Phenol	0.1	nil
Ammonia-N	80% removal	nil
Sulfide	0.1	nil
Cr, tertiary	0.25	nil
Cr, hexavalent	0.005	nil

*Average attainable concentrations from the application of best
practicable control technology currently available
(EPA-440/1-74-014a)

The possibility of leaching of trace metals from the ash into ground or
surface waters has been questioned. The difference in physical properties
between slag and fly ash would suggest a different leaching behavior; slagged
ash exhibits a glass matrix which possibly would inhibit leaching. Experi-
mental studies have been carried out on the leaching of power plant fly ash
or unslagged bottom ash. According to the results of a recent study,[4]
selenium, chromium, and boron (and occasionally mercury and barium) were
released on simulated leaching, and the concentrations reached exceeded the
values recommended by EPA for public water supplies. To our knowledge, no
leaching tests of slagged ash have been carried out. Experiments using the
slag generated by a slagging gasifier, such as the Bi-Gas pilot plant or a
Koppers-Totzek unit, would be very useful.

TRACE ELEMENTS

Due to its organic origin and its intimate commixture with crustal formations,
coal contains a large number of elements in minor or trace quantities.[5]
Actually, out of 92 known non-transuranic elements, only 15 (shown in Fig-
ure 6) have not yet been found in coal.

Table 5. Aqueous Effluent Standards, State of Illinois

Constituent	Maximum Concentration (mg/l)
Arsenic (total)	0.25
Barium (total)	2.0
BOD-5	10.0
Cadmium (total)	0.15
Chromium (total hexavalent)	0.3
Chromium (total trivalent)	1.0
Copper (total)	1.0
Cyanide	0.025
Fluoride (total)	15.0
Iron (total)	2.0
Iron (dissolved)	0.5
Lead (total)	0.1
Manganese (total)	1.0
Mercury (total)	0.0005
Nickel (total)	1.0
Oil (hexane solubles or equivalent)	15.0
pH	range 5-10
Phenols	0.3
Selenium (total)	1.0
Silver	0.1
Zinc (total)	1.0
Total Suspended Solids	12.0

A number of studies have analyzed the behavior of trace elements in coal-fired power plants.[6,7] In general, the elements have been divided into two groups, those appearing mainly in the bottom ash (elements or oxides having lower volatility) and those appearing mainly in the fly ash (elements or oxides having higher volatility). For power plants using dry particulate collection devices (e.g., electrostatic precipitators), it was believed that the most volatile elements (such as mercury and selenium) could actually escape at the elemental state with the flue gas; wet scrubbers, however, were believed capable of removing most of the elements from the gas streams and transfering them to the liquid effluent.

In the Oil/Gas plant, no particulates from coal combustion escape into the atmosphere; all particulate streams are collected quantitatively and either returned to the lower section of the gasifiers, where they melt and are removed as slag, or removed as fly ash. Any eventual dispersion of the elements present depends on the possibility of leaching, discussed above. The only concern, therefore, is to identify elements which may be occurring in the gaseous state. The reducing atmosphere present in the middle and top part of the gasifier may also favor different chemical combinations, such as hydrides, absent in the oxidizing atmosphere of a power plant.

Among the trace elements present in coal with recognized toxic properties, high volatility elements (beryllium, mercury and lead), do not form gaseous hydrides, will condense on cooling, and very likely be almost completely removed by the aqueous condensates formed on gas cooling and/or purification. Arsenic, antimony, and selenium have lower volatility but can form gaseous (covalent) hydrides: arsine, stibine, and hydrogen selenide. These hydrides, however, have stability characteristics which preclude their formation at the temperature and pressure prevailing in the Oil/Gas plant gasifiers. From general chemical principles, it would appear, therefore, that harmful trace elements are not released to the atmosphere. Experimental confirmation, however, is desirable and should be obtained from specific pilot plant studies.

OCCUPATIONAL SAFETY

Of particular interest in coal conversion projects is the possible formation of carcinogenic compounds on hydrogenation and pyrolysis of coal. These compounds are usually found in coal tars and coal-derived oils with boiling point higher than 480°F. They consist mainly of polycyclic aromatic hydrocarbons and amines, which are lipid soluble, and can enter cells easily. The carcinogenic activity is believed due to their molecular shape, which permits them to fit into the structure of DNA, and cause self-producing mutations.

Statistically significant increases in the incidence of skin and lung cancer were observed especially for coke oven workers who are exposed to contact and inhalation of coal tar products. These findings led the Federal Government to issue an OSHA Standard of 0.2 mg/m^3 (8-hour average) for coal tar pitch volatiles (anthracene, benzo(a)pyrene, phenanthrene, acridine, chrysene, pyrene).

For both men and laboratory animals, occasional exposure to the carcinogens is not sufficient for cancer development. Rats developed tumors after the chemical agents were applied 2 to 3 times per week to the shaved skin for approximately one year. The shortest exposure time recorded for the development of skin cancer in workers handling coal hydrogenation products was nine months.[8] The Federal Standard mentioned represents the consensus of Governmental and Industrial Hygienists on a threshold limit value which would minimize exposure risks.

Oils and tars are not expected to be formed under the operating conditions of the entrained gasifiers used in the Oil/Gas plant. The entire dissolver train, however, handles coal-derived oils and will therefore require strict application of industrial hygiene practices.

SUMMARY AND CONCLUSIONS

The conceptual commercial design of an Oil/Gas plant capable of converting approximately 35,000 tons of coal per day into clean boiler fuel, LPG, and SNG has been completed.

Design and mode of operation of the facility to assure compliance with environmental requirements was an integral part of the design program. The environmental acceptability of the plant was achieved by purification of gaseous and liquid streams; all effluents released to the environment were predicted to satisfy environmental standards and requirements.

Other environmental areas specific to coal conversion processes, such as disposal of slagged ash, the fate of trace elements, and occupational safety were also included in the design effort. Experimental programs required to provide additional data and information were recommended.

ACKNOWLEDGEMENT

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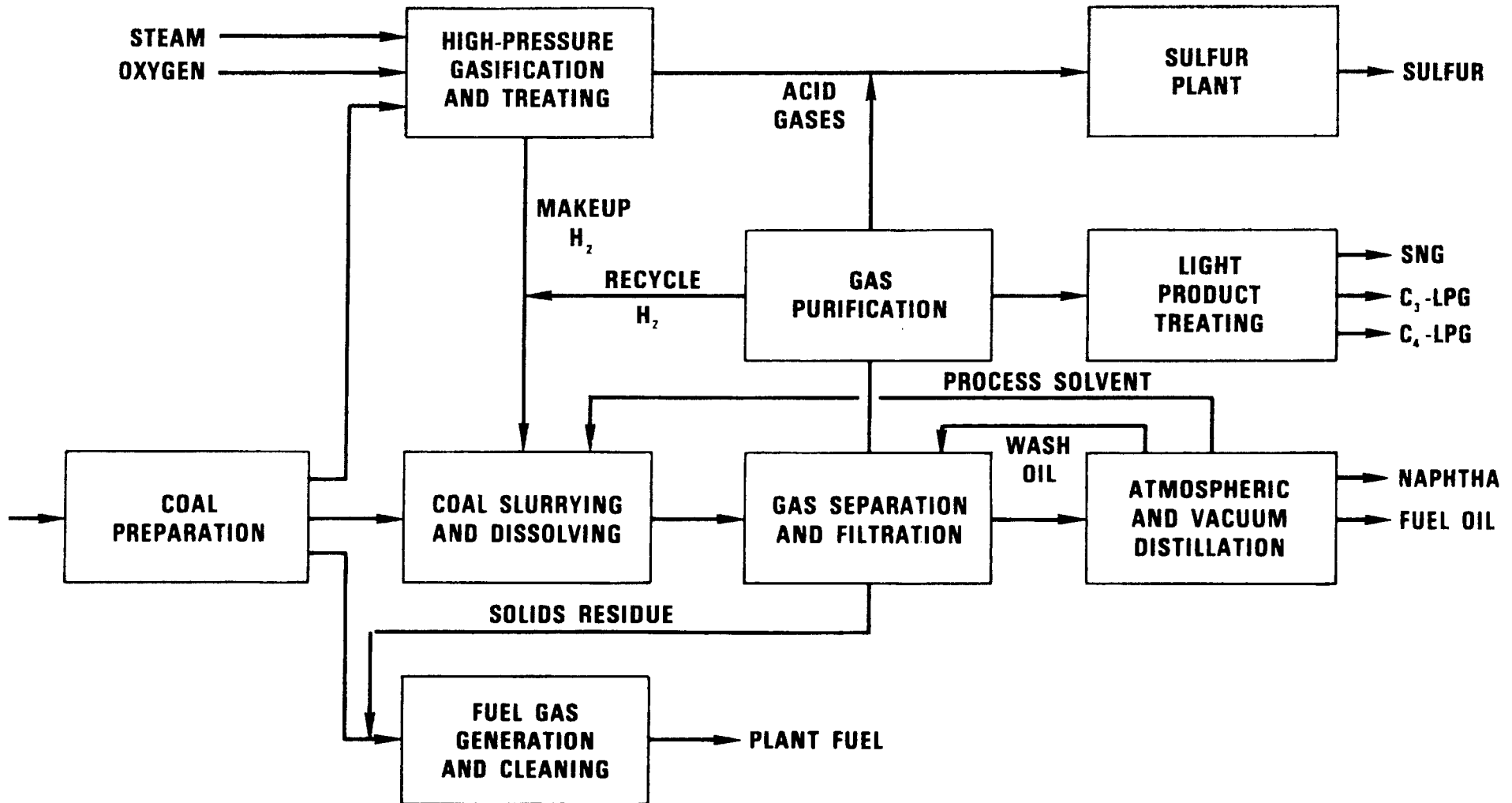
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Figure 1 - Simplified Block Flow Diagram,
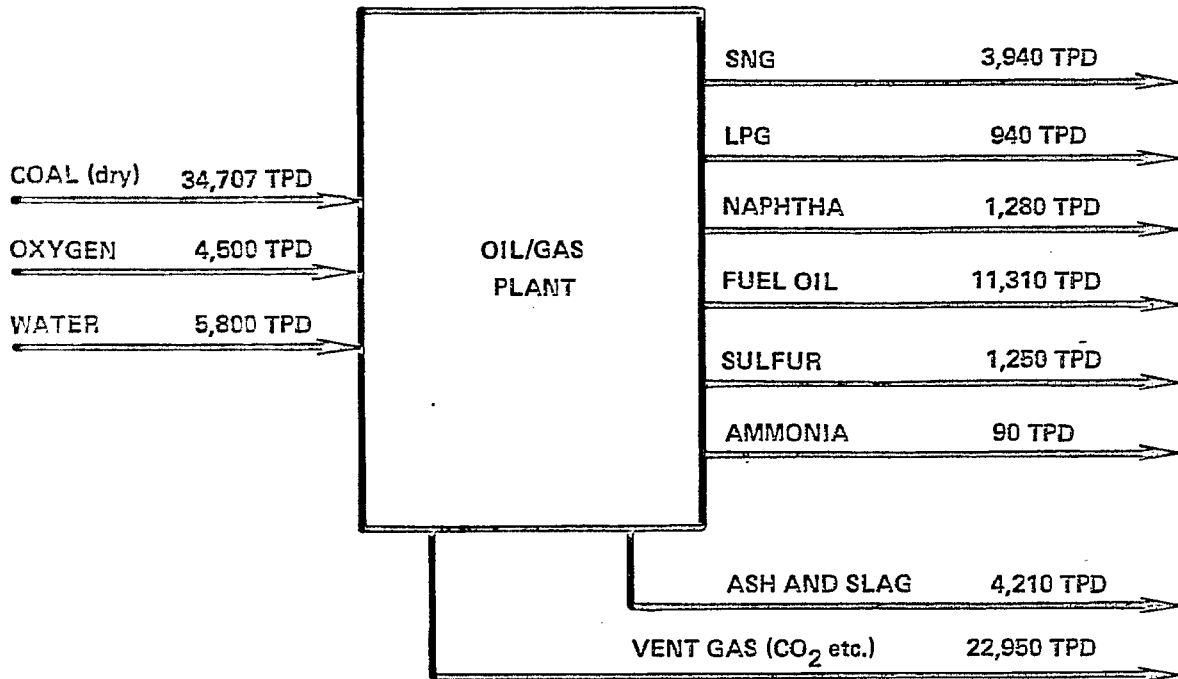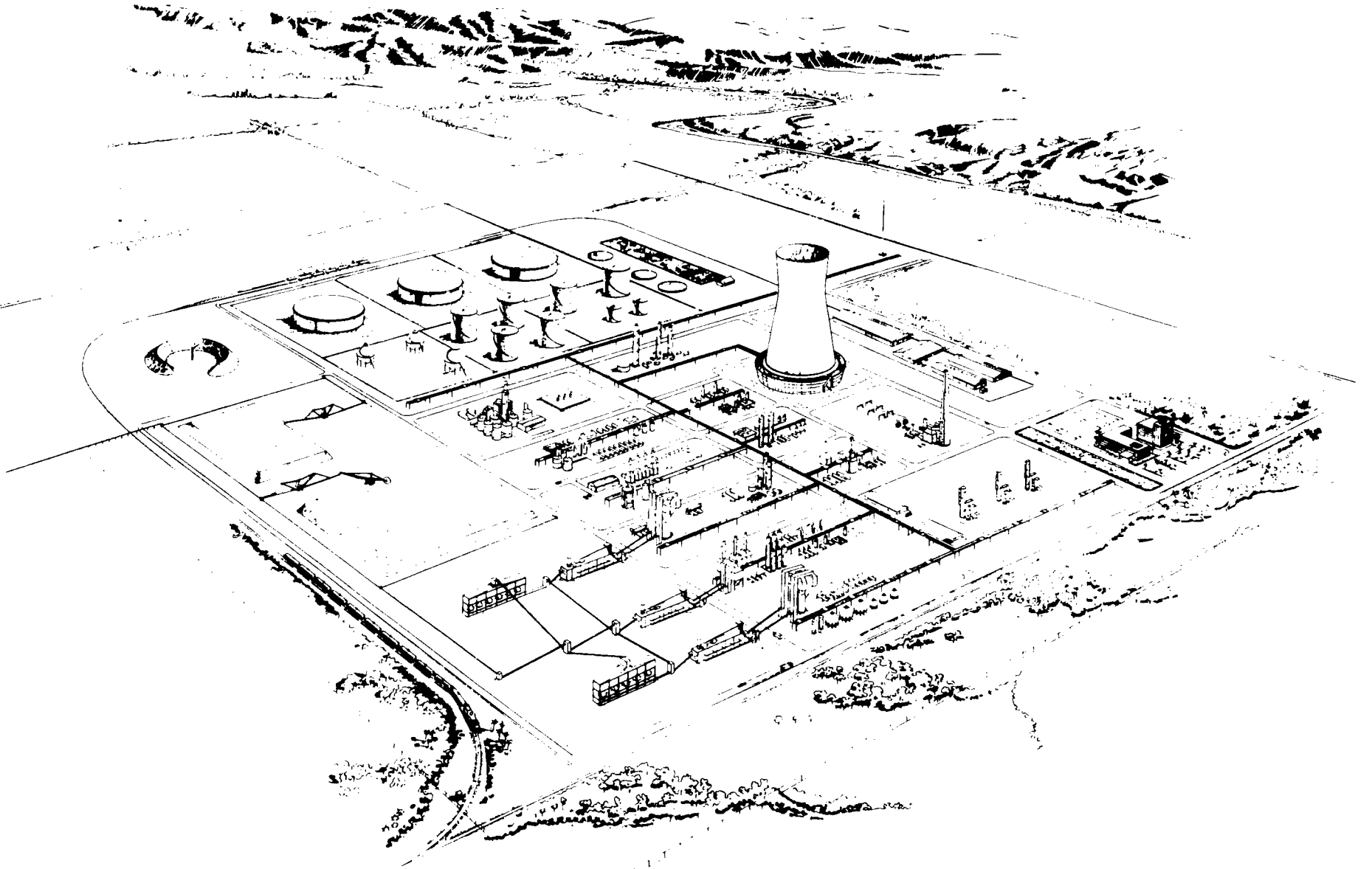Conceptual Design, Commercial Oil/Gas Plant

Figure 2 - Typical Overall Material Balance   (TPD = tons per day)

18

Figure 3 - Artist's Concept, Oil/Gas Plant

FUGITIVE DUST
(controlled)

COAL MINE

COAL CLEANING AND SIZING

COAL DRYING → Coal, 35,670 TPD

CY

BH

VENT TO AIR
DUST, 0.95 TPD

10,000 TPD → PROCESS GASIFIER → CY → DF → SHIFT CONVERTER → SELECTIVE ACID GAS REMOVAL

VENT TO AIR
CO₂, 17,353 TPD
CO, 10.6 TPD (833 ppm)
H₂S, 310 lb/day (10 ppm)

SELECTIVE ACID GAS REMOVAL → H₂, CO, CH₄ (to dissolver)

H₂S ↓

SULFUR RECOVERY → SULFUR, 818 TPD

TAIL GAS TREATMENT ← SULFUR RECOVERY

CO₂, 1440 TPD
CO, 1.08 TPD (412 ppm)
COS, 0.45 TPD (80 ppm)
H₂S, 6.4 lb/day (1 ppm)

VENT TO AIR ← TAIL GAS TREATMENT

SULFUR, 43 TPD

H₂S ↓

SOUR WATER STRIPPING → NH₃ → PURIFICATION → ANHYDROUS AMMONIA, 90 TPD

Gases → ACID GAS REMOVAL → CRYOGENIC SEPARATION

H₂S

SNG (S, nil)
LPG (S, 1 ppm)
NAPHTHA (S, 1ppm)

H₂
20,000 TPD → DISSOLVER

Slurry Solvent →

Liquid Slurry → FRACTIONATION → FILTRATION → FUEL OIL (S, 0.5%, 60 TPD; N, 1 TO 1.5%)

Filter cake ↓

5,670 TPD → FUEL GAS GASIFIER → CY → EP → SULFUR REMOVAL → STEAM GENERATION AND PROCESS HEATERS

SULFUR, 392 TPD

Combustion Gases ↓

VENT TO AIR
CO₂, 15,287 TPD
SO₂, 141 lb/day
NOₓ, 5.7 TPD
SP, nil

LEGEND

BH - BAGHOUSE
CY - CYCLONE
DF - DUST FILTER
EP - ELECTROSTATIC PRECIPITATOR
SP - SUSPENDED PARTICULATES

Figure 4 - Block Flow Diagram, Air
Pollution Abatement, Oil/Gas Plant
(See text for stack arrangement)

GASIFIERS, DISSOLVER → sour water → **SOUR WATER STRIPPER** → H₂S, NH₃ → **AMMONIA ABSORBER** → NH₃ → **AMMONIA PURIFICATION** → anhydrous ammonia

H_2S, NH_3

(to sulfur recovery) ↑ H_2S

stripped water (to process gasifier)

NH_3

wastewater (to slag quench)

OILY WATER →
RUNOFF FROM PROCESS AREAS → **PRIMARY OIL-WATER SEPARATOR** → water → **OILY WATER POND** → water → to slag quench

oil fraction

oil fraction

PRIMARY OIL-WATER SEPARATOR → oil fraction → **SECONDARY OIL-WATER SEPARATOR** → oil → to fractionation

water

SLAG SETTLING BASIN OVERFLOW

SANITARY SEWAGE → 50 gpm → **SEWAGE TREATMENT PLANT** → **BIOPOND** → water → to slag quench

firewater

sludge (to landfill)

sludge (to landfill)

DEIONIZER WASTES → 75 gpm

COOLING TOWER BLOWDOWN → 2875 gpm → **NEUTRALIZATION** → **SETTLER CLARIFIER** → 3100 gpm → to slag quench (as required)

sludge (to landfill)

BOILER BLOWDOWN → 150 gpm

RUNOFF FROM CLEAN AREAS

← RIVER

17,500 gpm →

wastes, 75 gpm

DEIONIZER → boiler feedwater makeup, 2910 gpm → **BOILERS** → steam and power

blowdown, 150 gpm

SAND FILTER

drift, 440 gpm
evaporation, 11,200 gpm

SETTLER CLARIFIER → cooling water makeup, 14,515 gpm → **COOLING TOWER** → cooling water

sludge (to mine)

blowdown, 2875 gpm

Figure 5 - Block Flow Diagram
Water Treatment and Supply
Oil/Gas Plant

Figure 6 - Periodic Table of the Elements. The Elements Shaded Have <u>Not</u> Been Found in Coal.

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ENVIRONMENTAL FACTORS FOR FISCHER-TROPSCH COAL CONVERSION TECHNOLOGY

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ABSTRACT

The environmental factors of a conceptual commercial Fischer-Tropsch coal conversion plant are discussed. The Fischer-Tropsch process, which converts coal into gaseous and liquid hydrocarbons, is briefly reviewed. The removal of sulfur and particulates from the syngas generated, the sulfur balance of the conversion process, and the quantity and types of effluent streams projected to be released are described. Estimated air emissions and aqueous effluents are compared with applicable standards and found capable of meeting the present and projected regulations. The fate of trace elements present in the coal and occupational safety aspects are also briefly considered.

INTRODUCTION

The diminishing national resources of oil and natural gas have made the development of a viable coal conversion technology increasingly important. One of the processes being considered generates synthetic hydrocarbons by Fischer-Tropsch indirect coal liquefaction. A version of this technology is presently applied on a commercial scale in the Republic of South Africa.

In the United States, prime responsibility for development of coal conversion technology rests with the Energy Research and Development Administration - Fossil Energy (ERDA-FE). The Ralph M. Parsons Company is assisting ERDA-FE with preliminary designs and economic evaluations for synthetic fuel facilities. Integral to the design effort is the definition of control equipment and procedures assuring that the plants designed and operated will be environmentally acceptable.

The conceptual commercial design of a Fischer-Tropsch facility incorporates second or third generation technology such as gasifiers based on Bi-Gas principles and a flame-sprayed catalytic reactor for Fischer-Tropsch conversion. Both of these are in the development stage and require further work prior to the design and construction of commercial plants. Successful application of these technologies could lead to conversion of coal to liquid and gaseous fuels with an overall thermal efficiency of 70%. A report describing the conceptual design and economic analysis of the facility has been published [1].

Creation of future synfuel supplies will undoubtedly require large innovative projects with management, technical and logistical challenges similar to the North Slope project in which crude oil from the Prudhoe Bay area in Alaska is gathered and prepared for transport to the lower 48 states, for which Parsons has been managing contractor.

OBJECTIVES

The purpose of this paper is to describe the environmental factors of a commercial Fischer-Tropsch plant, and also the processes and operating procedures required to assure environmental acceptability of the plant.

OUTLINE OF THE PROCESS

A report describing a preliminary design and economic evaluation of a conceptual commercial Fischer-Tropsch plant to convert coal to both liquid and gaseous fuels has been published [1]. A brief process description is presented here for orientation purposes.

As conceived, the plant will be located adjacent to a coal mine in the Eastern Region of the Interior (coal) Province of the United States. The design is based on use of 27,000 metric tons per day (MgPD) [30,000 U.S. tons per day (TPD)] of cleaned bituminous coal, containing 1.1% nitrogen and 3.4% sulfur. The simplified block flow diagram in Figure 1 depicts the conceptual design. The plant includes facilities to wash the coal, grind it, then dry it indirectly with steam. An artist's concept of the Fischer-Tropsch complex is shown in Figure 2.

The process consists of gasification of coal by reaction with oxygen and steam at elevated temperature and pressure to produce a synthesis gas, purification and adjustment of composition of the gas, and catalytic reaction of the gas to form principally hydrocarbon liquids. These premium products, containing nil sulfur or nitrogen, consist of 2200 MgPD (2400 TPD) of naphthas, 1900 MgPD (2100 TPD) of diesel fuel, and 650 MgPD (700 TPD) of fuel oil. Unreacted tail gas and methane are further processed to produce 6000 MgPD (6600 TPD) of substitute natural gas (SNG).

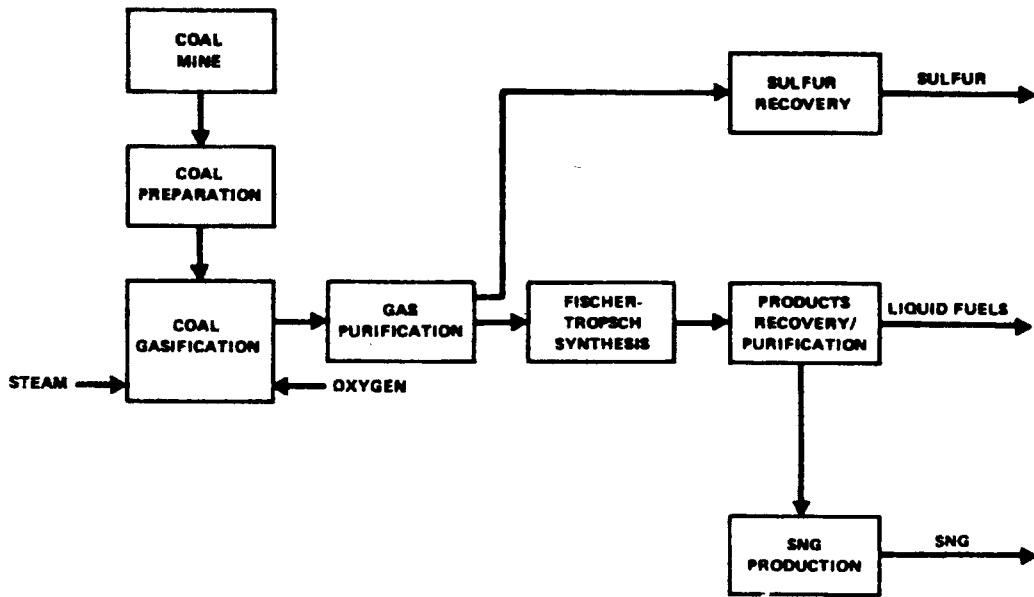Approximately one-half of the carbon in the coal fed to the process units is converted to

Figure 1. Simplified Block Flow Diagram, Fischer-Tropsch Conceptual Plant
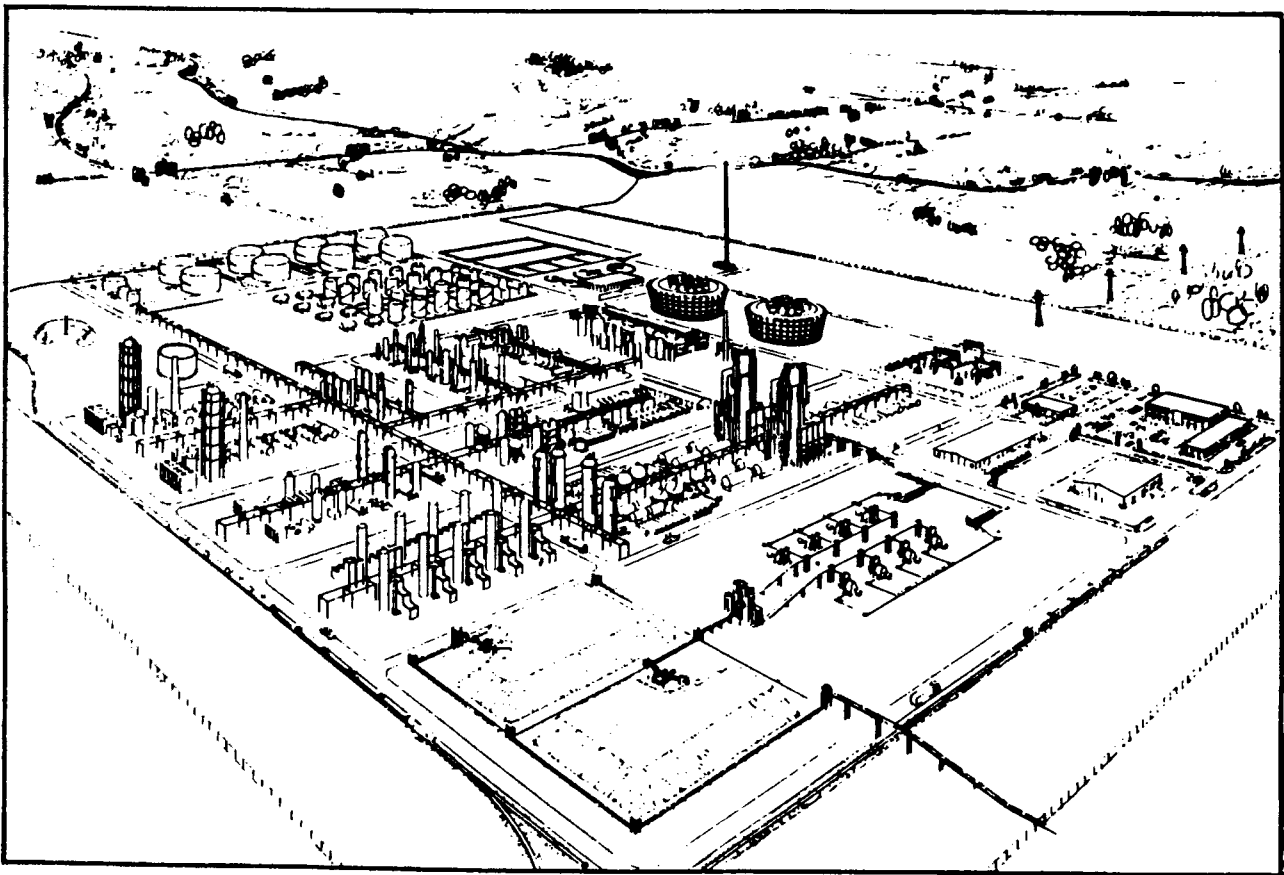
Figure 2. Artist's Concept, Fischer-Tropsch Plant

hydrocarbons having greater hydrogen content than the feed coal with heat being supplied primarily by conversion of carbon to carbon dioxide in the gasifier and the Fischer-Tropsch synthesis reaction. Efficient heat recovery provides all power and steam required to operate the complex; excess electric power for sale (140 megawatts) is also produced.

The control of all contaminants released to the environment had a high priority in plant and process design. Applicable standards covering the process operations were used in design and engineering of the process and equipment.

AIR POLLUTION ABATEMENT

The major air pollution abatement effort is aimed at desulfurizing the gases generated during the coal conversion process to make the fuels produced environmentally acceptable. In a Fischer-Tropsch plant, environmental and process goals coincide because the presence of sulfur inhibits the effectiveness of Fischer-Tropsch catalysts.

The air pollution abatement procedure is outlined in Figure 3, which shows the nature and amount of all streams vented to the air; these streams consist for the major part of inert gases (nitrogen and carbon dioxide). The effluent gases are shown vented separately to the air to identify the contribution of specific process units. In reality, however, all streams with the exception of the particulates from the coal drying plant are combined into a single stack before venting to the air.

The coal grinding and drying unit is the only source of particulate emissions. A baghouse system removes most of the particulates from the vent streams, with emissions to the air meeting both the Federal standard for thermal dryer gases and other standards related to coal gasification plants. The source of heat for the drying process is excess steam from the Fischer-Tropsch plant; no combustion gases are generated by the operation.

The coal gasifier receives powdered coal, steam, and oxygen and generates hydrogen, carbon monoxide, carbon dioxide, methane, hydrogen sulfide, and minor amounts of ammonia, carbon oxysulfide, cyanides, and sulfur dioxide. At the elevated reactor temperature, nil oils or tars are produced. The gaseous stream carries all the char and ash produced on gasification of the coal; the largest part of these materials is removed by a series of cyclones, followed by a hot electrostatic precipitator. Recovered char is returned to the lower section of the gasifier, where char gasification occurs by reaction with steam and oxygen while the accompanying ash melts and is removed as slag. The small amount of char and ash particles still accompanying the gases after passage through the cyclones and hot precipitator is removed by two wet scrubbers followed by a cold electrostatic precipitator. All the

ammonia and part of the hydrogen sulfide present are also removed by the scrubbers; most cyanides present, however, remain in the gas stream because of the acidic conditions of the sour water generated.

The next treatment step concerns the removal of acid gases (carbon dioxide and hydrogen sulfide). A physical solvent process removes these gases from the main stream, then, on selective regeneration, releases a stream of hydrogen sulfide containing part of the carbon dioxide and a stream of nearly pure carbon dioxide. The hydrogen sulfide stream is sent to the sulfur recovery plant. Hydrogen cyanide is also absorbed by the solvent; on regeneration, it joins the hydrogen sulfide stream and is conveyed to the sulfur recovery plant, where cyanides are destroyed by thermal oxidation. The carbon dioxide stream is vented to the air and small amounts of carbon monoxide and hydrogen sulfide are vented to the air with it.

The sulfur recovery plant oxidizes 95% of the hydrogen sulfide to high-purity elemental sulfur. The remaining 5% is present in the tail gas, which is treated in a tail gas unit where all sulfur species are reduced to hydrogen sulfide, then absorbed by an alkaline solution, and oxidized to also give high-purity sulfur. The final vent gas contains carbon dioxide plus traces of carbon oxysulfide, hydrogen sulfide, and carbon monoxide. The sulfur balance for the plant is detailed in Table I; a total of 98% of the coal sulfur content is recovered as elemental sulfur.

The purified gas is now suitable for conversion to hydrocarbon fuels in a Fischer-Tropsch reactor. Carbon dioxide generated at the same time is removed by absorption in a caustic solution and is then vented to the air on regeneration of the absorbent. The vent stream contains traces of carbon monoxide together with traces of light boiling hydrocarbons and methane (a nonpollutant). The Fischer-Tropsch catalyst absorbs the last traces of sulfur present; therefore, all fuels produced, gaseous and liquid, and the chemical byproducts (alcohols) contain nil sulfur.

The streams shown vented separately to the air in Figure 3 from the plant proper (acid gas removal, tail gas treatment, and carbon dioxide removal units) are actually combined in a single stack before venting. The overall amounts and concentrations become, therefore, the ones shown in Table II.

Source emission standards for coal conversion plants have not been issued by the Federal Government. Of the states, only New Mexico has issued specific regulations covering coal gasification plants; these regulations can be considered for illustrative purposes only because the Fischer-Tropsch plant, as conceived, would be located in the U.S. Eastern Interior (coal) Region. The State of Illinois has issued standards for petrochemicals; this
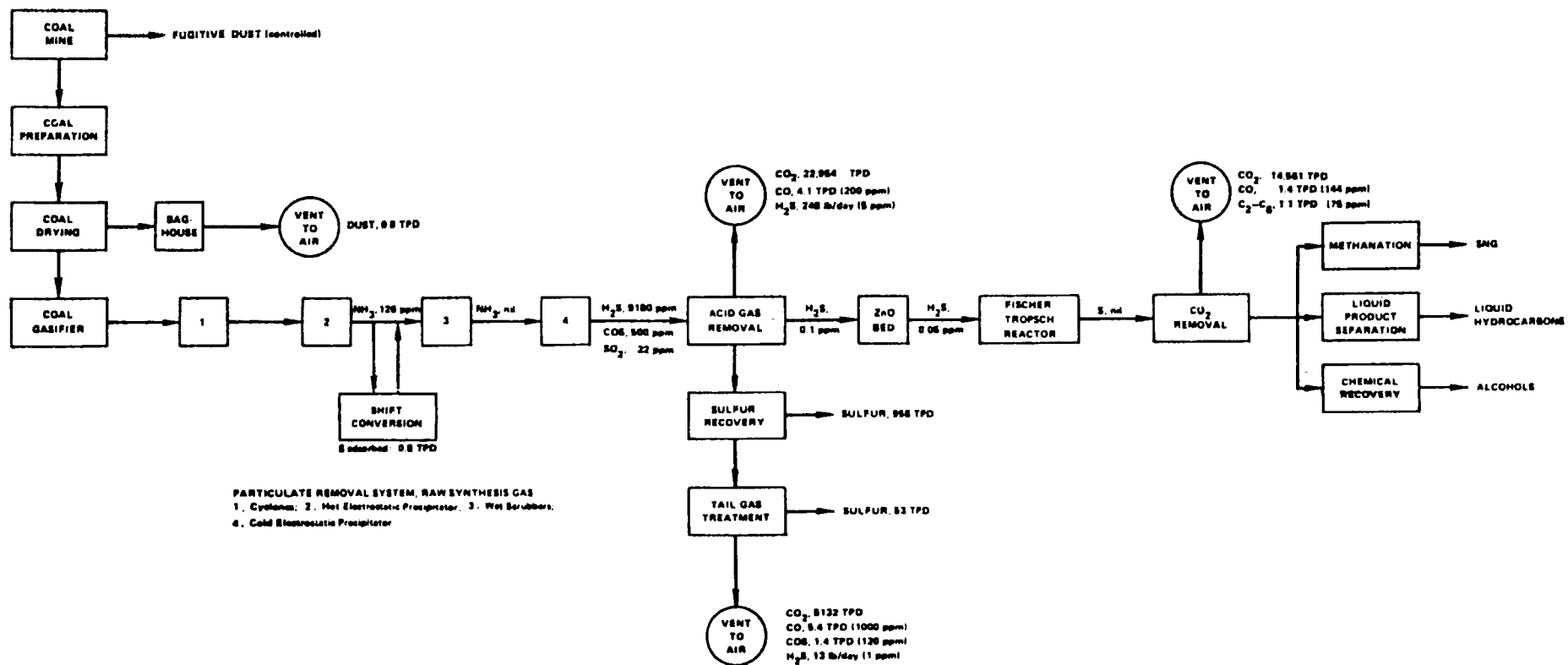
Figure 3. Block Flow Diagram, Air Pollution Abatement, Fischer-Tropsch Plant (1 TPD = 0.9 MgPD)

Table I. Sulfur Balance

Sulfur Contributions	MgPD	TPD
Total Input from the Typical Feed Coal	925.3	1020.0
Outputs: As Elemental Sulfur from Coal Gasifier Gas	917.5	1011.4
As Reduced Sulfur Emissions (19% H_2S, 81% COS)	0.7	0.8
As Sulfur Dioxide Emissions (actually emitted every six months on regeneration of the shift catalyst)	0.7	0.8
In the Ash	6.4	7.0
	925.3	1020.0

Table II. Combined Gaseous Effluents

Gaseous Effluent	MgPD	TPD	ppm
Carbon Dioxide	36,688	42,647	-
Carbon Monoxide	9.9	10.9	306
Carbon Oxysulfide	1.3	1.4	18
Organics (C_2 - C_6 Hydrocarbons)	1.0	1.1	21
Hydrogen Sulfide	0.12	0.13	3

technology is somewhat related to a Fischer-Tropsch operation. The standards are strict or stricter than the Federal standards for petroleum refining. For illustration purposes only, the Illinois and the New Mexico source emission standards are compared in Table III with the emissions from conceptual Fischer-Tropsch coal conversion plant. As shown in the table, all estimated emissions are projected to either meet or be below the standards.

AQUEOUS EFFLUENTS

The plant design is based on availability of an adequate supply of water. The wastewater treatment is therefore a combination of recycling and discharge of aqueous effluents. The most heavily contaminated streams are concentrated by evaporation, with residuals undergoing thermal destruction in the coal gasifier. The medium-contaminated streams are purified by oxidation and then reused as makeup for boiler feedwater. The lightly polluted streams are treated to make them acceptable to the environment and then are discharged to a river. The generation and control of aqueous contaminants is outlined in Figure 4, which shows the sources of wastewater (listed on the left-hand side) and their progressive treatment and disposition.

The river water supply provides 12,000 gpm of raw water, which, after purification by settling and sand filtration, is used for cooling water makeup and, after further deionization, for boiler feedwater makeup. Potable and sanitary water (75 gpm) is supplied by wells. The water supply from the river is not used for coal sizing and handling (a captive system feeding on a mine-based pond is used for this unit) or for coal grinding and drying, where no wet systems are employed.

One of the major contaminated streams is the sour water generated by the wet scrubbers cleaning the gases produced by the coal gasifier. The major contaminants present are hydrogen sulfide, ammonium sulfide, oil, phenols, thiocyanates, cyanides, and solids (ash and char particles). After removal of any oily materials by extraction, most of the gaseous contaminants (hydrogen sulfide and ammonia) are removed by a reboiler-stripper, and then conveyed to the sulfur plant where the hydrogen sulfide is converted to elemental sulfur and the ammonia is oxidized to nitrogen. The stripped aqueous stream is now treated in an oxidizer with oxygen at high pressure to convert most of the organics present (including cyanides) to inorganic gases such as carbon dioxide, nitric oxide, and sulfur dioxide. These are led back to the coal gasifier; the reducing atmosphere prevailing there is expected to reduce nitric oxide and sulfur dioxide to nitrogen and hydrogen sulfide. After settling and filtration, the aqueous effluent stream from the oxidizer is deionized and reused as boiler feedwater makeup.

The Fischer-Tropsch reactor produces, besides the desired hydrocarbon fuels, a number of alcohols and organic acids. When the product stream is purified by treating with caustic, a waste stream containing alkaline salts of low-molecular weight organic acids is produced. This stream is combined with the boiler water blowdown and the solids slurry obtained as a residue from the settling of the treated sour water, and then concentrated in a triple-effect evaporator. The evaporator condensate is used for boiler feedwater, while the residue is sprayed on the feed coal at the entrance to the coal dryer. A more thorough evaporation occurs in the latter unit; the organic materials are then destroyed when the coal is fed to the gasifier, while the inorganic materials are removed with the ash.
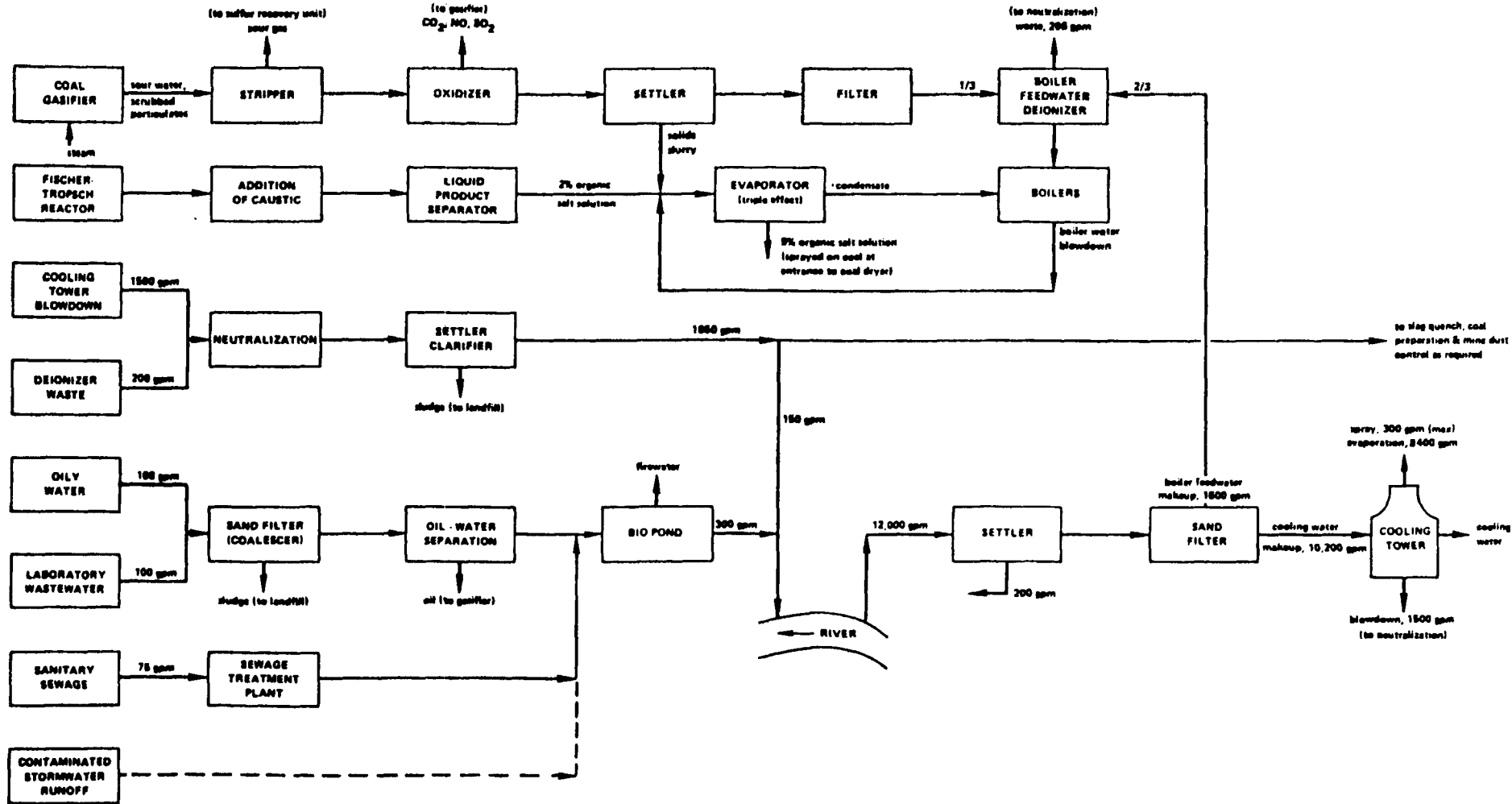
(to sulfur recovery unit)
sour gas

(to gasifier)
CO₂, NO, SO₂

(to neutralization)
waste, 295 gpm

| COAL GASIFIER | → sour water, scrubbed particulates → | STRIPPER | → | OXIDIZER | → | SETTLER | → | FILTER | → 1/3 | BOILER FEEDWATER DEIONIZER | 2/3 |

steam

| FISCHER-TROPSCH REACTOR | → | ADDITION OF CAUSTIC | → | LIQUID PRODUCT SEPARATOR | → 2% organic salt solution → | EVAPORATOR (triple effect) | condensate → | BOILERS |

solids slurry

9% organic salt solution (sprayed on coal at entrance to coal dryer)

boiler water blowdown

| COOLING TOWER BLOWDOWN | 1500 gpm |
| DEIONIZER WASTE | 200 gpm |

| NEUTRALIZATION | → | SETTLER CLARIFIER | → 1050 gpm →

sludge (to landfill)

to slag quench, coal preparation & mine dust control as required

150 gpm

spray, 300 gpm (max)
evaporation, 8400 gpm

firewater

| OILY WATER | 100 gpm |
| LABORATORY WASTEWATER | 100 gpm |

| SAND FILTER (COALESCER) | → | OIL-WATER SEPARATION | → | BIO POND | 300 gpm | 12,000 gpm | SETTLER | → | SAND FILTER | → cooling water makeup, 10,200 gpm → | COOLING TOWER | → cooling water

boiler feedwater makeup, 1600 gpm

sludge (to landfill)

oil (to gasifier)

RIVER

200 gpm

blowdown, 1500 gpm
(to neutralization)

| SANITARY SEWAGE | 75 gpm | → | SEWAGE TREATMENT PLANT |

| CONTAMINATED STORMWATER RUNOFF |

Figure 4. Block Flow Diagram, Water Treatment and Supply, Fischer-Tropsch Plant (1 gpm = 0.227 m³/hr)

Table III. Comparison of Gaseous Emissions with Illinois and New Mexico Source Emission Standards (The standards are expressed in the units issued by the states. 1 lb = 453.6 g; 1 gr = 64.8 mg; 1 Btu = 1055 J; 1 ft^3 = 0.028 m^3; MM = million; HHV = higher heating value; L = lower.)

Pollutant	Illinois Standards, Petrochemical Plant	New Mexico Standards, Coal Gasification Plant	Gaseous Effluents, Fischer-Tropsch Plant
Particulate Matter	78 lb/hr	0.03 gr/ft^3	67 lb/hr,[a] 0.03 gr/ft^3
Sulfur Dioxide	1.2 lb/MM Btu	-	Nil[b]
Carbon Monoxide	200 ppm, 50% xs air	-	164 ppm[c]
Nitrogen Oxides	0.7 lb/MM Btu	-	Nil
Organics (methane excluded)	100 ppm (CH$_4$ equivalent)	-	55 ppm
Total Reduced Sulfur (H$_2$S + COS + CS$_2$)	-	100 ppm	21 ppm
Hydrogen Sulfide	-	10 ppm	3 ppm
Hydrogen Cyanide	-	10 ppm	Nil
Hydrogen Chloride/ Hydrochloric Acid	-	5 ppm	Nil
Ammonia	-	25 ppm	Nil
Gas Burning Process Boilers, Particulate Matter	-	0.03 lb/MM Btu, LHV	-[d]
Gas Burning Process Boilers, Sulfur Dioxide	-	0.16 lb/MM Btu, LHV	-[d]
Total Sulfur	-	0.008 lb/MM Btu of feed (coal) heat input, HHV	0.003 lb/MM Btu[e]

[a] From coal-drying plant

[b] 47.4 tons of sulfur dioxide emitted twice a year, over 24-48 hours, on regeneration of the catalyst of each shift reactor (six reactors total). If this value were averaged out over the year, it would correspond to 0.004 lb/MM Btu/day.

[c] Value obtained on application of the 50% excess air correction to the streams originating from the acid gas removal unit and from the sulfur plant.

[d] Not applicable (none included in the design).

[e] Includes the sulfur dioxide emitted occasionally on regeneration of the shift reactor catalyst (see Note[b] above).

The cooling-tower blowdown stream is the largest in volume, and is only lightly contaminated by corrosion inhibitors (zinc salts and inorganic phosphates) and scale control agents (organic phosphate esters); this stream is mixed with deionizer wastes containing mainly sodium sulfate and other inorganic salts. After neutralization, this stream is treated with lime in a settler-clarifier. The lime sludge, containing most of the zinc and phosphates, is disposed of in a landfill, while the treated stream is returned to the river.

Any oily water streams produced during plant operation are combined with laboratory wastewater, and then passed through a sand filter to coalesce the oil particles. After physical separation of the oil (returned to the gasifier), the aqueous effluent is led to a biopond, where the organic materials present are converted to inorganics by bacterial activity. The biopond also receives a minor stream from the sewage-treatment plant, and is used as firewater supply, with any overflow discharged to the river. Strict housekeeping is expected to contain contamination of stormwater to very small volumes; any contaminated water is collected in a stormwater pond (not shown in Figure 4) for subsequent metered feeding to the biopond for treatment.

No aqueous effluent standards specifically addressed to coal conversion plants have been issued by the Federal government or by state legislatures. Standards that are somewhat related to a Fischer-Tropsch process are the Federal standards issued for petroleum refining. Average obtainable concentrations that were the base for such standards are reported in Table IV, together with the corresponding

Table IV. Comparison of Aqueous Effluents with Federal
Petroleum Refinery Standards* (mg/1)

Parameter	Federal Standards, Petroleum Refinery	Aqueous Effluents, Fischer-Tropsch Plant
BOD 5	15	10
COD	100	100
Total Organic Carbon	33	33
Suspended Solids	10	10
Oil and Grease	5	5
Phenol	0.1	nil
Ammonia-N	80% removal	nil
Sulfide	0.1	nil
Cr. tertiary	0.25	nil
Cr. hexavalent	0.005	nil

*Average attainable concentrations from the application of best practicable control technology currently available [2].

values for the aqueous effluents estimated for the Fischer-Tropsch plant. As shown in the table, these estimated values are either the same or lower than the Federal parameters [2].

SOLID WASTES

The Fischer-Tropsch plant generates two main types of solid waste materials: slagged ash from the coal gasifier [2132 MgPD (2350 TPD)], which is returned to the mine for burial with the mine spoils, and sludges from various wastewater treatment units, which are disposed of in a landfill. The mining and coal cleaning and sizing operations generate sizable amounts of solid wastes, which are disposed of at the mine site.

The possibility of leaching of trace metals from the ash into ground or surface waters has been questioned. Experimental studies have been carried out on the leaching of power plant fly ash or unslagged bottom ash [3]; the studies showed that selenium, chromium and boron, and occasionally mercury and barium, were released on simulated leaching, and the concentrations reached exceeded the values recommended by EPA for public water supplies. Possibly, slagged ash features a glass matrix which would inhibit leaching. Experiments using the slag generated by a slagging gasifier, such as the Bi-Gas pilot plant or a Koppers-Totzek unit, would be very useful.

TRACE ELEMENTS

Due to its organic origin and its intimate commixture with crustal formations, coal contains a large number of elements in minor or trace quantities [4]. Actually, out of 92 known non-transuranic elements, only 15 have not yet been found in coal.

A number of studies have analyzed the behavior of trace elements in coal-fired power plants [5,6]. In general, the elements have been

divided into two groups, those appearing mainly in the bottom ash (elements or oxides having lower volatility) and those appearing mainly in the fly ash (elements or oxides having higher volatility). For power plants using dry particulate collection devices (e.g., electrostatic precipitators), it was believed that the most volatile elements (such as mercury and selenium) could actually escape in the elemental state with the flue gas; wet scrubbers, however, were believed capable of removing most of the elements from the gas streams and transferring them to the liquid effluent.

In the Fischer-Tropsch process, no particulates from coal combustion escape into the atmosphere. Particulate streams, wet or dry, are returned to the bottom of the gasifier, where ash and salts melt and are removed as slag. Any eventual dispersion of the elements present depends on the possibility of leaching, mentioned above. The only concern, therefore, is to identify elements which may be occurring in the gaseous state. The reducing atmosphere present in the middle and top part of the gasifier may also favor different combinations, absent in the oxidizing atmosphere of a power plant boiler.

Among the trace elements present in coal with recognized toxic properties, high volatility elements (beryllium, mercury and lead), do not form gaseous hydrides, will condense on cooling, and very likely be almost completely removed by the aqueous condensates formed on gas cooling and/or purification. Arsenic, antimony, and selenium have lower volatility but can form gaseous (covalent) hydrides: arsine, stibine, and hydrogen selenide. These hydrides however, have stability characteristics which preclude their formation at the temperature and pressure prevailing in the Fischer-Tropsch gasifier. From general chemical principles, it would appear, therefore, that harmful trace elements are not released to the atmosphere.

Experimental confirmation, however, is desirable and should be obtained from specific pilot plant studies.

OCCUPATIONAL SAFETY

Of particular interest in coal conversion projects is the possible formation of carcinogenic compounds on hydrogenation and pyrolysis of coal. These compounds are usually found in coal tars, and are not expected to be formed under the operating conditions of the entrained coal gasifier used in the Fischer-Tropsch plant.

Carcinogenic activity for laboratory animals has also been observed for higher boiling fractions obtained from petroleum refining [7]. Similar fractions are obtained on distillation of the liquid hydrocarbons produced by the Fischer-Tropsch reactor, and Fischer-Tropsch oils boiling above 250°C were found carcinogenic in mice [8]. A corresponding activity in man, however, has not been shown; cancer frequency in oil refinery workers is the same as for other industrial occupations. The amount of known carcinogens, such as benzo(a)pyrene, in high boiling petroleum fractions is much lower than in coal tar; the products are also maintained in close systems, so that very little contact of workers with the product occurs. It is felt that similar conditions will exist in Fischer-Tropsch operations, thereby minimizing any environmental risks.

ACKNOWLEDGEMENT

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SPECIFIC ENVIRONMENTAL ASPECTS OF FISCHER-TROPSCH COAL CONVERSION TECHNOLOGY

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A preliminary design of a commercial-scale Fischer-Tropsch plant producing liquid hydrocarbons plus substitute natural gas by indirect coal liquefaction has been completed. The units and processes utilized are reviewed to highlight the progressive removal from the streams of compounds or materials capable of contributing to air and water pollution. All final effluents released to the environment are estimated to be in compliance with applicable or related Federal and State standards.

Methods of environmental control for the following specific areas are discussed:

- Fate of trace elements present in coal.
- Formation and destruction of metal carbonyls.
- Cyanide formation, partitioning among effluent streams, and final decomposition.
- Formation of coal-tar carcinogens and biohazards involved.

There still exist some environmental aspects specific to coal conversion for which additional experimental data are required. Research and development programs that can provide this additional information are defined.

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Environmental Aspects of Fuel Conversion Technology

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SPECIFIC ENVIRONMENTAL ASPECTS OF
FISCHER-TROPSCH COAL CONVERSION TECHNOLOGY

INTRODUCTION

Development of viable coal conversion technology is a national priority. A prime responsibility for development of this technology rests with the Energy Research and Development Administration - Fossil Energy (ERDA-FE). The Ralph M. Parsons Company is assisting ERDA-FE in reaching this objective by developing preliminary designs and economic evaluations for commercial coal conversion facilities. Preliminary commercial designs for four of these facilities have been completed so far, namely for a Demonstration Plant producing clean boiler fuels from coal, for a complex producing oil and power by COED (Coal Oil Energy Development) based pyrolysis coal conversion, for an Oil/Gas Plant using integrated coal conversion technology, and for a Fischer-Tropsch facility producing liquid hydrocarbons plus substitute natural gas by indirect coal liquefaction.

The definition of facilities and procedures to assure that environmentally acceptable plants can be designed and operated is integral to the design effort. The basis for establishing environmental control facilities and operating procedures is the many coal conversion process development units and pilot plants being operated in the United States plus experience gained from related industries such as petroleum processing.

This paper concerns specific environmental aspects of a Fischer-Tropsch facility. The technology involved, outlined in Figure 1, consists of coal gasification to produce a carbon dioxide/carbon monoxide/hydrogen syngas, purification of this gas to remove carbon dioxide and hydrogen sulfide, adjustment of composition to increase the hydrogen content, and catalytic conversion of the gas to form principally hydrocarbon liquids. Part of the unreacted syngas is upgraded by methanation to substitute natural gas (SNG). A version of this technology is presently applied on a commercial scale in the Republic of South Africa.

The Parsons conceptual commercial design incorporates advanced technology such as a high temperature-high pressure gasifier based on Bi-Gas principles and a flame-sprayed catalytic reactor for Fischer-Tropsch conversion. Both of these are in the development stage and require further work prior to the design and construction of commercial plants. Successful application of these technologies could lead to conversion of coal to liquid and gaseous fuels with an overall thermal efficiency of 70%. A report describing the conceptual design and economic analysis of the facility has been published[1].

As conceived, the plant will be located adjacent to a coal mine in the Eastern Region of the Interior (coal) Province of the United States. The design is based on use of 27,000 metric tons per day (MgPD) [corresponding to 30,000 U.S. tons per day (TPD)] of cleaned bituminous coal, containing 1.1% nitrogen and 3.4% sulfur. The premium products obtained, containing nil sulfur or nitrogen, consist of 2200 MgPD (2400 TPD) of naphthas, 1900 MgPD (2100 TPD) of diesel fuel,
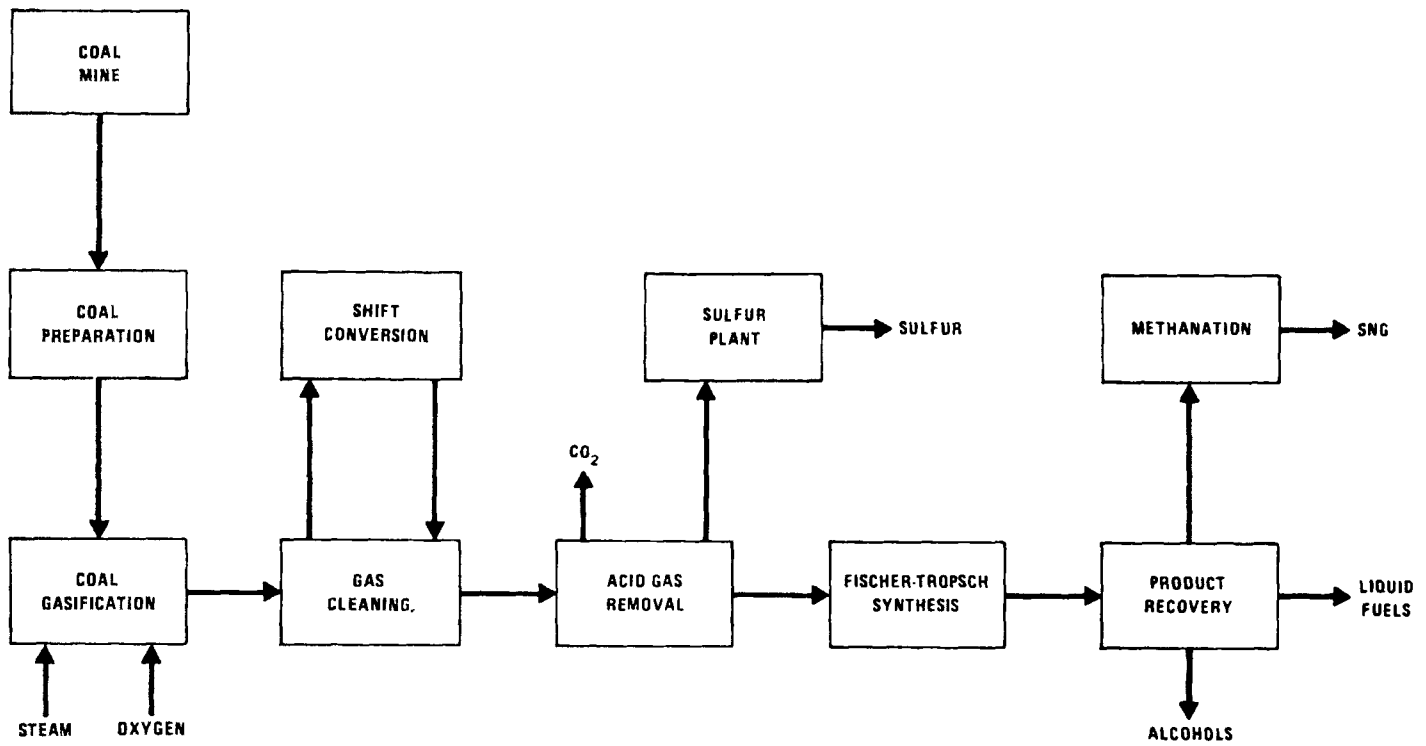
1

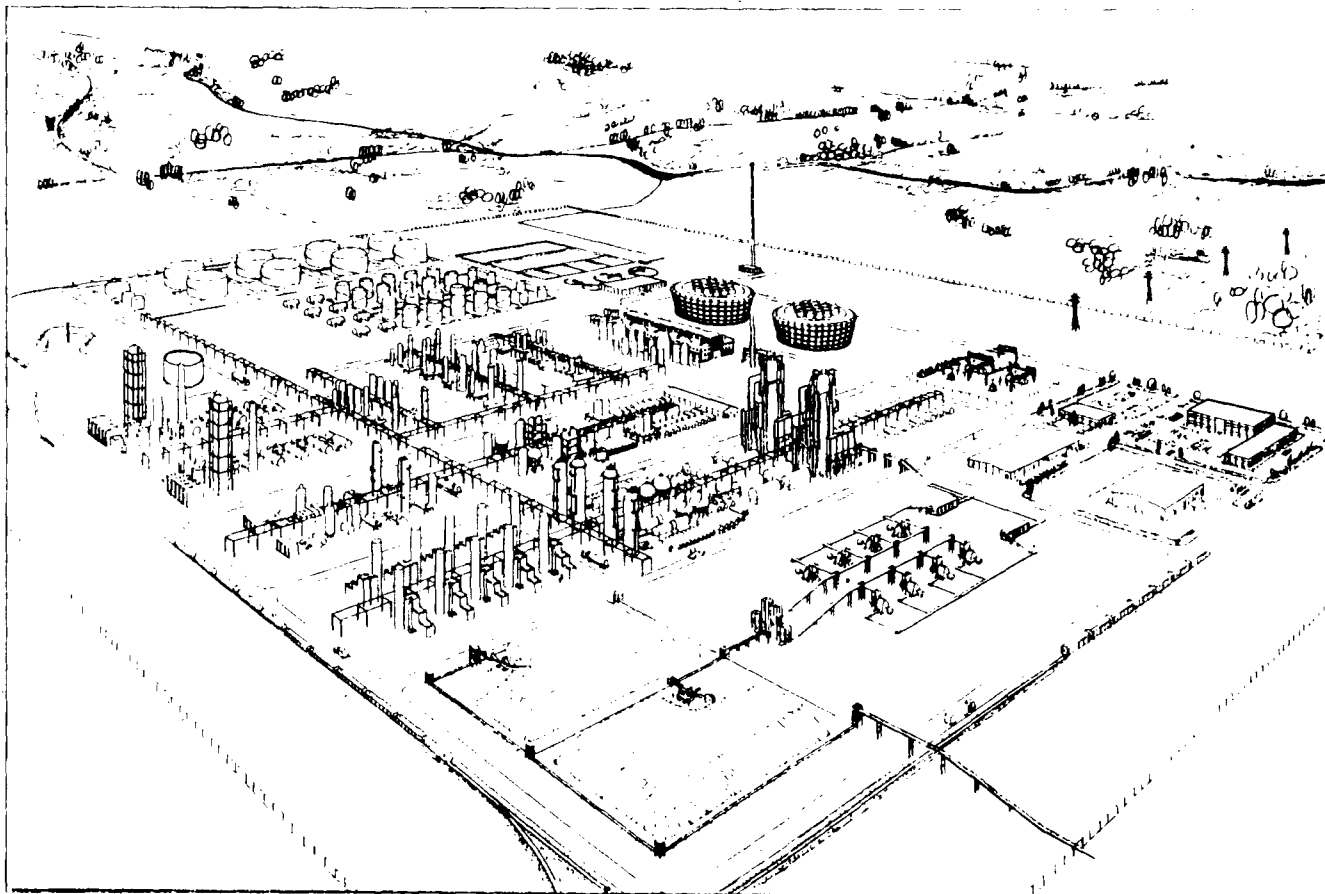Figure 1.   Simplified Block Flow Diagram, Fischer-Tropsch Conceptual Plant

Figure 2.   Artist's Concept, Fischer-Tropsch Plant

650 MgPD (700 TPD) of fuel oil, and 6000 MgPD (6600 TPD) of SNG. Heat recovery provides all power and steam required to operate the complex; excess electric power for sale (140 megawatts) is also produced. An artist's concept of the Fischer-Tropsch complex is shown in Figure 2.

AIR POLLUTION ABATEMENT

The major air pollution abatement effort is aimed at desulfurizing the gases generated during the coal conversion process to make the fuels produced environmentally acceptable. In a Fischer-Tropsch plant, environmental and process goals coincide because the presence of sulfur inhibits the effectiveness of Fischer-Tropsch catalysts.

The air pollution abatement procedure is outlined in Figure 3, which shows the nature and amount of all streams vented to the air; these streams consist for the major part of inert gases (nitrogen and carbon dioxide). The effluent gases are shown vented separately to the air to identify the contribution of specific process units. In reality, however, all streams with the exception of the particulates from the coal drying plant are combined into a single stack before venting to the air.

The coal grinding and drying unit is the only source of particulate emissions. A baghouse system removes most of the particulates from the vent streams, with emissions to the air meeting both the Federal standard for thermal dryer gases and other standards related to coal gasification plants. The source of heat for the drying process is excess steam from the Fischer-Tropsch plant; no combustion gases are generated by the operation.

The coal gasifier receives powdered coal, steam, and oxygen and generates hydrogen, carbon monoxide, carbon dioxide, methane, hydrogen sulfide, and minor amounts of ammonia, carbon oxysulfide, cyanides, and sulfur dioxide. The reactor operates at high pressure (3.5 MPa, 500 psia) and temperatures (1650°C, 3000°F in the lower stage and 930°C, 1700°F in the upper stage). At these elevated temperatures, nil oils or tars are produced.

The gaseous stream carries all the char and ash produced on gasification of the coal; the largest part of these materials is removed by a series of cyclones, followed by a hot electrostatic precipitator. Recovered char is returned to the lower section of the gasifier, where char gasification occurs by reaction with steam and oxygen while the accompanying ash melts and is removed as slag. The small amount of char and ash particles still accompanying the gases after passing through the cyclones and hot precipitator is removed by two wet scrubbers followed by a cold electrostatic precipitator. All the ammonia and part of the hydrogen sulfide present are also removed by the scrubbers.

The next treatment step concerns the removal of acid gases (carbon dioxide and hydrogen sulfide). A physical solvent process removes these gases from the main stream, then, on selective regeneration, releases a stream of hydrogen sulfide containing part of the carbon dioxide. The hydrogen sulfide stream is sent to the sulfur recovery plant. The carbon dioxide stream is vented to the air together with very small amounts of carbon monoxide and hydrogen sulfide.
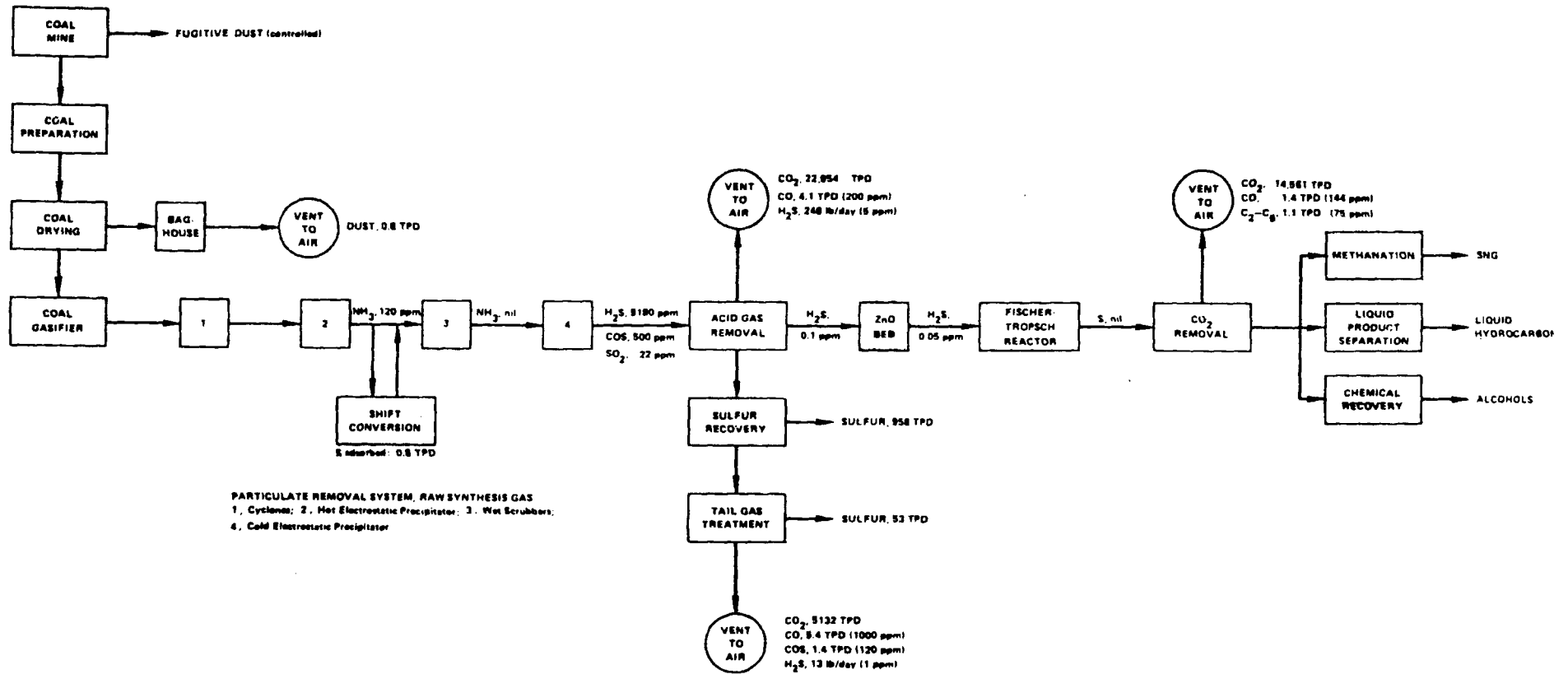
COAL MINE → FUGITIVE DUST (controlled)

COAL PREPARATION

COAL DRYING → BAG HOUSE → VENT TO AIR — DUST, 0.6 TPD

COAL GASIFIER → 1 → 2 —NH$_3$, 120 ppm→ 3 —NH$_3$, nil→ 4

SHIFT CONVERSION
S adsorbed: 0.6 TPD

PARTICULATE REMOVAL SYSTEM, RAW SYNTHESIS GAS
1. Cyclones; 2. Hot Electrostatic Precipitator; 3. Wet Scrubbers;
4. Cold Electrostatic Precipitator

H$_2$S, 5190 ppm
COS, 500 ppm
SO$_2$, 22 ppm

ACID GAS REMOVAL —H$_2$S, 0.1 ppm→ ZnO BED —H$_2$S, 0.05 ppm→ FISCHER-TROPSCH REACTOR —S, nil→ CO$_2$ REMOVAL

VENT TO AIR —
CO$_2$, 22,954 TPD
CO, 4.1 TPD (200 ppm)
H$_2$S, 248 lb/day (5 ppm)

SULFUR RECOVERY → SULFUR, 958 TPD

TAIL GAS TREATMENT → SULFUR, 53 TPD

VENT TO AIR —
CO$_2$, 5132 TPD
CO, 5.4 TPD (1000 ppm)
COS, 1.4 TPD (120 ppm)
H$_2$S, 13 lb/day (1 ppm)

VENT TO AIR —
CO$_2$, 14,561 TPD
CO, 1.4 TPD (144 ppm)
C$_2$–C$_6$, 1.1 TPD (75 ppm)

METHANATION → SNG

LIQUID PRODUCT SEPARATION → LIQUID HYDROCARBON

CHEMICAL RECOVERY → ALCOHOLS

Figure 3. Block Flow Diagram, Air Pollution Abatement, Fischer-Tropsch Plant (1 TPD = 0.9 MgPD)

The sulfur recovery plant oxidizes 95% of the hydrogen sulfide to high-purity elemental sulfur. The remaining 5% is present in the tail gas, which is treated in a tail gas unit where all sulfur species are reduced to hydrogen sulfide, then absorbed by an alkaline solution, and oxidized to also give high-purity sulfur. The final vent gas contains carbon dioxide plus traces of carbon oxysulfide, hydrogen sulfide, and carbon monoxide. The sulfur balance for the plant is detailed in Table 1; a total of 98% of the coal sulfur content is recovered as elemental sulfur.

Table 1. Sulfur Balance

Sulfur Contributions	MgPD	TPD
Total Input from the Typical Feed Coal	925.3	1020.0
Outputs: As elemental Sulfur from Coal Gasifier Gas	917.5	1011.4
As Reduced Sulfur Emissions (19% H_2S, 81% COS)	0.7	0.8
As Sulfur Dioxide Emissions (actually emitted every six months on regeneration of the shift catalyst)	0.7	0.8
In the Ash	6.4	7.0
	925.3	1020.0

The purified gas is now suitable for conversion to hydrocarbon fuels in a Fischer-Tropsch reactor. Carbon dioxide generated at the same time is removed by absorption in a caustic solution and is then vented to the air on regeneration of the absorbent. The vent stream contains traces of carbon monoxide together with traces of light boiling hydrocarbons and methane (a nonpollutant). The Fischer-Tropsch catalyst absorbs the last traces of sulfur present; therefore, all fuels produced, gaseous and liquid, and the chemical byproducts (alcohols) contain nil sulfur.

The streams released to the air are combined in a single stack before venting. The overall amounts and concentrations are shown in Table 2.

Table 2. Combined Gaseous Effluents

Gaseous Effluent	MgPD	TPD	ppm
Carbon Dioxide	36,688	42,647	-
Carbon Monoxide	9.9	10.9	306
Carbon Oxysulfide	1.3	1.4	18
Organics (C2 - C6 Hydrocarbons)	1.0	1.1	21
Hydrogen Sulfide	0.12	0.13	3

Source Emission Standards for coal conversion plants have not been issued by the Federal Government. Guidelines for hydrocarbon (100 ppm) and sulfur dioxide (250 ppm) have been proposed by EPA for Lurgi coal gasification plants. These guidelines are not applicable to the Fischer-Tropsch plant because a different technology is utilized; they are, however, met by the plant effluents.

Of the states, only New Mexico has issued specific regulations covering coal gasification plants; these regulations can be considered for illustrative purposes only because the Fischer-Tropsch plant, as conceived, would be located in the U.S. Eastern Interior (coal) Region. The State of Illinois has issued standards for petrochemicals; this technology is somewhat related to a Fischer-Tropsch operation. Federal standards for petroleum refinery sulfur recovery plants have been proposed[3]; Fischer-Tropsch technology utilizes similar sulfur recovery procedures. For illustration purposes only, the Federal, Illinois, and the New Mexico source emission standards are compared in Table 3 with the emissions from the conceptual Fischer-Tropsch coal conversion plant. As shown in the table, all estimated emissions are projected to either meet or be below the standards.

A dispersion modeling study, using average atmospheric conditions and the EPA-developed PTMAX computer program, was carried out; the results obtained show that the Fischer-Tropsch emissions can meet ambient air quality standards after atmospheric dispersion.

As shown in Table 2, significant carbon dioxide emissions would be generated by the Fischer-Tropsch commercial plant; therefore, it appeared desirable to investigate the possible effects of these emissions. Carbon dioxide is not toxic, and the natural background concentration in the atmosphere has been estimated at 300 to 500 ppm.

Global weather modification effects have been attributed to increased carbon dioxide generation by fossil-fuel combustion. A gradual warming trend on the order of 0.5°C in 25 years has been predicted; however, actual temperature trends have shown a cooling of 0.3°C from 1945 to the present.

On a localized scale, no micrometeorological effects due to increased carbon dioxide have been reported. Emissions from the Fischer-Tropsch facility could approximately double the average atmospheric carbon dioxide concentrations to 600 to 1000 ppm in the vicinity of the plant. The lowest concentration at which some physiological effects (dyspnea and headache) have been observed is 30,000 ppm; therefore, no effects are expected at the levels mentioned. However, vegetable life has been reported to benefit from increased atmospheric concentrations of carbon dioxide.

AQUEOUS EFFLUENTS

The plant design is based on availability of an adequate supply of water. The wastewater treatment is therefore a combination of recycling and discharge of aqueous effluents. The most heavily contaminated streams are concentrated by evaporation, with residuals undergoing thermal destruction in the coal gasifier. The medium-contaminated streams are purified by oxidation and then reused as makeup for boiler feedwater. The lightly polluted streams are treated to

Table 3. Comparison of Gaseous Emissions with Federal, Illinois and New Mexico Source Emission Standards. (State standards are expressed in the units issued. 1 lb = 453.6 g; 1 gr - 64.8 mg; 1 Btu = 1055 J; 1 ft^3 = 0.028 m^3; MM - million; HHV = higher heating value; L - lower.)

Pollutant	Federal Standards, Petroleum Refinery Sulfur Recovery Plant	Illinois Standards, Petrochemical Plant	New Mexico Standards Coal Gasification Plant	Gaseous Effluents, Fischer-Tropsch Plant
Particulate Matter	-	78 lb/hr	0.03 gr/ft^3	67 lb/hr[a], 0.03 gr/ft^3
Surfur Dioxide	250 ppm	1.2 lb/MM Btu	-	Nil[b]
Carbon Monoxide	-	200 ppm, 50% xs air	-	164 ppm[c]
Nitrogen Oxides	-	0.7 lb/MM Btu	-	Nil
Organics (methane excluded)	-	100 ppm (CH_4 equivalent)	-	55 ppm
Total Reduced Sulfur (H_2S + COS + CS_2)	300 ppm	-	100 ppm	21 ppm
Hydrogen Sulfide	10 ppm	-	10 ppm	3 ppm
Hydrogen Cyanide	-	-	10 ppm	Nil
Hydrogen Chloride/ Hydrochloric Acid	-	-	5 ppm	Nil
Ammonia	-	-	25 ppm	Nil
Gas Burning Process Boilers, Particulate Matter	-	-	0.03 lb/MM Btu, LHV	-[d]
Gas Burning Process Boilers, Sulfur Dioxide	-	-	0.16 lb/MM Btu, LHV	-[d]
Total Sulfur	-	-	0.008 lb/MM Btu of feed	0.003 lb/MM Btu[e]

[a]From coal-drying plant

[b]47.4 tons of sulfur dioxide emitted twice a year, over 24-48 hours, on regeneration of the catalyst of each shift reactor (six reactors total). If this value were averaged out over the year, it would correspond to 0.004 lb/MM Btu/day.

[c]Value obtained on application of the 50% excess air correction to the streams originating from the acid gas removal unit and from the sulfur plant.

[d]Not applicable (none included in the design).

[e]Includes the sulfur dioxide emitted occasionally on regeneration of the shift reactor catalyst (see Note[b] above).

make them acceptable to the environment and then are discharged to a river. The generation and control of aqueous contaminants is outlined in Figure 4, which shows the sources of wastewater (listed on the left-hand side) and their progressive treatment and disposition.

The river water supply provides 2,725 m^3/hr (12,000 gpm) of raw water, which, after purification by settling and sand filtration, is used for cooling water makeup and, after further deionization, for boiler feedwater makeup. Potable and sanitary water is supplied by wells. The water supply from the river is not used for coal sizing and handling (a captive system feeding on a mine-based pond is used for this unit) or for coal grinding and drying, where no wet systems are employed.

One of the major contaminated streams is the sour water generated by the wet scrubbers cleaning the gases produced by the coal gasifier. The major contaminants present are hydrogen sulfide, ammonium sulfide, oil, phenols, thiocyanates, cyanides, and solids (ash and char particles). After removal of any oily materials by extraction, most of the gaseous contaminants (hydrogen sulfide and ammonia) are removed by a reboiler-stripper, and then conveyed to the sulfur plant where the hydrogen sulfide is converted to elemental sulfur and the ammonia is oxidized to nitrogen. The stripped aqueous stream is now treated in an oxidizer with oxygen at high pressure to convert most of the organics present to inorganic gases such as carbon dioxide, nitric oxide, and sulfur dioxide. These are led back to the coal gasifier; the reducing atmosphere prevailing there is expected to reduce nitric acids and sulfur dioxide to nitrogen and hydrogen sulfide. After settling and filtration, the aqueous effluent stream from the oxidizer is deionized and reused as boiler feedwater makeup.

The Fischer-Tropsch reactor produces, besides the desired hydrocarbon fuels, a number of alcohols and organic acids. When the product stream is purified by treating with caustic, a waste stream containing alkaline salts of low-molecular weight organic acids is produced. This stream is combined with the boiler water blowdown and the solids slurry obtained as a residue from the settling of the treated sour water, and then concentrated in a triple-effect evaporator. The evaporator condensate is used for boiler feedwater, while the residue is sprayed on the feed coal at the entrance to the coal dryer. A more thorough evaporation occurs in the latter unit; the organic materials are then destroyed when the coal is fed to the gasifier, while the inorganic materials are removed with the ash.

The cooling-tower blowdown stream is the largest in volume, and is only lightly contaminated by corrosion inhibitors (zinc salts and inorganic phosphates) and scale control agents (organic phosphate esters); this stream is mixed with deionizer wastes containing mainly sodium sulfate and other inorganic salts. After neutralization, this stream is treated with lime in a settler-clarifier. The lime sludge, containing most of the zinc and phosphates, is disposed of in a landfill, while the treated stream is returned to the river.

Any oily water streams produced during plant operation are combined with laboratory wastewater, and then passed through a sand filter to coalesce the oil particles. After physical separation of the oil (returned to the gasifier), the aqueous effluent is led to a biopond, where the organic materials present are converted to inorganics by bacterial activity. The biopond also receives a
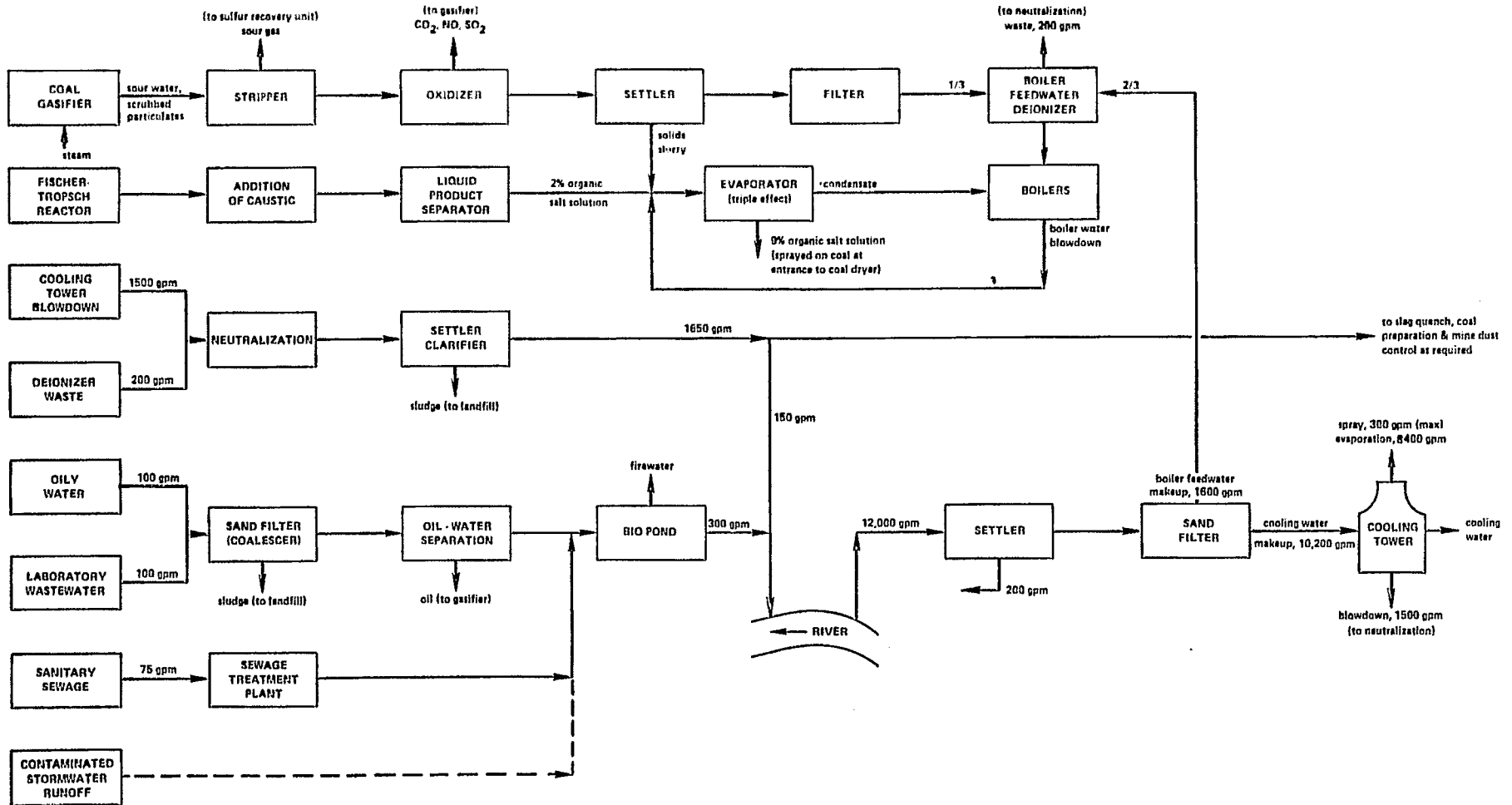
Figure 4. Block Flow Diagram, Water Treatment and Supply, Fischer-Tropsch Plant (1 gpm = 0.227 m³/hr)

minor stream from the sewage-treatment plant, and is used as firewater supply, with any overflow discharged to the river. Strict housekeeping is expected to contain contamination of stormwater to very small volumes; any contaminated water is collected in a stormwater pond (not shown in Figure 4) for subsequent metered feeding to the biopond for treatment.

No aqueous effluent standards specifically addressed to coal conversion plants have been issued by the Federal government or by state legislatures. Standards that are somewhat related to a Fischer-Tropsch process are the Federal standards issued for petroleum refining. Average obtainable concentrations that were the base for such standards are reported in Table 4, together with the corresponding values for the aqueous effluents estimated for the Fischer-Tropsch plant. As shown in the table, these estimated values are either the same or lower than the Federal parameters[4].

Table 4. Comparison of Aqueous Effluents with
Federal Petroleum Refinery Standards*

Parameter	Federal Standards, Petroleum Refinery	Aqueous Effluents, Fischer-Tropsch Plant
BOD 5	15	10
COD	100	100
Total Organic Carbon	33	33
Suspended Solids	10	10
Oil and Grease	5	5
Phenol	0.1	nil
Ammonia-N	80% removal	nil
Sulfide	0.1	nil
Cr. tertiary	0.25	nil
Cr. hexavalent	0.005	nil
*Average attainable concentrations from the application of best practicable control technology currently available[4].		

The State of Illinois has issued aqueous effluent standards applicable to all sources discharging to the natural waters of the state. These standards are reported for illustration purposes in Table 5. All Fischer-Tropsch effluents are estimated to either meet, or be lower than such standards.

Table 5. Aqueous Effluent Standards, State of Illinois

Constituent	Maximum Concentration (mg/1)
Arsenic (total)	0.25
Barium (total)	2.0
BOD-5	10.0
Cadmium (total)	0.15
Chromium (total hexavalent)	0.3
Chromium (total trivalent)	1.0
Copper (total)	1.0
Cyanide	0.025
Fluoride (total)	15.0
Iron (total)	2.0
Iron (dissolved)	0.5
Lead (total)	0.1
Manganese (total)	1.0
Mercury (total)	0.0005
Nickel (total)	1.0
Oil (hexane solubles or equivalent)	15.0
pH	range 5-10
Phenols	0.3
Selenium (total)	1.0
Silver	0.1
Zinc (total)	1.0
Total Suspended Solids	12.0

SOLID WASTES

The Fischer-Tropsch plant generates two main types of solid waste materials:
slagged ash from the coal gasifier, and sludges from various wastewater treat-
ment units. All of the ash produced during coal gasification is returned to
the bottom of the gasifier together with carbon residues (char); on combustion
of the char with oxygen, the temperature produced is sufficient for melting the
ash to a slag, which is withdrawn from the bottom of the gasifier. It is esti-
mated that 2132 MgPD (2350 TPD) of slag are produced. On quenching with water,
the slag is fragmented into vitrified granules, which are returned to the mine
for burial with the mine spoils. If outlets exist nearby, this material could
also be utilized as filler in aggregates for construction blocks or road building.

The sludges from the wastewater treatment units contain mainly inorganic salts, such as calcium and zinc phosphates, which are added to cooling water as corrosion inhibitors. If these sludges were buried with mine spoils, possible contamination of groundwater by zinc could result; they are therefore disposed of in a secure landfill.

The mining and coal cleaning and sizing operations generate sizable amounts of solid wastes which are disposed of at the mine site. The surface mining operation proceeds in an orderly fashion, following an environmentally sound mining plan. The topsoil is removed and stored, then the overburden is stripped and used for refilling of the previous pit, in combination with the inorganic wastes from the coal cleaning and sizing plant (rocks, clay and mud) and the vitrified ash from the coal gasifier. The mined out area is restored to approximately the original surface contour, then the topsoil is replaced, fertilized, and reseeded, completing the land reclamation cycle.

The coal cleaning and sizing plant is located in proximity of the mine. This arrangement minimizes the exposure to the air of mine spoils, with consequent negligible oxidation of coal pyrites to oxygenated sulfur acids.

FATE OF TRACE ELEMENTS PRESENT IN COAL

Due to its organic origin and its intimate commixture with crustal formations, coal contains a large number of elements in minor or trace quantities. Actually, out of 92 known non-transuranic elements, only 14 (shown in Figure 5) have not yet been found in coal.

Average amounts of trace and other elements for 82 coals from the Eastern Region of the Interior Coal Province are shown in Table 6. These values were developed during a recent study[5] carried out with thorough analytical procedures; the coals analyzed were mainly composite face channel samples.

A number of studies have analyzed the behavior of trace elements in coal-fired power plants[6,7]. In general, the elements have been divided into two groups, the ones appearing mainly in the bottom ash (elements or oxides having lower volatility) and the ones appearing mainly in the fly ash (elements or oxides having higher volatility). For power plants using dry particulate collection devices (e.g., electrostatic precipitators), it was believed that the most volatile elements, such as mercury and selenium, could actually escape at the elemental state with the flue gas. Wet scrubbers, however, were believed capable of removing most of the elements from the gas streams and transferring them to the liquid effluent.

Very few data are available for coal conversion plants. A study on trace element disposition for the Sasol (South Africa) facility, reported by the Los Alamos Scientific Laboratory[8] was able to follow the partitioning of trace elements between solid residue (ash), liquid streams, and gases. Among the elements studied, lead, arsenic and beryllium were found mainly in the ash, selenium and tellurium in the liquid streams, fluorine two-thirds in the ash and one-third in the liquids. Mercury was found present in all phases, but concentrated mainly in the gas; however, 50% of the mercury and 17% of the beryllium could not be accounted for.

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Figure 5 - Periodic Table of the Elements. The Elements Shaded Have Not Been Found in Coal.

Table 6. Mean Analytical Values for 82 Coals from
the Illinois Basin (From Reference 5)*

Constituent	Mean	Constituent	Mean (%)
As	14.91 ppm	Cl	0.15
B	113.79 ppm	Fe	2.06
Be	1.72 ppm	K	0.16
Br	15.27 ppm	Mg	0.05
Cd	2.89 ppm	Na	0.05
Co	9.15 ppm	Si	2.39
Cr	14.10 ppm	Ti	0.06
Cu	14.09 ppm	ORS	1.54
F	59.30 ppm	PYS	1.88
Ga	3.04 ppm	SUS	0.09
Ge	7.51 ppm	TOS	3.51
Hg	0.21 ppm	SXRF	3.19
Mn	53.16 ppm	ADL	7.70
Mo	7.96 ppm	MOIS	10.02
Ni	22.35 ppm	VOL	39.80
P	62.77 ppm	FIXC	48.98
Pb	39.83 ppm	ASH	11.28
Sb	1.35 ppm	Btu/lb	12748.91
Se	1.99 ppm	C	70.69
Sn	4.56 ppm	H	4.98
V	33.13 ppm	N	1.35
Zn	313.04 ppm	O	8.19
Zr	72.10 ppm	HTA	11.18
Al	1.22 %	LTA	15.22
Ca	0.74 %		

*Abbreviations other than standard chemical symbols: organic
sulfur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total
sulfur (TOS), sulfur by X-ray fluorescence (SXRF), air-dry loss
(ADL), moisture (MOIS), volatile matter (VOL), fixed carbon (FIXC),
high-temperature ash (HTA), low-temperature ash (LTA).

The possibility of leaching of trace metals from the ash into ground or surface waters has been questioned. Experimental studies have been carried out on the leaching of power plant fly ash or unslagged bottom ash[9]; the studies showed that selenium, chromium and boron, and occasionally mercury and barium, were released on simulated leaching, and the concentrations reached exceeded the values recommended by EPA for public water supplies.

An on-going study at the University of Montana[10] is investigating leaching of trace elements from solid residues of coal conversion plants under neutral, acidic, and basic conditions. Preliminary results indicate that manganese, mercury and nickel are occasionally released in amounts exceeding recommended potable water standards. The study is hampered by the unavailability of typical residue specimens.

In the Fischer-Tropsch process, essentially nil particulates from coal combustion escape into the atmosphere. Particulate streams, wet or dry, are returned to the bottom of the gasifier, where ash and salts melt and are removed as slag. Any eventual dispersion of the elements present in the slag depends on the possibility of leaching. Possibly, slagged ash features a glass matrix which would inhibit leaching. Leaching experiments using the slag generated by a slagging gasifier, such as the Bi-Gas pilot plant or a Koppers-Totzek unit, would be very useful.

The major concern, therefore, is to identify trace elements which may be occurring in the gaseous state. The reducing atmosphere present in the middle and top part of the gasifier may also favor different combinations, absent in the oxidizing atmosphere of a power plant boiler.

Among the trace elements present in coal with recognized toxic properties, high volatility elements (beryllium, mercury and lead), do not form gaseous hydrides, will condense on cooling, and very likely be removed by the aqueous condensates formed on gas cooling and/or purification. Arsenic, antimony, and selenium have lower volatility but can form gaseous (covalent) hydrides: arsine, stibine, and hydrogen selenide. These hydrides however, have stability characteristics which preclude their formation at the temperature and pressure prevailing in the Fischer-Tropsch gasifier. From general chemical principles, it would appear, therefore, that harmful trace elements are not released to the atmosphere. Experimental confirmation, however, is desirable, especially for mercury, and should be obtained from specific pilot plant studies.

FORMATION AND DESTRUCTION OF METAL CARBONYLS

Metal carbonyls form by reaction of carbon monoxide with free metals in the 40-300°C (100-570°F) temperature range. Carbonyls form with all transition metals; nickel, cobalt, and iron carbonyls are most significant since the metals from which they are derived are used as catalysts or for structural equipment[11,12]. Higher pressures [of the order of 100 MPa (15,000 psi)] and the presence of hydrogen favor their formation, while oxygen represses it. They decompose readily in air with half-lives estimated at 10-15 seconds for cobalt carbonyl, 10 minutes for nickel carbonyl, and a few hours for iron carbonyl.

These carbonyls are volatile liquids at room temperature. They all exhibit toxicity, directed at the respiratory system. The most harmful among the three carbonyls is the nickel derivative; for this carbonyl only, chronic effects and carcinogenic activity have been observed. Suggested exposure guidelines and chemical formulas are reported in Table 7.

Table 7. Suggested Exposure Guidelines
for Metal Carbonyls (from Reference 11)

Metal Carbonyl	Air Concentration (ppm)	
	Single Short Term Exposure	Eight-Hour Day
$Ni(CO)_4$	0.04	0.001
$Co(CO)_x + CoH(CO)_4$	0.10	-
$Fe(CO)_5$	0.10	0.01

Iron, nickel, and cobalt catalysts are used in the Fischer-Tropsch process, and low carbon steel is employed for structural equipment. However, at the relatively low pressures and high temperatures prevailing, nil metal carbonyls are expected to be formed. In shutdown operations, however, conditions under which metal carbonyls can form may be experienced for short periods of time. In these cases the normal safe practice of flaring vent streams, along with operation of all contaminant removal systems, will prevent release of carbonyls to the atmosphere. Plant personnel who may be entering vessels or handling catalysts, however, will need to be trained in the proper procedures and supplied with adequate protective equipment to safeguard their health.

FORMATION, PARTITION, AND DISPOSITION OF CYANIDE

The question of the generation of cyanide, a highly toxic ion, and of its possible release to the environment, was explored for the Fischer-Tropsch process. Under the chemical and physical conditions experienced in the coal gasifier, nearly all of the nitrogen content of the coal is converted to molecular nitrogen. The remainder is distributed between ammonia and hydrogen cyanide, according to an equilibrium relationship.

This relationship was investigated using a Parsons-modified computer program for the calculation of complex chemical equilibrium compositions, originally developed by NASA[13] for aerospace applications. The equilibrium calculations were made over the 930°C (1700°F, upper stage) to 1650°C (3000°F, lower stage) temperature range and at the 3.5 MPa (500 psia) pressure which are representative of the conditions expected in the gasifier. The equilibria considered involved a series of molecular and ionic components compatible with the elemental analysis of the charge to the gasifier and with the probability of their occurrence in the effluent gas.

The results obtained, plotted in Figure 6, show that very small amounts of cyanide, of the order of 0.7 mole/hour, are produced at the outlet temperature (950°C, 1700°F) of the gasifier. Even if complete equilibrium were not achieved but were equivalent for example to that calculated for 1100°C (2000°F), the quantities of cyanide in the gases would still be quite small.
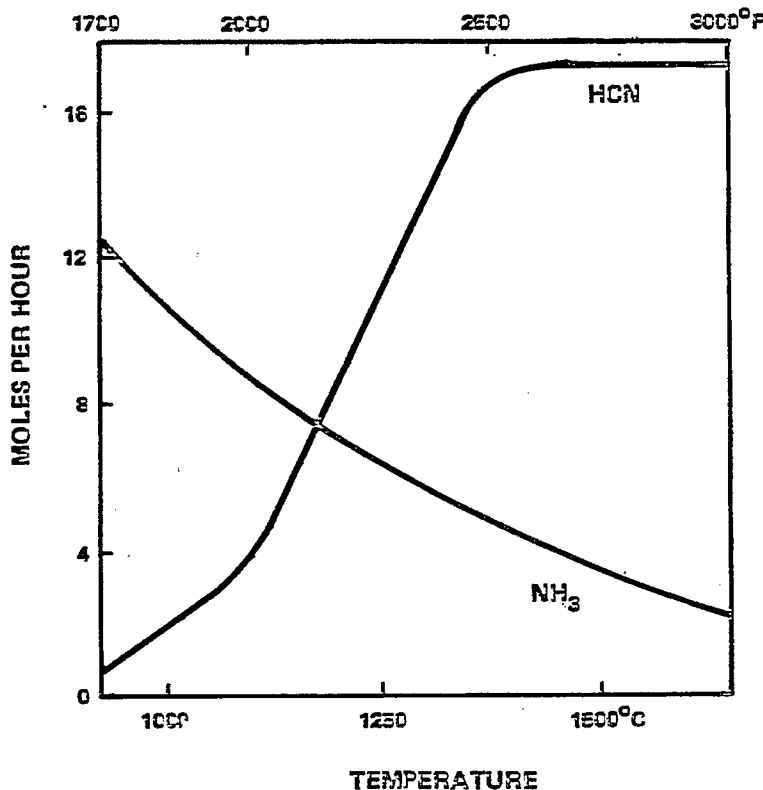

Figure 6. Ammonia-Cyanide Equilibria

When the effluent gas undergoes wet scrubbing, most of the cyanide remains in the gas stream because the sour water generated is only slightly alkaline. It is then adsorbed, together with hydrogen sulfide, by the physical solvent process; on regeneration, it is conveyed to the sulfur recovery plant, where it undergoes thermal oxidation to nitrogen and carbon dioxide. The cyanide fraction which had remained in the aqueous stream is treated, together with other organics, with oxygen at high pressure in the oxidizer unit; there these compounds are converted to inorganic gases such as carbon dioxide and nitric oxide. These are led back to the coal gasifier, where under the prevailing reducing conditions nitric oxide is expected to be reduced to nitrogen.

It appears therefore that very little cyanide is generated, and any amounts produced are destroyed within the Fischer-Tropsch process, so that nil cyanide is released to the environment.

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FORMATION OF COAL TAR CARCINOGENS AND BIOHAZARDS INVOLVED

Of particular interest in coal conversion projects is the possible formation of carcinogenic compounds on hydrogenation and pyrolysis of coal. These compounds are polynuclear aromatic hydrocarbons and heterocyclics usually found in coal tar. Nil coal oils and coal tars are expected to 'be produced under the operating conditions of the entrained coal gasifier used in the Fischer-Tropsch plant.

Carcinogenic activity for laboratory animals has been observed for distillation residuals obtained from petroleum refining[14]. Similar fractions are obtained on distillation of the liquid hydrocarbons produced by the Fischer-Tropsch reactor, and Fischer-Tropsch oils boiling above 250°C (480°F) were found carcinogenic in mice[15]. However, the carcinogenic activity is much smaller than observed for coal tar products because Fischer-Tropsch fuels consist essentially of aliphatic compounds. Crudes also contain less aromatics than coal oils and tars; the refining process occurs in close systems, so that very little contact of workers with products occurs; equipment handling residual oil is often color coded, so that workers are warned of avoiding direct contact. As a consequence, cancer frequency in oil refinery workers is the same as for other industrial occupations. Equally efficient occupational safety procedures will be maintained in Fischer-Tropsch operations, thereby minimizing any environmental risks.

ACKNOWLEDGEMENT

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SECTION 6
MATERIAL CONSIDERATIONS

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