

SPECIFIC ENVIRONMENTAL ASPECTS OF FISCHER-TROPSCH COAL CONVERSION TECHNOLOGY

by

B. I. Loran and J. B. O'Hara
The Ralph M. Parsons Company
Pasadena, California

Abstract

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.

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 percent. 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

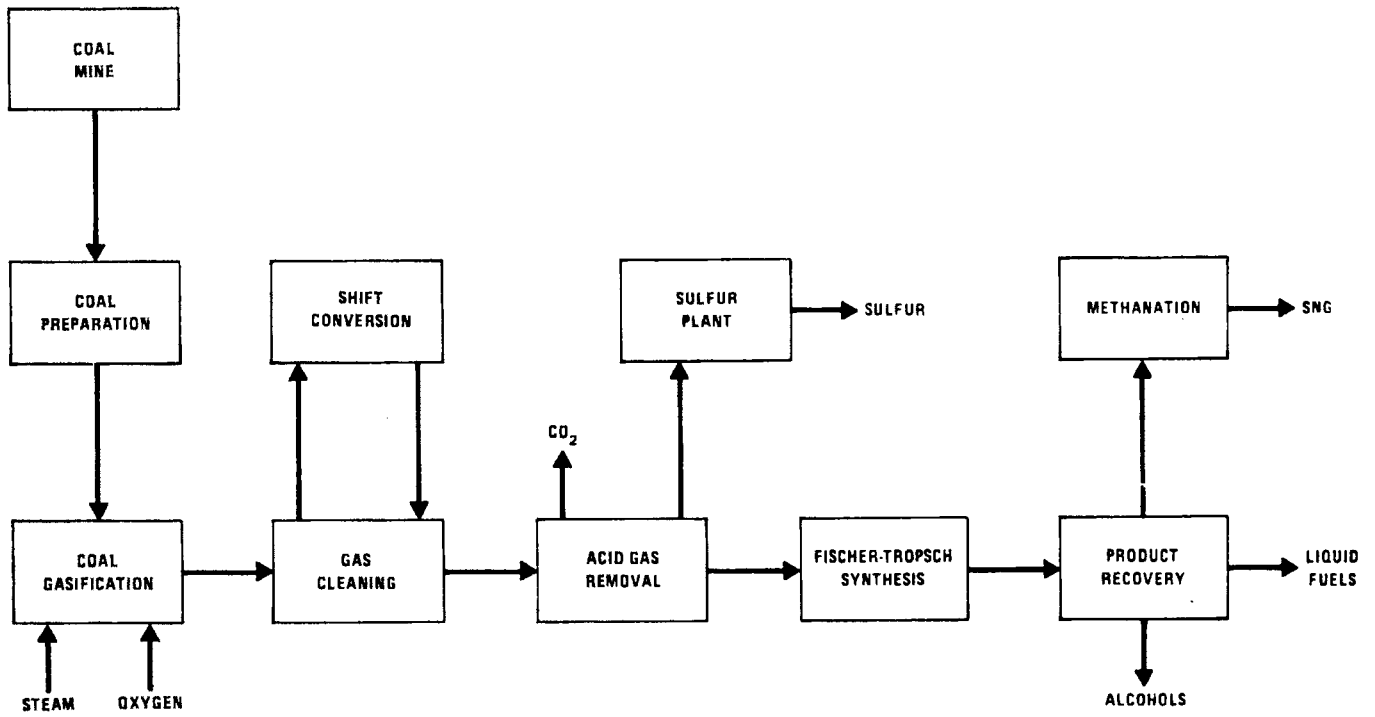


Figure 1. Simplified block flow diagram, Fischer-Tropsch conceptual plant.

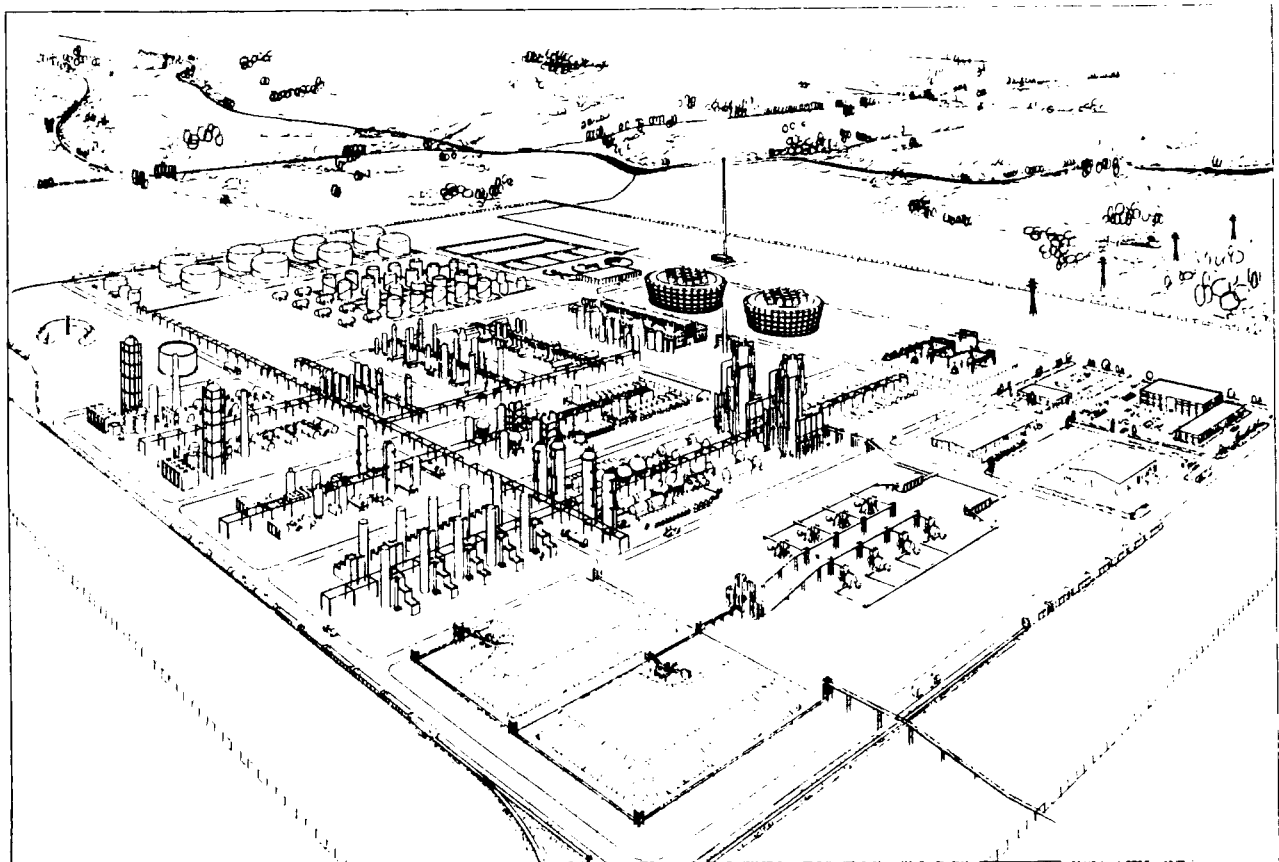


Figure 2. Artist's concept, Fischer-Tropsch plant.

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 percent nitrogen and 3.4 percent sulfur. The premium products obtained, containing nil sulfur or nitrogen, consist of 2,200 MgPD (2,400 TPD) naphthas, 1,900 MgPD (2,100 TPD) of diesel fuel, 650 MgPD (700 TPD) of fuel oil, and 6,000 MgPD (6,600 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 am-

monia, 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.

The sulfur recovery plant oxidizes 95 percent of the hydrogen sulfide to high-purity elemental sulfur. The remaining 5 percent 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 percent 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 regenera-

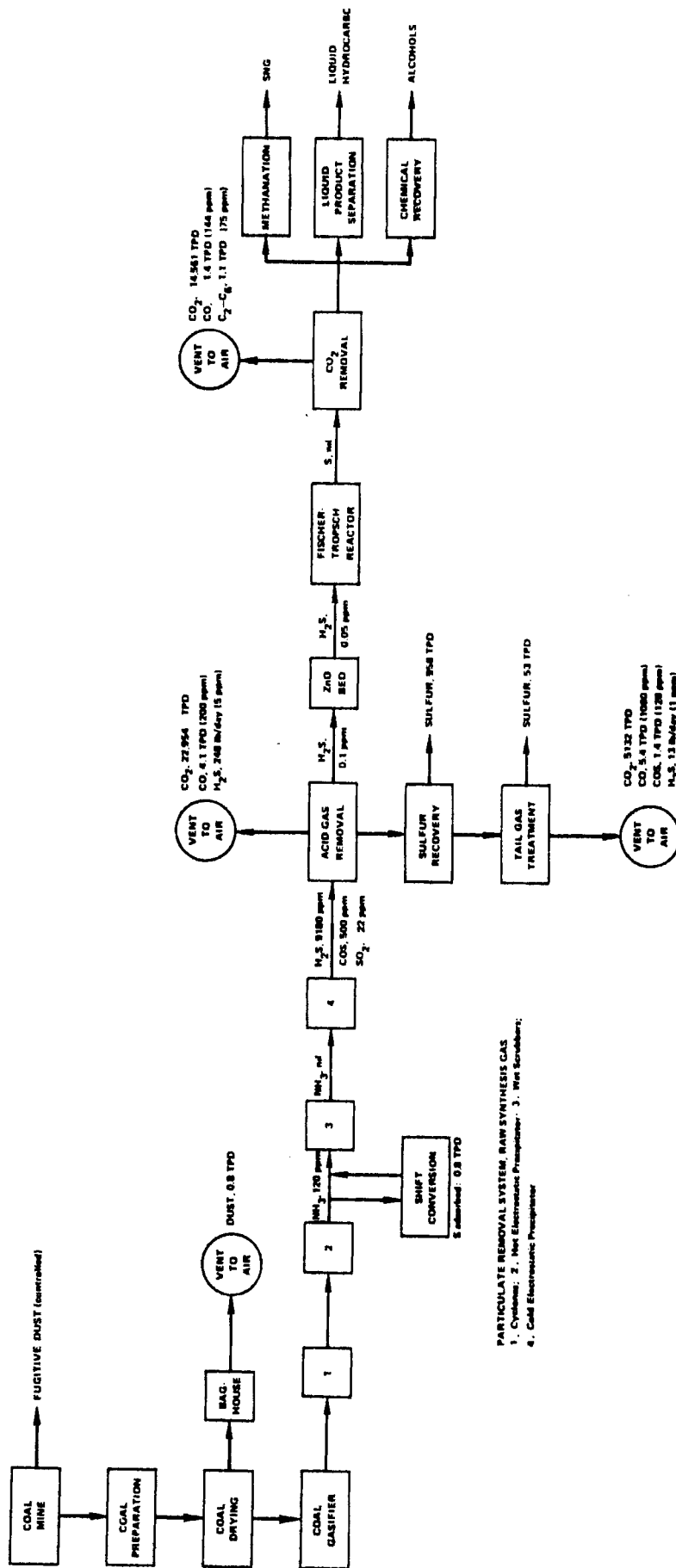


Figure 3. Block flow diagram, air pollution abatement, Fischer-Tropsch plant (1 TPD = 0.9 MgPD)

TABLE 1
SULFUR BALANCE

Sulfur Contributions	MgPD	TPD
Total Input from the Typical Feed Coal	925.3	1,020.0
Outputs: As Elemental Sulfur from Coal Gasifier Gas	917.5	1,011.4
As Reduced Sulfur Emissions (19% H ₂ S, 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	1,020.0

tion 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.

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

TABLE 2
COMBINED GASEOUS EFFLUENTS

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

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 concentra-

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 ft³ = 0.028 m³; MM = million; HHV = higher heating value; L = lower.)

Pollutant	Federal Standards,			New Mexico Standards, Coal Gasification Plant	Gaseous Effluents, Fischer-Tropsch Plant
	Petroleum Refinery Sulfur Recovery Plant	Illinois Standards, Petrochemical Plant			
Particulate Matter	--	78 lb/hr	0.03 gr/ft ³	67 lb/hr ^(a) , 0.03 gr/ft ³	
Sulfur 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	--	55 ppm	
Total Reduced Sulfur (H ₂ S + COS + CS ₂)	300 ppm	(CH ₄ equivalent)	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).

tions 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 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 m³/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

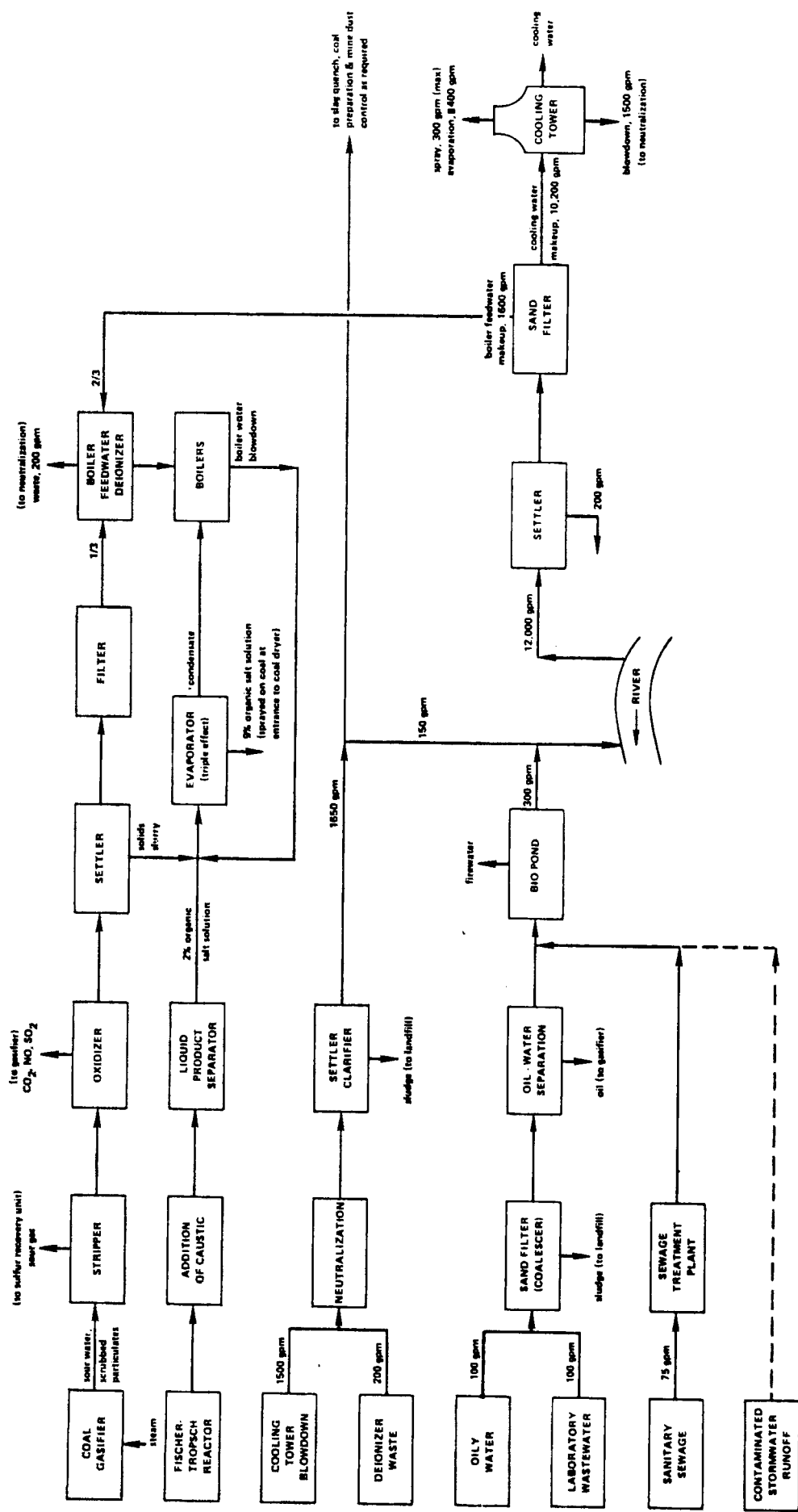


Figure 4. Block flow diagram, water treatment and supply, Fischer-Tropsch plant (1 gpm = 0.227 m³/hr)

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 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

The State of Illinois has issued aqueous effluent standards applicable to all sources discharging to the natural waters of the state.

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 available⁴.

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.

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 treatment 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 estimated that 2132 MgPD (2350 TPD) of slag are produced. On quenching with water, the

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

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 nontransuranic 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 study⁵ carried out with thorough analytical procedures; the coals analyzed were mainly composite face channel samples.

A number of studies have analyzed the

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	12,748.91
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).

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

1 H 1.00797	2 He 4.0026	3 Li 6.939	4 Be 9.0122	5 B 10.811	6 C 12.01115	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.179	11 Na 22.98976	12 Mg 24.305	13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948	19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.63	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80	37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc 98.906	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.6	53 I 126.9044	54 Xe 131.29	55 Cs 132.905	56 Ba 137.34	57 La 138.905	58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm 144.9126	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.930	70 Yb 173.04	71 Lu 174.967	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po 209	85 At 210	86 Rn 222	87 Fr 223	88 Ra 226	89 Ac 227	90 Th 232.038	91 Pa 231	92 U 238.03	93 Np 237	94 Pu 239	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 262	104 Rf 261	105 Db 262	106 Sg 266	107 Bh 264	108 Hs 269	109 Mt 268	110 Ds 271	111 Rg 272	112 Cn 285	113 Nh 286	114 Fl 289	115 Mc 290	116 Lv 293	117 Ts 294	118 Og 294
-------------------	-------------------	------------------	-------------------	------------------	--------------------	-------------------	-------------------	-------------------	--------------------	----------------------	--------------------	---------------------	--------------------	--------------------	-------------------	--------------------	--------------------	-------------------	-------------------	--------------------	-------------------	-------------------	--------------------	--------------------	--------------------	---------------------	-------------------	-------------------	-------------------	-------------------	-------------------	---------------------	-------------------	--------------------	-------------------	-------------------	-------------------	-------------------	-------------------	--------------------	-------------------	--------------------	--------------------	---------------------	-------------------	--------------------	--------------------	--------------------	--------------------	--------------------	-------------------	---------------------	--------------------	---------------------	--------------------	---------------------	--------------------	---------------------	--------------------	----------------------	--------------------	--------------------	--------------------	---------------------	--------------------	---------------------	--------------------	---------------------	--------------------	---------------------	--------------------	---------------------	-------------------	---------------------	--------------------	--------------------	--------------------	---------------------	--------------------	--------------------	--------------------	---------------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	---------------------	-----------------	-------------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------

Figure 5. Periodic table of the elements. The elements shaded have NOT been found in coal.

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 Laboratory⁸ 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 percent of the mercury and 17 percent of the beryllium could not be accounted for.

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 Montana¹⁰ 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 will very likely be removed by the aqueous condensates formed in 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

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

derivative; for this carbonyl only, chronic effects and carcinogenic activity have been observed. Suggested exposure guidelines and chemical formulas are reported in Table 7.

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 NASA¹³ 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 (930° 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.

When the effluent gas undergoes wet scrubbing, most of the cyanide remains in the gas

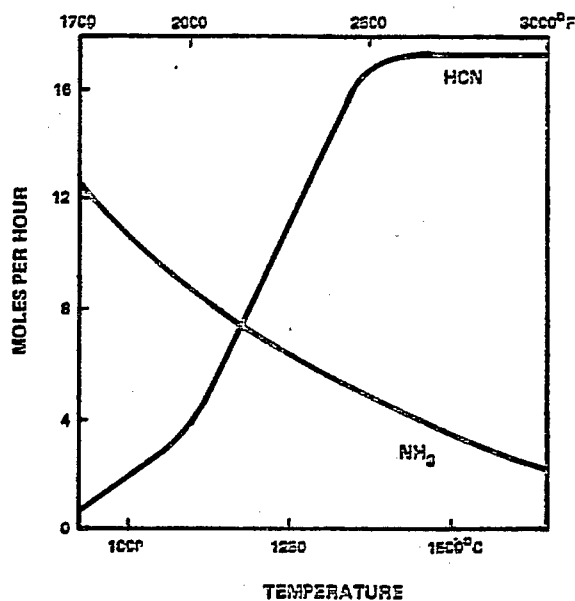


Figure 6. Ammonia-cyanide equilibria.

stream because the sour water generated is only slightly alkaline. It is then absorbed, 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.

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 to avoid 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

We gratefully acknowledge the support and guidance of ERDA-FE in our work, and the contribution of the many people at Parsons who participate in coal conversion activities.

REFERENCES

1. J. B. O'Hara et al., "Fischer-Tropsch Complex: Conceptual Design/Economic Analysis. Oil and SNG Production," R&D Report No. 114 - Interim Report No. 3. Energy Research and Development Administration, Washington, D.C., January 1977.
2. "Draft Standards Support and Environmental Impact Statement, Volume I: Proposed Standards of Performance for Lurgi Coal Gasification Plants," EPA Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, November 1976 (will be reissued as "Guidelines" in late 1977).
3. "Proposed EPA Performance Standards for Petroleum Refinery Sulfur Recovery Plants," Federal Register, 41, 43866, October 4, 1976.
4. "Development Document for Effluent Guidelines and New Source Performance Standards for the Petroleum Refining Point Source Category," U.S. Environmental Protection Agency, Report EPA-440/1-74-014a, Washington, D.C., April 1974.
5. R. R. Ruch et al., "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," Illinois State Geological Survey, Environmental Geology Note No. 72, August 1974 (NTIS Report No. PB 238091).
6. J. W. Kaakinen et al., "Trace Element Behavior in Coal-Fired Power Plant," Environ. Sci. Technol., 9, 862-869 (1975).

7. D. H. Klein et al., "Pathways of Thirty-Seven Trace Elements Through Coal-Fired Power Plant," *Environ. Sci. Technol.*, **9**, 973-979 (1975).
8. W. S. Bennett et al., "WESCO Coal Gasification Plant: Navajo Considerations." Los Alamos Scientific Laboratory Report No. LA-6247-MS, February 1976.
9. W. F. Holland et al., "The Environmental Effects of Trace Elements in the Pond Disposal of Ash and Flue Gas Desulfurization Sludge," Research Project 202 by the Radian Corp. for the Electric Power Research Institute, Sept. 1975 (NTIS Report No. PB 252090/6WP).
10. W. P. Van Meter and R. E. Erickson, "Environmental Effects from Leaching of Coal Conversion By-Products," ERDA Report Series FE-2019, 1977.
11. R. S. Brief et al., "Metal Carbonyls in the Petroleum Industry," *Archives of Environmental Health, Amer. Ind. Hygiene Assn.*, **23**, 373-384 (1971).
12. J. Brinestad, "Iron and Nickel Carbonyl Formation in Steel Pipes and Its Prevention-Literature Survey," Oak Ridge National Laboratory Report No. ORNL/TM-5499, September 1976.
13. S. Gordon, and B. J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations," NASA Special Publication SP-273, Washington, D.C., 1971.
14. E. Bingham, "Carcinogenic Investigation of Oils from Fossil Fuels," University of Cincinnati Kettering Laboratory, Cincinnati, Ohio, 1974.
15. W. C. Hueper, "Experimental Carcinogenic Studies on Hydrogenated Coal Oils. II. Fischer-Tropsch Oils," *Industrial Medicine and Surgery*, **25**, 459-62 (1956).