

Table 22

Coal Preparation for COED Plant

Inlet Streams:

- (1) Coal, Illinois No. 6 Seam, 14% moisture; 1237 tph.
- (2) Influence of weather on coal stockpiles and open coal operations.
- (3) Clean fuel gas to dryer; 455 MM Btu/Hr.

Outlet Streams:

- (4) Precipitation runoff to holding ponds. May include wet scrubber aqueous effluents.
- *(5) Dust and Fumes. Atmosphere in enclosed working areas to be analyzed per Table 35 for particulates. Discrete stack emissions to atmosphere from enclosed spaces from dust collection equipment to be analyzed per Table 35 for particulates. Atmosphere in vicinity of coal stockpiles, open conveying and handling equipment, and coal fines product collection system to be analyzed per Table 35 for particulates.
- *(6) Sized Coal to Pyrolysis, 5.9% moisture; 1063 tph. To be analyzed as feed coal per Table 35.
- *(7) Vent gas from dryer containing 108 tph water. Gas stream may require treatment to limit CO content. To be analyzed per Table 35 for particulates, trace sulfur compounds, and CO content.
- (8) Product coal fines, 4% moisture; 66 tph.

* Analytical Sample

4.4 Drying and Stage 1 Pyrolysis (Figure 20 and Table 23)

Clean fuel gas is burned substoichiometrically both to dry feed coal and to heat fluidizing gas for the first stage of pyrolysis. Both gas and air feeds to the heaters must be raised in pressure to match the operating pressures of the coal dryer and first stage, nominally 7-8 psig.

Coal is fed from storage hoppers by mechanical feeders into a mixing tee from which it is blown into the dryer with heated transport (recirculated) gas.

A cascade of two internal gas cyclones is provided both the coal dryer and the first pyrolysis reactor. Gas which issues from the first pyrolyzer is circulated through the fluidizing-gas heater for the coal dryer. Gas which issues from the coal dryer passes through an external cyclone and is then scrubbed in venturi scrubber-coolers, which serve to complete the removal of coal and char fines, as well as traces of coal liquids from the gas stream. Fines which are recovered in the external cyclone are passed through a mechanical feeder to a mixing tee where they are injected into the first-stage pyrolyzer by recirculated gas. Water equivalent to that introduced with coal and formed in the combustion processes is condensed from the gas in the scrubbing process.

Scrubber effluent passes into a gas-liquid separator, and the liquor stream is decanted and filtered to remove solids. The solids removed by filtration are indicated to amount to about 1 percent of the coal feed, and the wet filter cake is indicated to be recycled back to coal feed. The decanted liquor, except for a purge stream which, along with the filtrate from the fines filter, balances the removal of water from the section, is pumped back to the venturi scrubbers through water-cooled heat exchangers.

The gas stream which issues from the separator, except for a purge stream which removes the nitrogen introduced in the combustion processes, is compressed and recirculated to the gas heaters. This purge gas stream is essentially the only gaseous release from this section. Like the gas stream envisioned for the coal preparation section (see above), it is indicated to contain about 3.7 percent carbon monoxide, and will probably require further treatment before it may be released to the atmosphere. It may be possible to inject it into a boiler stack(s) along with air or oxygen to reduce CO emission. Alternatively the stream(s) may have to be incinerated in specific equipment for this purpose with additional fuel. The gas stream in this case is indicated to be sulfur-free.

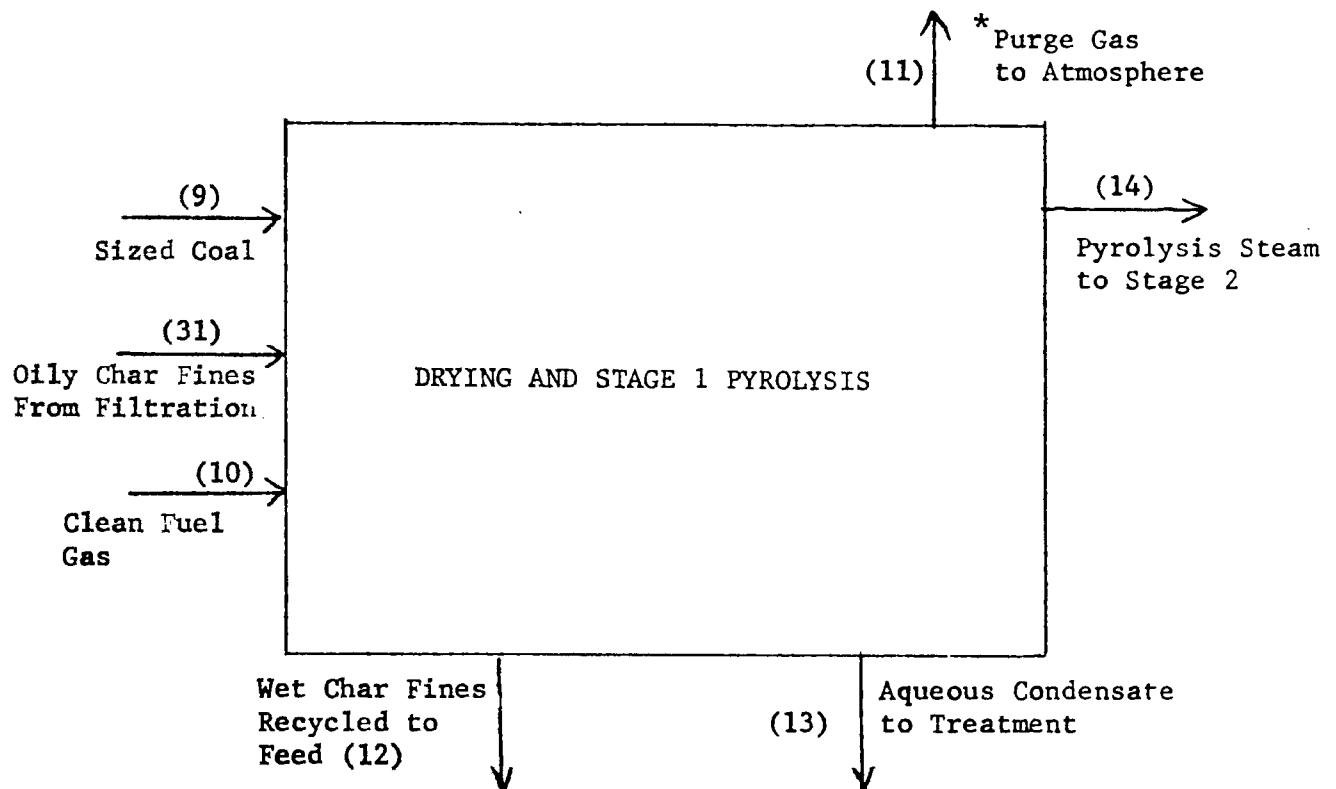


Figure 20

Drying and Stage 1 Pyrolysis

Table 23

Drying and Stage 1 Pyrolysis

Inlet Streams:

- (9) Sized Coal; 1063 tph; plus Recycle Wet Char Fines; 22 tph.
- (10) Clean Fuel Gas; 25 tph.
- (31) Oily Char Fines from Filtration; 15.2 tph.

Outlet Streams:

- *(11) Purge gas to atmosphere; 366 tph. May require treatment to limit CO content. To be analyzed for particulates, trace sulfur compounds, and CO content per Table 35.
- (12) Wet, oily char fines separated at fines filter; 22 tph. Recycled to coal feed.
- (13) Aqueous condensate; 93.5 tph. 83.3 tph directed to last pyrolyzer. 10.2 tph directed to water treatment.
- (14) Pyrolysis Stream to Stage 2; 978 tph.

* Analytical Sample.

4.5 Stages 2,3,4 Pyrolysis (Figure 21 and Table 24)

Coal which has undergone first-stage pyrolysis (at temperatures of about 550-600°F) is passed out of the stage into a mixing tee, from which it is transported into the second stage by heated recycle gas. Pyrolysis stages 2,3, and 4 are cascaded such that pyrolyzed solids pass through the stages in sequence in transport gas streams. Superheated steam and oxygen are injected into the last stage, where heat is released by partial combustion. Substantial recycle of hot ($\sim 1550^\circ\text{F}$) char from this last stage is used to supply heat to stages 2 and 3, in which it otherwise serves as an inert diluent. Similarly, hot gas which issues from the last stage is passed countercurrently through the cascade, serving also as the primary fluidizing medium in these reactors. Stages 2 and 3 operate at about 850° and 1050°F respectively.

The pyrolyzer vessels are each about 60-70 feet in diameter. A total of eight pyrolyzers in two trains is required to process the indicated feed coal. All fluidized vessels are equipped with internal dual-cascade cyclone systems.

Gas which issues from the second pyrolyzer passes through an external cyclone before being directed to the product recovery system. Fines which are separated are directed, along with product char from the last stage, to a fluidized bed cooler, which is used to generate 265,000 lb/hr of 600 psia steam. First-stage recycle gas is used to fluidize the char cooler, and the gas which issues from the cooler is directed back to the venturi scrubbers in the first section after it has passed through an external cyclone. Fines from this cyclone are added to the char make from the last stage. Product char is available at this point at 800°F. About 180,000 lb/hr of 150 psia steam may additionally be generated from the char if suitable equipment can be designed to abstract its sensible heat.

Because the system is otherwise closed, the only possible major atmospheric effluents from this section are the products of combustion from the heaters used to superheat the steam and oxygen feeds to the last pyrolysis stage. We have assumed clean product gas for this service also. About 10.5 tons of gas is required, along with about 105 tons of air per hour. The combustion products should be dischargeable directly in this case without further treatment.

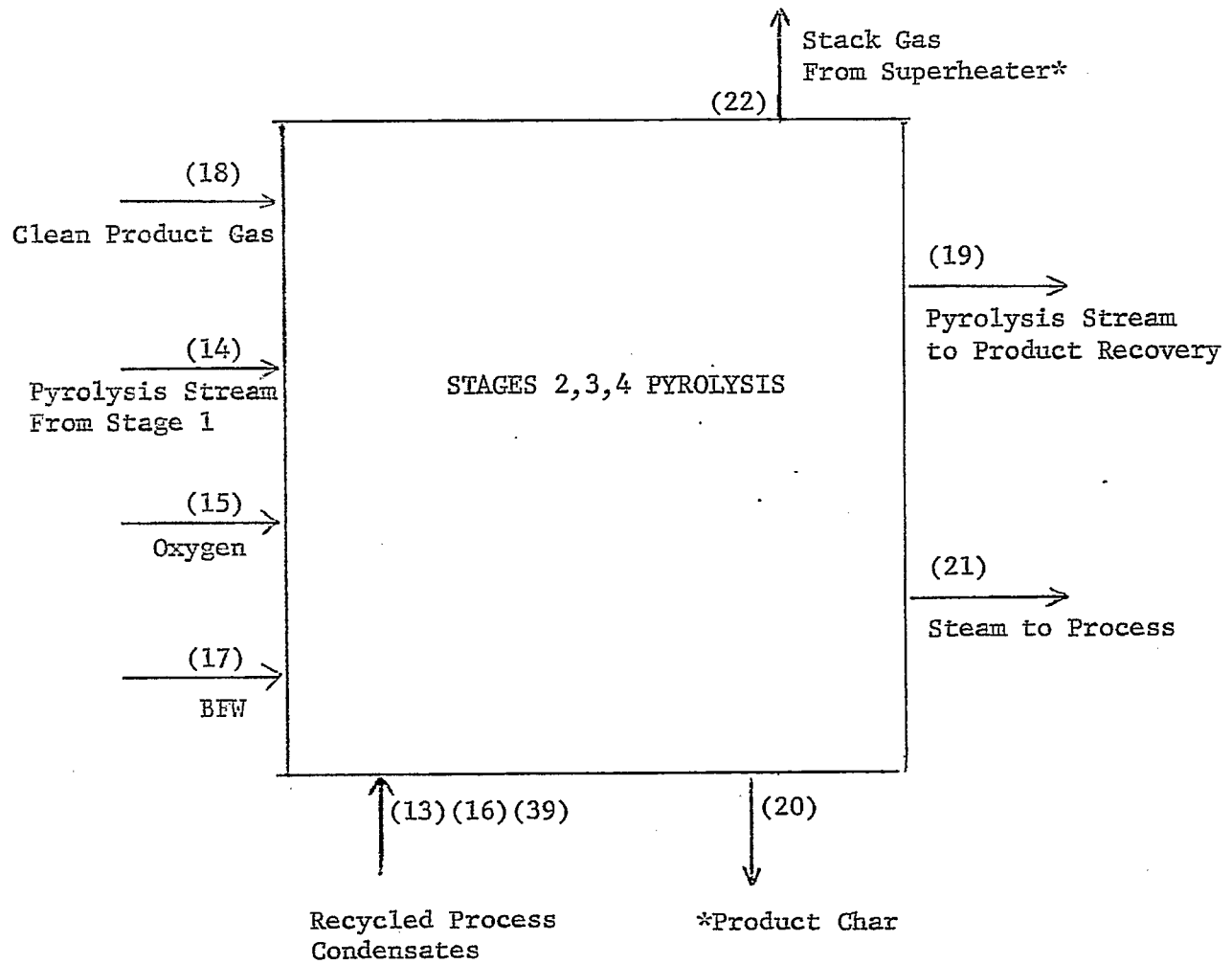


Figure 21

Stages 2,3,4 Pyrolysis

Table 24

Stages 2,3,4 Pyrolysis

Inlet Streams:

- (14) Pyrolysis Stream from Stage 1; 978 tph.
- (15) Oxygen from Oxygen Plant; 156.5 tph.
- (39)(13)(16) Recycled process liquors as steam to last pyrolyzer; 337 tph.
- (17) BFW to fluidized bed char cooler and aftercooler; 900 gpm.
- (18) Clean Product Gas to Superheaters; 10.5 tph.

Outlet Streams:

- (19) Pyrolysis Stream to Product Recovery; 1088 tph.
- *(20) Product char; 521 tph. To be analyzed for trace sulfur and trace elements per Table 35.
- (21) 600 psia steam; 265,000 lb/hr and 150 psia steam; 180,000 lb/hr from char cooling to process.
- *(22) Stack gas from superheaters; 115 tph. To be analyzed per Table 35 for particulates and trace sulfur compounds.

* Analytical Sample.

24

4.6 Product Recovery (Figure 22 and Table 25)

Gas from the pyrolysis section is cooled and washed in two cascaded venturi scrubber stages to condense oil and solid components from the gas stream. The gas which issues from the second scrubber gas-liquid separator is passed through an electrostatic precipitator to remove microscopic droplets, and is then cooled to 110°F by cold-water exchange to condense water. About a quarter of the gas stream is compressed and reheated for use as transport gas in the pyrolysis train. The remainder issues from the system as raw product gas, which is to be directed to an acid-gas removal system.

The oil and water condensed from the gas stream in the scrubber-coolers is decanted and separates into three phases: a light oil phase, a middle (aqueous phase), and a heavy oil phase. The oil phases are collected separately for dehydration in steam-jacketed vessels. The combined dehydrated oil is pumped to the COED oil filtration system.

A recycle liquor pump takes suction from the middle phase in the decanter. Recycle liquor is cooled in cold-water exchangers before being injected into the venturi scrubbers. Water condensed from the incoming gas leaves the section as a purge ahead of the recycle liquor coolers, and is indicated to be recirculated to the last pyrolysis stage.

The only major effluents to the atmosphere from this section are the combustion gases from the recycle transport-gas heater. Since clean product gas is fired in this heater, the combustion gases should be dischargeable directly.

Vents from the oil decanters and dehydrators are indicated to be directed to an incinerator. Under normal operation, and with adequate condensing capacity in the vapor takeoffs from the dehydrators, vent flow should be minimal.

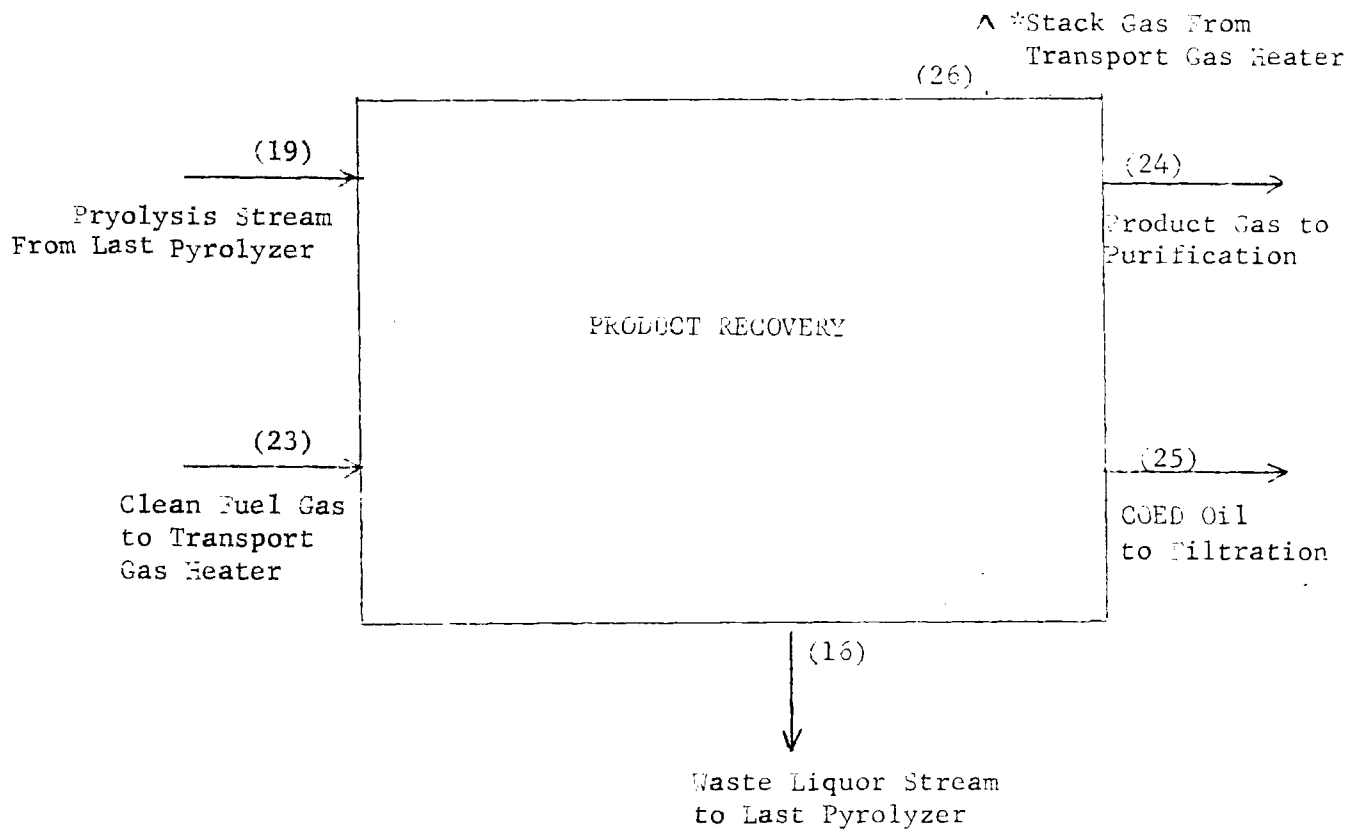


Figure 22

Product Recovery

Table 25

Product Recovery

Inlet Streams:

- (19) Pyrolysis Stream from Last Pyrolyzer; 1088 tph.
- (23) Clean Fuel Gas to Transport Gas Heater; 3.1 tph.

Outlet Streams:

- (16) Waste Liquor Stream to Last Pyrolyzer; 237 tph.
- (24) Product Gas to Gas Purification; 513 tph.
- (25) COED oil to Oil Filtration; 200 tph.
- *(26) Stack Gas from Transport Gas Heater; 35 tph, to be analyzed per Table 35 for particulates and trace sulfur compounds.

* Analytical Sample.

4.7 Oil Filtration (Figure 23 and Table 26)

FMC has designed a filtration plant to handle the COED raw oil output based on filtration rates demonstrated in its pilot plant. The system employs ten 700 ft² rotary-pressure precoat filters to remove char fines from the raw oil ahead of hydrotreating. Each filter is operated on a 7-hour precoat cycle, followed by a 41-hour filtration cycle.

Both the precoat and the raw oil to filtration are heated, using steam, to about 340°F. Inert gas (nitrogen) is compressed, heated, and recirculated for pressurizing the filters. The gas purge from the system, equivalent to the nitrogen makeup, is directed to a boiler stack. It is indicated to contain only trace quantities of combustibles and sulfur.

Hot filter cake (38% oil, 52% char, 10% filter aid at 350°F) is discharged at the rate of about 15 tph, and is indicated to be added to the plant's char output in the process basis. FMC has recently indicated that filter cake will instead be recycled to coal feed. Filtered oil is directed to the hydrotreating facility.

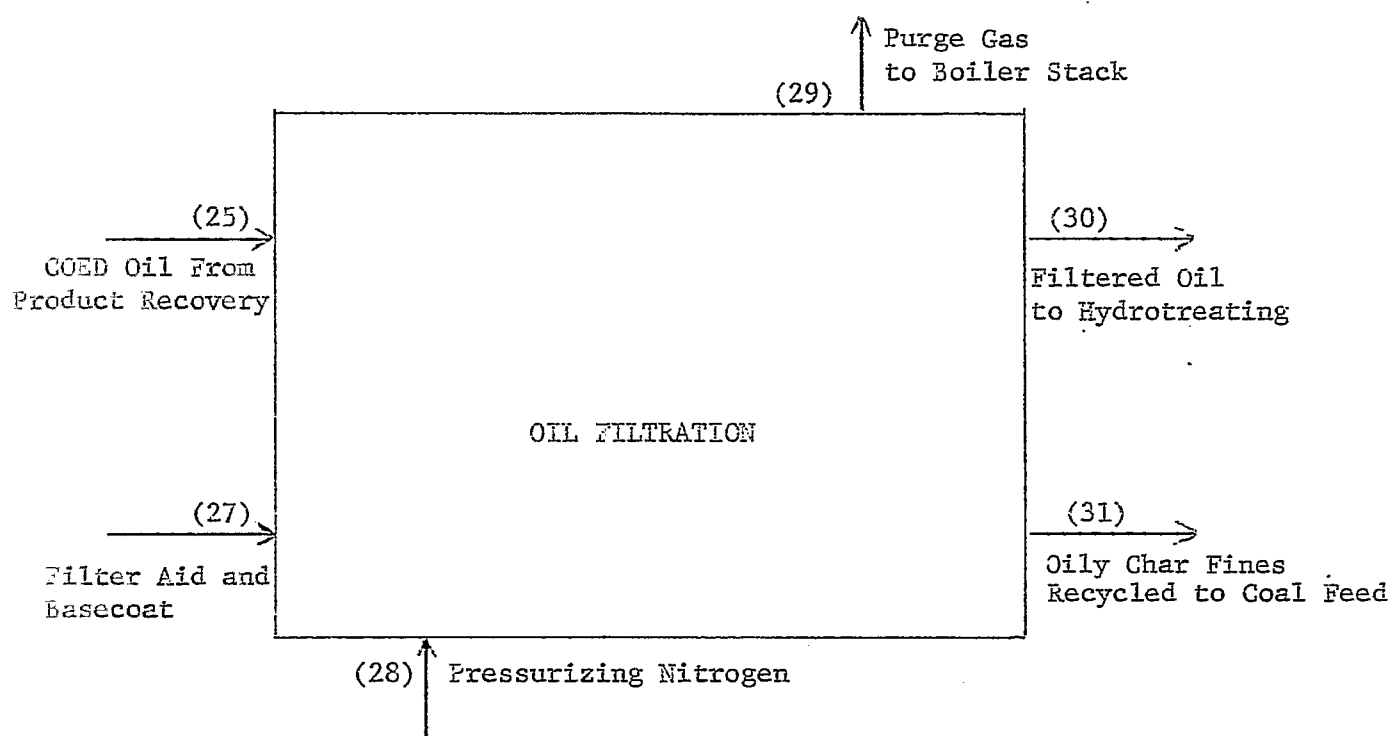


Figure 23

Oil Filtration

Table 26

Oil Filtration

Inlet Streams:

- (25) COED Oil from Product Recovery; 200 tph.
- (27) Filter aid and Basecoat during filter precoat cycle; 1.5 tph.
- (28) Pressurizing nitrogen from oxygen plant; 0.5 tph.

Outlet Streams:

- (29) Purge gas directed to incinerator or boiler stack; 0.5 tph.
- (30) Filtered Oil to Hydrotreating; 186 tph.
- (31) Oily char fines containing 1.5 tph filter aid; 15.2 tph. Recycled to coal feed.

4.8 Hydrotreating (Figure 24 and Table 27)

Hydrotreating is employed to upgrade the heavy pyrolysis oil through the addition of hydrogen, which serves to convert sulfur to hydrogen sulfide, nitrogen to ammonia, and oxygen to water, as well as to increase the oil's hydrogen content through saturation reactions. Hydro-treating is performed catalytically in the FMC pilot plant at 750 to 800°F and at total pressures of 2000-3000 psig; conditions which also promote some cracking reactions.

In the FMC base design, hydrotreating is indicated to be performed at 750°F and at a total pressure of 1710-1720 psia. Filtered oil from the filtration plant is pumped, along with hydrogen from a reforming plant and some recycled oil, through a gas-fired preheater into initial catalytic guard reactors. The guard reactors are intended to prevent plugging of the main hydrotreating reactors by providing for deposition of coke formed in the system on low surface-to-volume packing.

The hydrotreating reactors are indicated to be three-section, down flow devices. The gas-oil mixture from the guard bed is introduced at the reactor head along with additional recycle hydrogen. Recycled oil and hydrogen at low temperature (100-200°F) are introduced between the catalyst sections in the reactor to absorb some of the exothermic heat of reaction.

The hydrotreated effluent is cooled and flows into a high-pressure flash drum, where oil-water-gas separation is effected. About 60 percent of the gas which separates is recycled by compression to the hydrotreaters. The remainder is indicated to be directed to the hydrogen plant.

A little less than half of the oil which separates is recycled to the hydrotreaters. The remainder, taken as product, is depressured into a receiving tank. From the tank it is pumped into a stripping tower, where clean product gas is used to strip hydrogen sulfide and ammonia.

Clean product gas is used also to strip ammonia and H₂S from the water which separates from hydrotreater effluent. Stripped water is indicated to be recycled to the last pyrolysis stage. The gas effluents from the strippers are indicated to be directed to gas clean up.

The only major effluents to atmosphere from this section are the combustion gases from the hydrotreater preheater. About 4.5 tph of product gas is consumed, along with about 84 tph of combustion air. The products of combustion should be dischargeable directly without further treatment.

The process design basis does not provide for catalyst replacement in this section. Nor are facilities included for presulfiding catalyst, if this be required, or for regenerating catalyst.

We have assumed that regeneration, if it is practiced, will occur off site. Moreover, we have assumed that the hydrotreaters will be designed to run continuously between maintenance shutdowns.

Provisions for depressuring and inerting the hydrotreater preliminary to catalyst removal should not result in emissions to atmosphere, since gaseous effluents may be recycled to the hydrogen plant gas treatment section, or to the main gas-treating section. Ammonium sulfide, which is produced in the hydrotreater and which is stable at reaction conditions, decomposes at low temperatures and pressure to release additional ammonia and H_2S into the inerting medium. Metal carbonyls may also be present, and special precautions may be required if these are found in significant concentration.

Gaseous effluent which results from inerting the system after catalyst replacement may require treatment to remove particulates. In general, the same procedures used to replace catalyst in the hydrotreater may also be applied to changeout of the packing or catalyst in the guard reactors.

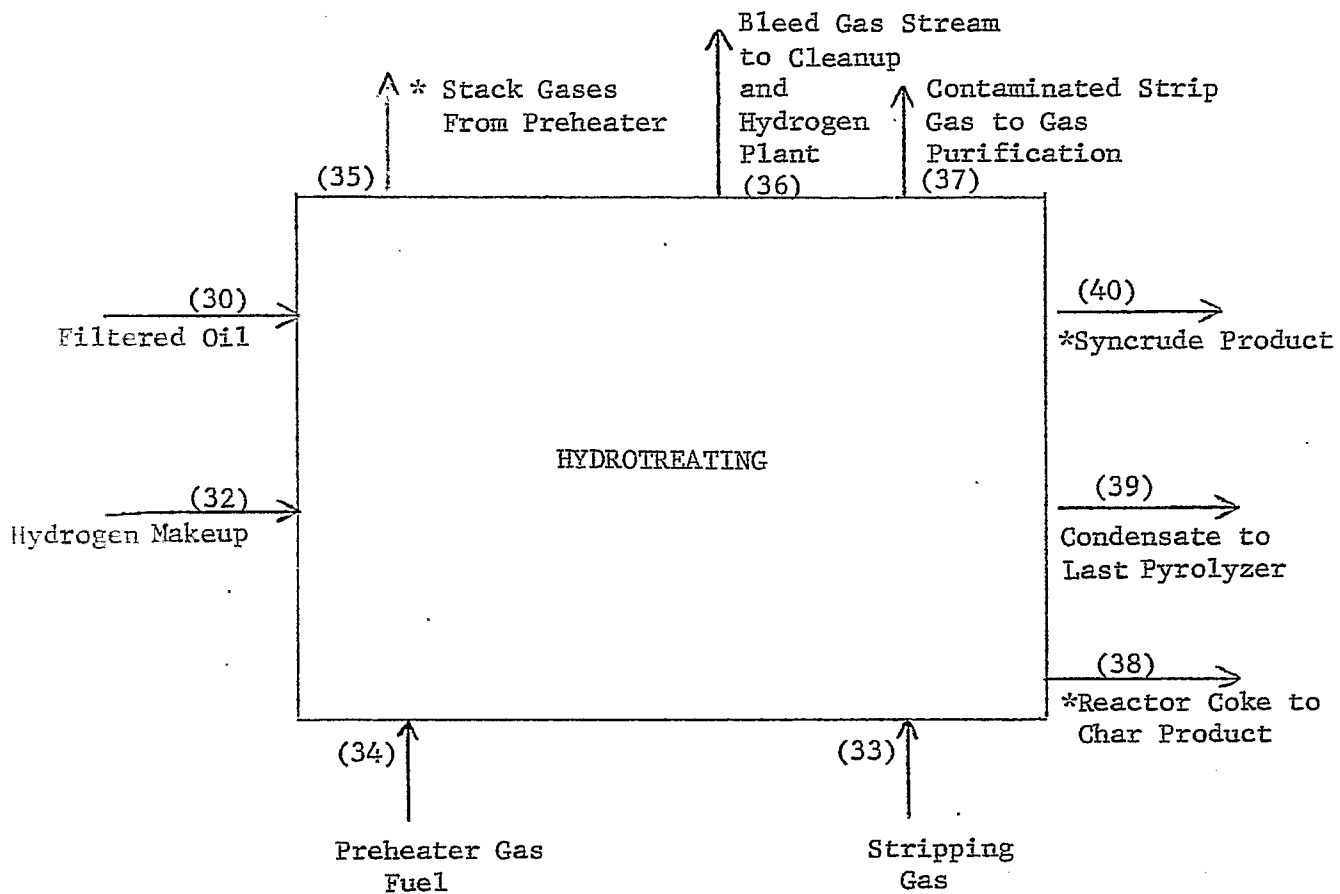


Figure 24
Hydrotreating

Table 27

Hydrotreating

Inlet Streams:

- (30) Filtered Oil from Filtration; 186 tph.
- (32) Hydrogen Makeup from Hydrogen Plant; 28.4 tph.
- (33) Clean Product Gas Stripping Medium; 103 tph.
- (34) Clean Product Gas to Preheater; 11.8 tph.

Outlet Streams:

- *(35) Stack Gases from Preheater; 130 tph. To be analyzed for particulates and trace sulfur compounds per Table 35.
 - (36) Bleed Gas Stream to Cleanup and Hydrogen Plant; 29 tph.
 - (37) Contaminated Stripping Gas to Gas Purification; 107 tph.
 - *(38) Reactor Coke to Product Char; 0.04 tph. To be analyzed for trace elements for Table 35.
 - (39) Contaminated Condensate to Last Pyrolyzer; 16.6 tph.
 - *(40) Syncrude Product; 164.4 tph. To be analyzed for trace sulfur compounds and trace elements per Table 35.
- * Analytical Sample.

4.9 Oxygen Plant (Figure 25 and Table 28)

The oxygen plant provides a total of 3760 tons per day of oxygen to the last pyrolysis stage. The only effluents to the air from this facility should be the other components of air, principally nitrogen. About 340 MM scfd of nitrogen will be separated. Some of this nitrogen may be used to advantage in the plant to inert vessels or conveyances, to serve as transport medium for combustible powders or dusts, to serve as an inert stripping agent in regeneration or distillation, or to dilute other effluent gas streams. Nitrogen is also indicated to be used to pressurize the rotary pressure raw-oil filters.

About 440 MM scfd of air is taken into the oxygen facility. Placement of the oxygen facility will depend in part on the desire to maintain the quality of the air drawn into the system and, especially, to minimize interference from plant effluents.

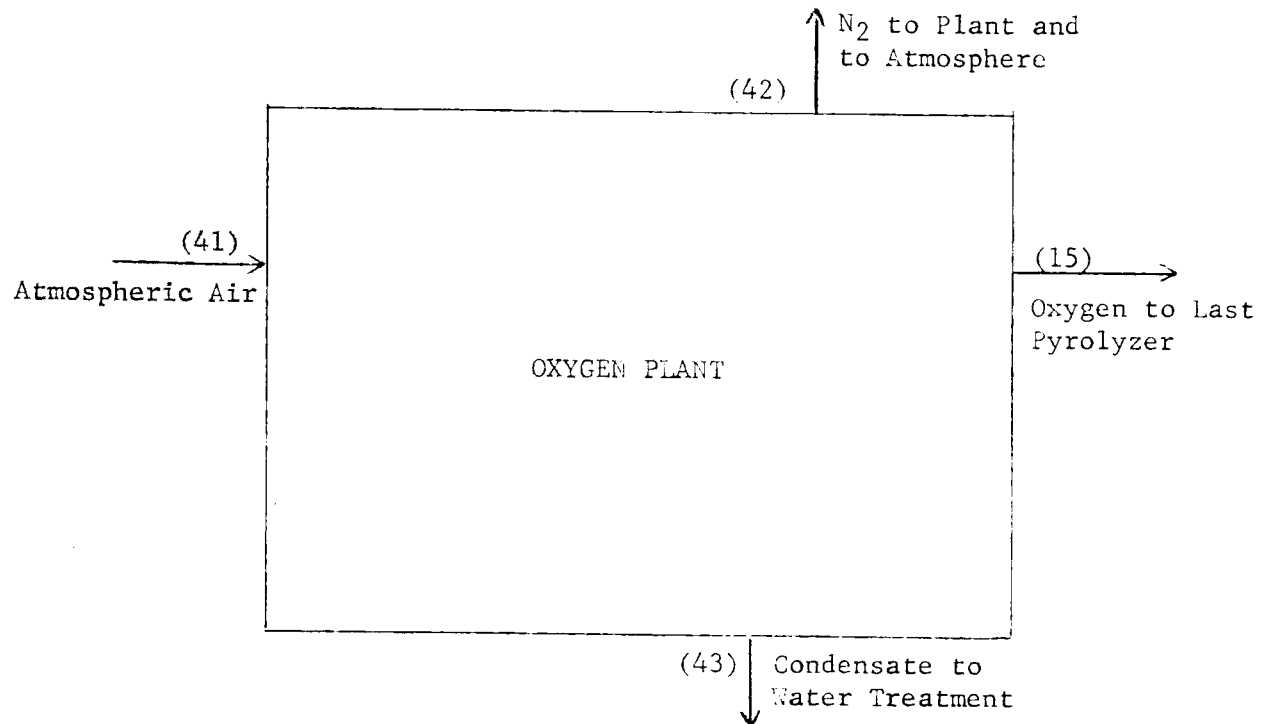


Figure 25

Oxygen Plant

Table 28

Oxygen Plant

Inlet Streams:

(41) Atmospheric air intake; 440 MM SCFD.

Outlet Streams:

(15) Oxygen to Last Pyrolyzer; 156.5 tph.

(42) Nitrogen to Atmosphere and/or Plant; 340 MM SCFD.

(43) Water Condensate to BFW Treatment; 17 gpm.

4.10 Gas Purification (Figure 26 and Table 29)

The acid-gas removal process to be used in this facility has not been specified by FMC. Sulfinol and hot carbonate have been tentatively considered.

The primary feed to this unit would be the product gas stream separated from the product recovery system (513 tph). Contaminated product gas used for stripping the water and oil effluents from hydro-treating (107 tph) may also be returned to this unit; however, since this stream contains ammonia, it may be preferable to treat it separately.

The particular choice of acid gas removal process may depend on the nature and quantity of "trace" contaminants present in the gas to be treated. FMC has not reported on the quantity and nature of the sulfurous contaminants in raw gas. COS has been found in some streams.

In our basis we have assumed that the "Benfield" hot potassium carbonate gas purification system will be used. In the Benfield system, gas absorption takes place in a concentrated aqueous solution of potassium carbonate which is maintained at above the atmospheric boiling point of the solution (225-240°F) in a pressurized absorber. The high solution temperature permits high concentrations of carbonate to exist without incurring precipitation of bicarbonate.

Partial regeneration of the rich carbonate solution is effected by flashing as the solution is depressured into the regenerators. Low-pressure steam is admitted to the regenerator and/or to the reboiler to supply the heat requirement. Regenerated solution is recirculated to the absorbers by solution pumps. Stripped acid gas flows to the sulfur recovery plant after condensation of excess water. Depressurization of the rich solution from the absorber through hydraulic turbines may recover some of the power required to circulate solution.

Raw product gas from the product recovery section must be compressed for effective scrubbing. We have estimated that the compressor driver will require the equivalent of 500,000 lb/hr of high-pressure steam to handle the primary raw gas stream. Some 1,400,000 gph of solution must be circulated, requiring the equivalent of 5700 kW. Some 450 MM Btu/hr is required for regeneration, supplied as steam, and about this same cooling duty will be required. Additionally, some 100,000 lb/hr of high-pressure steam, 1200 kW, and 95 MM Btu/hr as low-pressure steam, as well as the corresponding quantity of cooling water, will be required to treat the stripping gas from hydrotreating.

Clean gas may be directed to the various fired heaters throughout the plant, and to the utility boiler. There should be no discharge to the atmosphere from the acid-gas removal section.

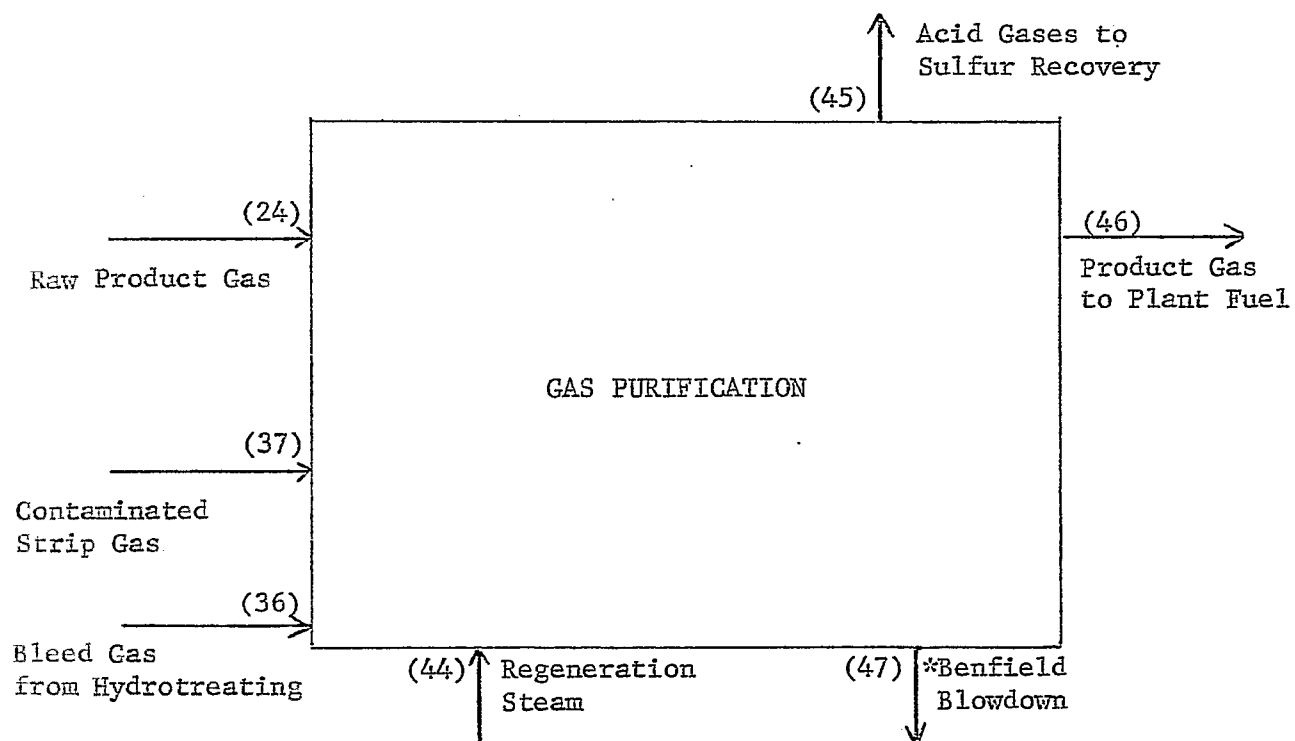


Figure 26

Gas Purification for COED Plant

Table 29

Gas Purification for COED Plant

Inlet Streams:

- (24) Product Gas from Product Recovery; 513 tph.
- (36) Bleed Gas from Hydrotreating; 29 tph.
- (37) Contaminated Stripping Gas from Hydrotreating; 107 tph.
- (44) 150 psia Steam to Regenerators; 381,000 lb/hr.

Outlet Streams:

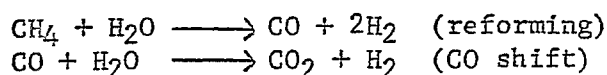
- (45) Acid gases to Sulfur Recovery; 315 tph.
- (46) Product Gas to Plant Fuel and to Hydrogen Plant; 171 tph dry basis.
- *(47) Spent Benfield blowdown requires special treatment. To be analyzed per Table 35 for trace sulfur compounds and trace elements.

* Analytical Sample.

4.11 Hydrogen Plant (Figure 27 and Table 30)

The COED process gas product is indicated to be the source of hydrogen for the hydrotreating of raw COED oil. We have assumed that steam reforming will be used to produce the hydrogen requirement.

COED process gas at 15 psia is compressed to 410 psia and passed through a sulfinol system to remove CO₂ and H₂S. Regenerated acid gases are directed to the sulfur recovery plant. The cleaned process gas containing about 1 ppm H₂S is divided into a fuel gas stream and a process feed gas stream. The process feed gas is passed over a zinc oxide sulfur guard bed to remove sulfur traces, and is then heated by combustion of the fuel gas and hydrogenated with recycle product hydrogen to remove unsaturates. Steam is injected, and reforming and shifting occur catalytically according to:



CO₂ formed in the reactions is removed in a second scrubber-absorber and the process gas is finally methanated catalytically to convert residual CO to methane according to $3\text{H}_2 + \text{CO} \longrightarrow \text{CH}_4 + \text{H}_2\text{O}$. Resulting product gas is available at 200 psig.

The bleed gas from the hydrotreating plant, containing about 2 percent H₂S and about 0.1 percent ammonia, is indicated to be returned to the hydrogen plant for reprocessing. It may be preferable to first scrub this stream with water separately to remove the ammonia trace. About 3.5 tph of H₂S must also be removed from this stream, and the H₂S residual, after water scrubbing, would be removed in an acid gas scrubber and directed to the sulfur recovery plant.

The major gaseous effluents from the hydrogen plant will be the products of combustion from the fired heaters and the CO₂ stream removed from the processed gas after reforming. Since clean product gas is consumed in the heaters, the products of combustion should be dischargeable directly. Some 23 tph of gas is fired.

About 60 tph of CO₂ will be removed from the process gas, and this too may be discharged, although there may be incentive to recover some or all of this stream for sale, since its purity should be high.

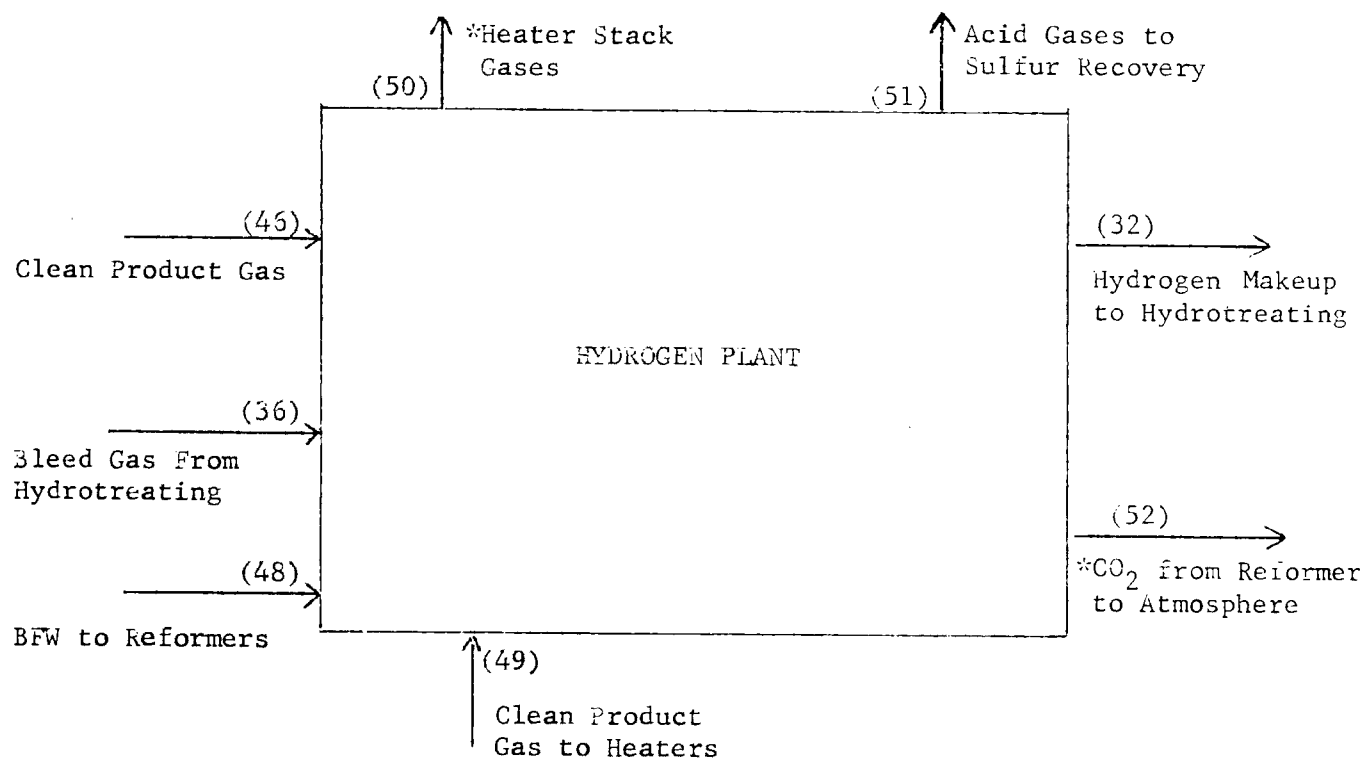


Figure 27
Hydrogen Plant

Table 30

Hydrogen Plant

Inlet Streams:

- (36) Bleed Gas from Hydrotreating; 29 tph.
- (46) Clean Product Gas to Reformers; 25 tph.
- (48) BFW to Reformers; 43 tph net consumption. Excess condensate returned to Water Treatment.
- (49) Clean Product Gas to Fired Heaters; 23 tph.

Outlet Streams:

- (32) Hydrogen Makeup to Hydrotreating; 28.4 tph.
- *(50) Stack Gases from Fired Heaters. To be analyzed for particulates and trace sulfur compounds per Table 35.
- (51) Acid Gases to Sulfur Recovery.
- *(52) CO₂ from reformers; 60 tph. To be analyzed for trace elements per Table 35.

4.12 Sulfur Recovery (Figure 28 and Table 31)

The type of sulfur plant that will be used has not been specified by FMC. The combined acid-gas streams resulting from treatment of raw product gas (pyrolysis gas) and hydrotreating bleed gas would appear to yield an H_2S concentration of about 7 percent based on gas analyses presented in the FMC design. Additional concentrated H_2S streams may result from treatment of sour water and stripping gas. FMC has indicated that high-sulfur Illinois coals will yield H_2S levels in the range of 10-20 percent.

We have assumed that acid gas will be sufficiently high in H_2S content to permit use of a Claus recovery system. Tail gas from the Claus unit must be desulfurized, however. Several processes have been developed for this purpose. FMC indicates that the Beavon or Shell Claus Off-Gas Treating (SCOT) process may be employed.

The Beavon system catalytically hydrogenates the SO_2 over cobalt-molybdate. The catalyst is also effective for reacting CO , which may be present, with water to form hydrogen and for the reaction of COS and CS_2 with water to form H_2S .

The hydrogenated stream is cooled to condense water, and the H_2S stream is fed into a Stretford unit to recover sulfur in elemental form. Treated tail gas may contain less than 200 ppm sulfur, with almost all of this being carbonyl sulfide. Condensate may be stripped of H_2S and directed to boiler feed water treatment.

About 500 tpd of elemental sulfur will be separated at the sulfur plant, depending on the sulfur content of the feed coal and on the processing employed. Total sulfur emission to the atmosphere may be held to less than 200 lbs/hr, and the treated tail gas may be directed to a boiler stack for disposal. The small air stream used to regenerate the Stretford solution in the tail gas treatment plant may also be so directed.

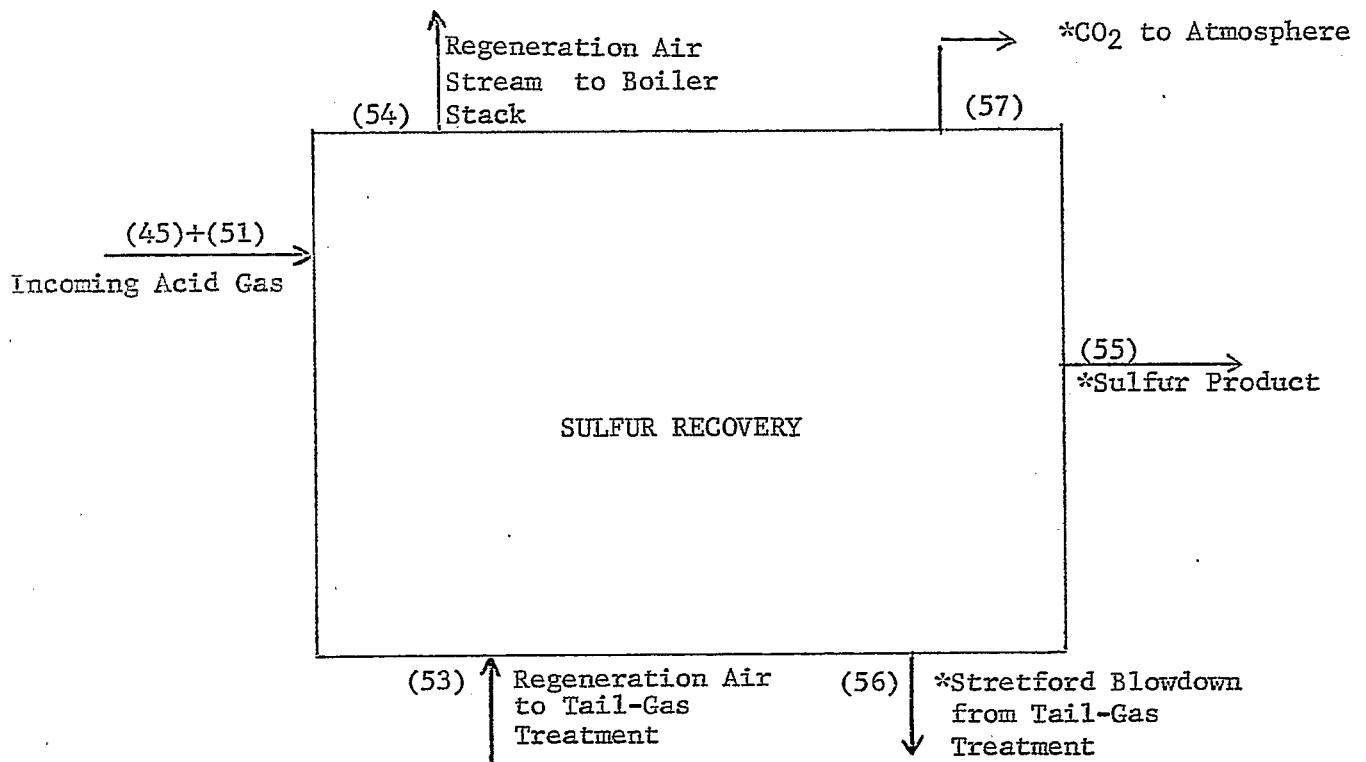


Figure 28

Sulfur Recovery for COED Plant

Table 31

Sulfur Recovery

Inlet Streams:

- (45)(51) Incoming Acid Gases (330 tph) containing 23 tph H₂S.
- (53) Regeneration Air to Tail-Gas Treatment; 0.7 MM SCFD.

Outlet Streams:

- (45) Regeneration Air Stream to Boiler Stack; 0.7 MM SCFD.
 - *(55) Sulfur Product; 510 tpd. To be analyzed for trace elements per Table 35.
 - *(56) Stretford blowdown from tail-gas treatment, to be analyzed for trace elements and trace sulfur compounds per Table 35. May require special treatment.
 - *(57) CO₂ stream to Atmosphere contains less than 200 ppm sulfur. To be analyzed for trace sulfur per Table 35.
- * Analytical Sample.

4.13 Power and Steam Generation (Figure 29 and Table 32)

We have in this study considered that dirty fuels would not be combusted in the plant; therefore, clean product gas would be used for the generation of steam and power requirements. However, the total utility balances require some additional fuel source. Of the 513 tph of contaminated product gas issuing from the product recovery system, there is net 171 tph of dry gas available from the acid-gas removal system. Some 25 tph is required as feed to the hydrogen plant, leaving the net available gas for fuel as 146 tph. The gas is estimated to have a higher heating value of 505 Btu per scf, so that the total available fuel gas equivalent is about 4180 MM Btu per hour.

Net steam requirements for the facility total 783,000 lb/hr, equivalent to a 1130 MM Btu/hr fuel requirement. Net electrical power requirements total 93,200 kW, equivalent to 902 MM Btu/hr of additional fuel. The plant otherwise fires fuel equivalent to 2842 MM Btu/hr in process heaters. Hence the total requirement, 4847 MM Btu per hour, cannot be supplied by the product gas stream alone. The shortfall, equivalent to 694 MM Btu/hr, would presumably come from char.

We have considered that the 2032 MM Btu/hr fuel equivalent required at the power plant could be supplied by the combinative firing of product char and product gas in suitably designed boilers. The fuel requirement is such that if all of the char required to supply the fuel shortfall, about 30 tph, is fired in the power plant along with about 47 tph of product gas, the sulfur emission would be such that flue-gas treatment would be required. About 2.1 tph of SO₂ would be emitted, equivalent to about 2.0 lb/MM Btu, which is above the level permitted by current standards for solid fuels.

We have assumed that char will be combusted in the power plant to make up the fuel shortfall and that flue gas will be treated with a lime-stone process. We recognize that some char treatment process is practically required in a commercial design, so that it is likely that clean fuel gas of low heating value will be available from char in an integrated facility.

We note, however, that only that portion of stack gases derived from char burning needs be treated in our assumed case. Only a small amount of product gas would be fired with char to stabilize the char combustion in order to minimize the volume of stack gas which is treated.

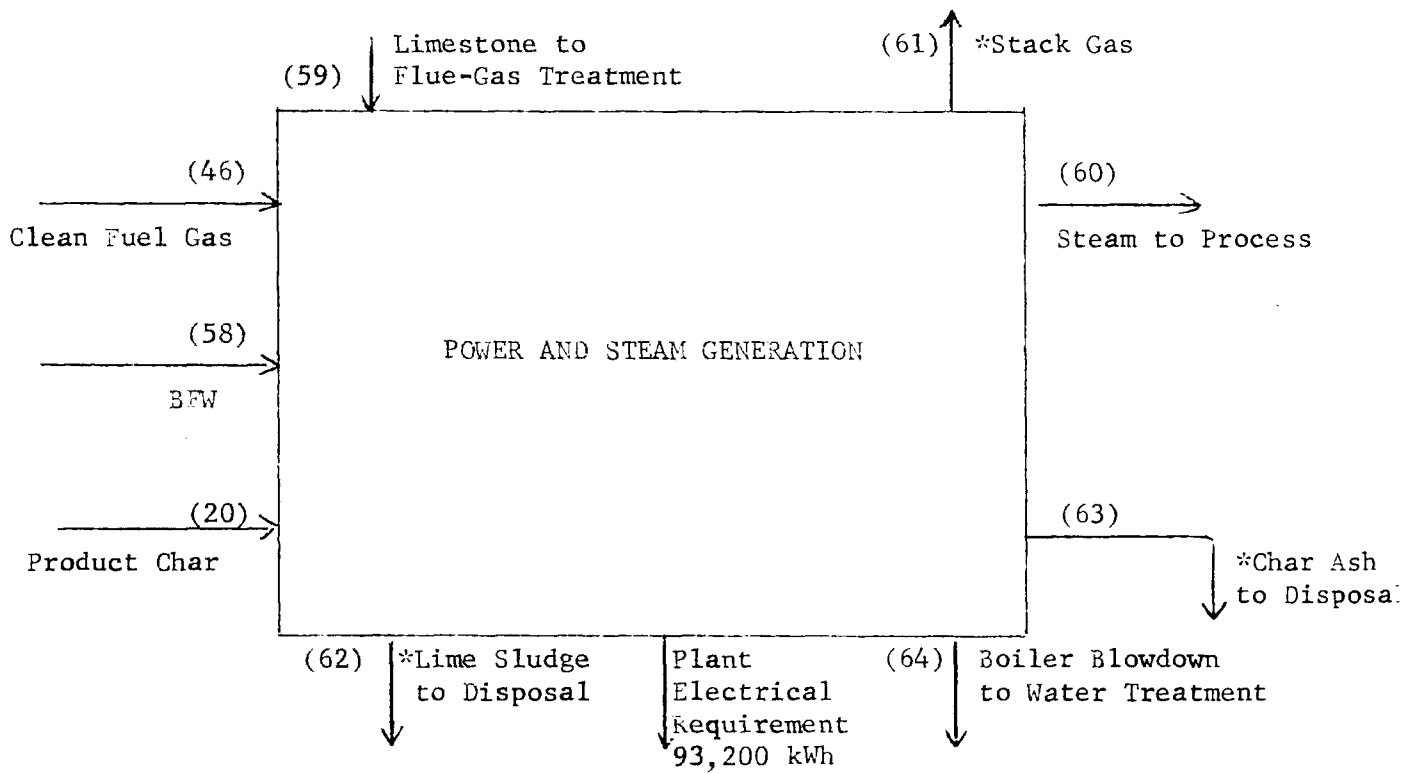


Figure 29

Power and Steam Generation

Table 32

Power and Steam Generation for COED Plant

Inlet Streams:

- (20) Product Char; 30 tph.
- (46) Clean Fuel Gas; 47 tph.
- (58) BFW; 783,000 lb/hr.
- (59) Limestone to Flue-Gas Treatment.

Outlet Streams:

- (60) Steam to Process; 277,000 lb/hr 150 psia and 506,000 lb/hr 600 psia.
- *(61) Stack Gases. Complete stack gas analysis, including particulates and trace sulfur compounds per Table 35.
- *(62) Lime Sludge to Disposal. To be analyzed for trace elements and trace sulfur compounds per Table 35. May require special treatment.
- *(63) Char Ash to Disposal; 6.4 tph. To be analyzed for trace elements and trace sulfur compounds per Table 35. May require special treatment
- (64) Boiler Blowdown to Water Treatment.
- * Analytical Sample.

4.14 Water Treatment (Figure 30 and Table 33)

Analyses of the aqueous condensates produced in the pyrolysis and hydrotreating plants have not been specified in the FMC design. FMC has indicated that these streams would be preferentially recycled to the last, or hottest pyrolyzer, or to char gasification if it be included, after minimal processing to strip ammonia and hydrogen sulfide.

Recycle to a high-temperature char gasification system should present no difficulty. However, the long-term recycle to pyrolysis requires additional study, since temperatures are rather low and there is no basis on which to estimate the degree of "bypass" through the fluidized bed system. The question may be largely academic, however, because it would appear that a large-scale installation, unless it were arranged to combust char locally, would include some form of high-temperature char gasification. We have assumed that pyrolysis liquor may be recycled in our design.

Facilities required to treat water, including raw water, boiler feed water, and aqueous effluents, will include the following separate collection facilities:

- Effluent or chemical sewer
- Oily water sewer
- Oily storm sewer
- Clean storm sewer
- Cooling tower blowdown
- Boiler blowdown
- Sanitary waste

Retention ponds for runoffs and for flow equalization within the system will be required. Runoff from the paved process area could easily exceed 15,000 gpm during rainstorms. Runoff from the unpaved process and storage areas could exceed 80,000 gpm in a maximum 1-hour period.

Pretreatment facilities will include sour water stripping for chemical effluents and Imhoff tanks or septic tanks and drainage fields for sanitary waste.

Gravity settling facilities for oily wastes will include API separators, skim ponds, or parallel plate separators.

Secondary treatment for oily and chemical wastes will include dissolved air-flotation units, granular-media filtration, or chemical flocculation units.

Oxygen demand reduction may be accomplished in activated sludge units, trickling filters, natural or aerated lagoons, or by activated carbon treatment.

Boiler feedwater treatment will in general involve use of ion-exchange resins. Reverse osmosis, electrodialysis, and ozonation may find special application.

Evaporation will of course occur throughout this system, and the concern of the designers will be to limit the coevolution of noxious or undesirable components which may be present. We note that it may be necessary to cover portions of the watertreatment facility and/or provide forced draft over some units to avoid undue discharge of hydrocarbons into the atmosphere. In the latter case, as with direct oxidation or ozonation, sweep gases would be ducted to an incinerator or boiler; and provisions for minimizing explosive hazard would be required.

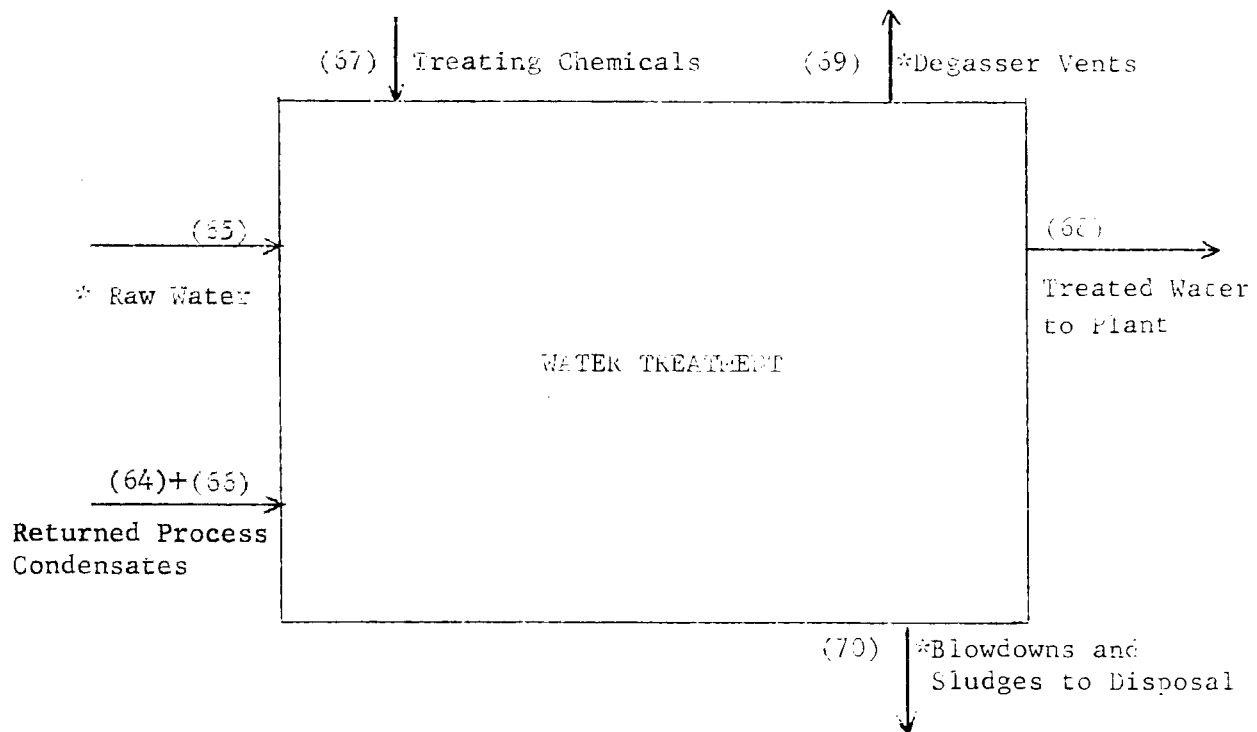


Figure 30
Water Treatment

Table 33

Water Treating

Inlet Streams:

- *(65) Raw Water Makeup; 7600 gpm. Complete water analysis per Table 35.
- (64)(66) Returned process condensates; 3000 gpm.
- (67) Water Treatment chemicals, including pebbled quicklime, sodium hydroxide solution, sulfuric acid, alum, polymer solution, chlorine, hypochlorite, demineralizer and zeolite polymers, salt, anthracite filter media.

Outlet Streams:

- (68) Treated Water to Users; 10,600 gpm.
- *(69) Vents from condensate degassers. To be analyzed for trace constituents per Table 35.
- *(70) Blowdowns and chemical sludges to disposal. To be analyzed for trace sulfur compounds and trace elements per Table 35. May require special treatment.

* Analytical Samples.

4.15 Cooling Water (Figure 31 and Table 34)

A total of 200,000 gpm of cooling water is indicated to be required for operating the FMC design. Because most of this requirement is used for thermal exchange against relatively low-pressure streams, the circuit should be relatively free from process contamination leakage.

A design wet bulb temperature of 77°F and an approach to the wet bulb temperature of 8°F was assumed, with a circulating water temperature rise of 30°F. 9,000 gpm is required as cooling tower make-up, equivalent to 4.5 percent of circulation. Some 3,000,000 pounds per hour of water is evaporated at the cooling tower, 600 gpm is lost as drift, and 2400 gpm is withdrawn as blowdown and is directed to the water treatment facility.

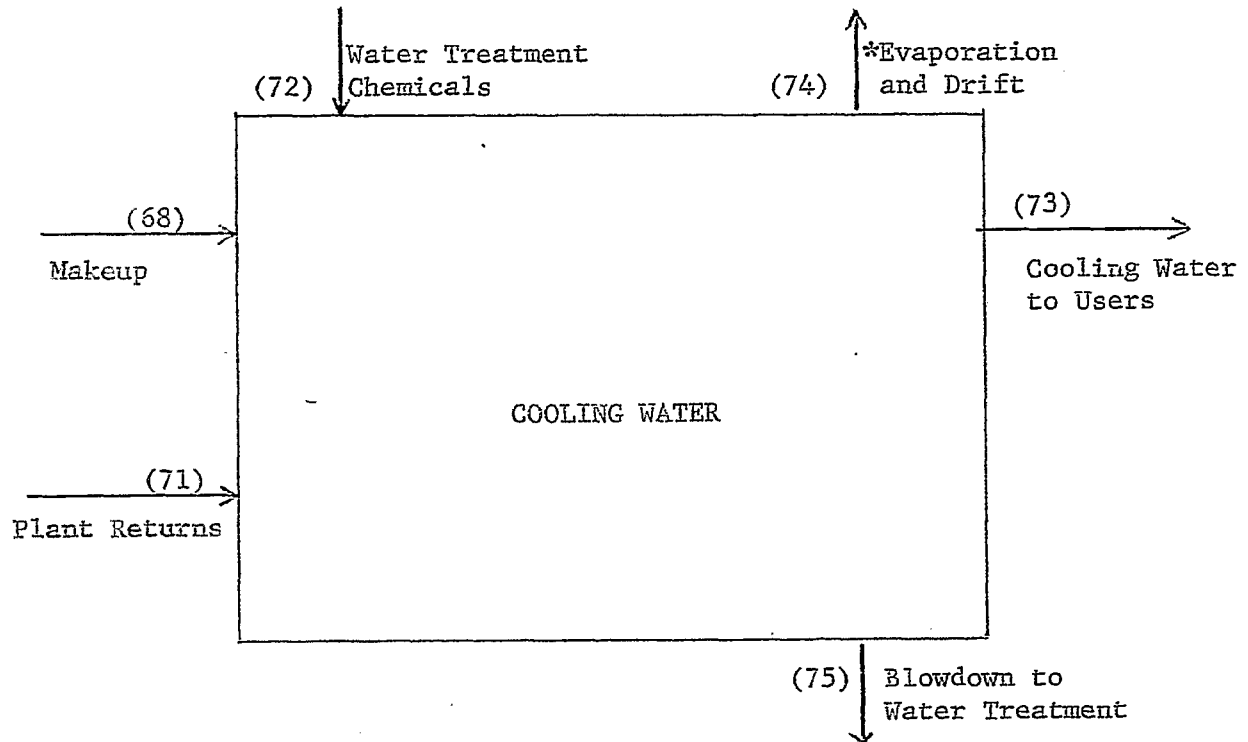


Figure 31
Cooling Water

Table 34

Cooling Water

Inlet Streams:

- (68) Makeup Water from Water Treatment; 9000 gpm.
- (71) Plant returns; 200,000 gpm.
- (72) Water Treatment chemicals including anti-foam package, biological (growth control) package, inhibitor feed package, pH (sulfuric acid) package.

Outlet Streams:

- (73) Cooling water to users; 200,000 gpm.
- *(74) Evaporation from Towers; 6000 gpm and Drift from Towers; 600 gpm.
Atmosphere downwind of towers to be analyzed for trace constituents
per Table 35.
- (75) Blowdown to Water Treatment; 2400 gpm.

* Analytical Sample.

4.16 Process Analytical Summary

The streams indicated for analysis around the COED Process model are summarized in Table 35, along with specific references to suggested sampling and analytical procedures described in the Analytical Sections 5-9.

The qualifications applicable to the analytical scheme for coal gasification described in Section 3.18 are likewise applicable to the liquefaction scheme. We note again that coal liquefaction encompasses a much wider variety of processing alternatives than does gasification, and that the processing sequence in a particular "liquefaction" system may differ considerably from the COED system. However, the integrated facility, when broken down into unit operations in the manner presented herein, will be found to differ generally only in the relative sizes and sequence of such operations, with special differences occurring mainly in the reactor module.

Table 35

Summary of Effluent Streams to be Analyzed for COED Plant

COAL LIQUEFACTION

COED PROCESS MODEL

<u>Stream No.</u>	<u>Stream Name</u>	<u>Analysis For</u>	<u>Analytical Section Reference</u>
5	Dust and Fumes in Coal Preparation Area	Atmosphere in enclosed spaces, discrete stack emissions from enclosed spaces and from dust collection equipment, and atmosphere in vicinity of coal piles, open conveying and handling equipment, and coal fines collection system to be analyzed for particulates.	Total particulates to be determined in enclosed spaces using a high volume sampler, Section 9; in stacks using EPA Method No. 5, Section 9; and the ASTM D 1739 dust fall test will be performed at various site locations.
6	Sized Coal to Pyrolysis	Complete coal analysis including trace elements.	Coal will be analyzed for the elements listed in Section 7, Table VI and will be analyzed to determine its gross composition as indicated in Section 7, Table VII.
7	Coal Dryer Vent Gas	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO ₂ /SO ₃ , NO _x , CO, CO ₂ , COS, H ₂ S, and CH ₃ SH and for particulates. Refer to Section 9.
11	Purge Gas from Stage 1 Pyrolysis	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO ₂ /SO ₃ , NO _x , CO, CO ₂ , COS, H ₂ S, and CH ₃ SH and for particulates. Refer to Section 9.
20	Product Char	Complete Coal Analysis Including Trace Elements	Coal will be analyzed for the elements listed in Section 7, Table VI and will be analyzed to determine its gross composition as indicated in Section 7, Table VII.
22	Stack Gas from Superheaters	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO ₂ /SO ₃ , NO _x , CO, CO ₂ , COS, H ₂ S, and CH ₃ SH and for particulates. Refer to Section 9.

Table 35 (Cont'd)

Summary of Effluent Streams to be Analyzed for COED Plant

COAL LIQUEFACTION

COED PROCESS MODEL

<u>Stream No.</u>	<u>Stream Name</u>	<u>Analysis For</u>	<u>Analytical Section Reference</u>
26	Stack Gas from Transport Gas Heater	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO ₂ /SO ₃ , NO _x , CO, CO ₂ , COS, H ₂ S, and CH ₃ SH and for particulates. Refer to Section 9.
35	Stack Gas From Preheater	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO ₂ /SO ₃ , NO _x , CO, CO ₂ , COS, H ₂ S, and CH ₃ SH and for particulates. Refer to Section 9.
38	Hydrotreating Reactor Coke Product	Complete Coal Analysis Including Trace Elements	Coke will be analyzed for the elements listed in Section 7, Table VI and will be analyzed to determine its gross composition as indicated in Section 7, Table VII.
40	Syncrude Product	Sulfur Trace Elements	This stream will be analyzed for the metals listed in Section 8, Table VIII and for total sulfur as indicated in Section 8, Table X.
47	Benfield Blowdown	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV. The high K ₂ CO ₃ and KHCO ₃ content of this stream may cause interferences in the analyses.

Table 35 (Cont'd)

Summary of Effluent Streams to be Analyzed for COED Plant

COAL LIQUEFACTION

COED PROCESS MODEL

<u>Stream No.</u>	<u>Stream Name</u>	<u>Analysis For</u>	<u>Analytical Section Reference</u>
50	Stack Gas from Hydrogen Plant Heaters	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO ₂ /SO ₃ , NO _x , CO, CO ₂ , COS, H ₂ S, and CH ₃ SH and for particulates. Refer to Section 9.
52	Separated CO ₂ from Reformed Stream	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO ₂ /SO ₃ , NO _x , CO, CO ₂ , COS, H ₂ S, and CH ₃ SH and for particulates. Refer to Section 9.
55	Sulfur Product	Trace Elements	Sulfur will be analyzed for the metals listed in Section 8, Table VIII, by adaptation of methods which were designed for oil analysis.
56	Stretford Blowdown	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV. The Na, V, and carbonate content of the stream may cause interferences in the analyses.
57	Sulfur Plant Off Gas	Trace Sulfur Compounds Particulates (V, Na)	Off-gases to be analyzed for particulates and for COS, H ₂ S, CH ₃ SH and SO ₂ /SO ₃ , see Section 9. In addition Na and V will be determined on particulates, see Section 7.
61	Boiler Stacks and Heaters (Multiple Stacks are Involved)	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gases will be analyzed for SO ₂ /SO ₃ , NO _x , CO, CO ₂ , COS, H ₂ S and CH ₃ SH and for particulates. Refer to Section 9.

Table 35 (Cont'd)

Summary of Effluent Streams to be Analyzed for COED PlantCOAL LIQUEFACTIONCOED PROCESS MODEL

<u>Stream No.</u>	<u>Stream Name</u>	<u>Analysis For</u>	<u>Analytical Section Reference</u>
62	Lime Sludge From Flue-Gas Treatment	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV. The high Ca content of the stream may cause interferences in the analyses.
63	Char Ash from Boilers	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV.
65	Raw Water to Process	Complete Water Analysis	Raw water will be analyzed for all components listed in Section 6, Table IV.
69	Degasser Vent Gases	Trace Sulfur Compounds Hydrocarbons	Vent gases will be analyzed for Thiophene, CO ₂ , SO ₂ /SO ₃ , COS, H ₂ S, and CH ₃ SH and for benzene, toluene, and other volatile organics. See Section 9.
70	Sludges from Water Treatment	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV. The chemicals used for water treatment may cause interferences in the analyses.
74	Evaporation and Drift from Cooling Towers	Atmosphere in vicinity of cooling towers to be sampled for: Trace Sulfur Compounds Trace Elements Hydrocarbons and PNA	A high volume sample will be collected and the particulates will be analyzed for the metals listed in Section 7, Table VI. In addition the atmosphere will be sampled for benzene, toluene and other volatile organics; polynuclear aromatics; and for thiophene, CS ₂ , SO ₂ /SO ₃ , COS, H ₂ S, and CH ₃ SH (Section 9).

4.17 Unit Material Balances

As indicated for gasification in Section 3.19 above, further analyses may be necessary if an over-all plant balance cannot be made using analyses of streams in table 35. Additional streams are listed below for critical units.

Coal Preparation - Streams 2 and 4.

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

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

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

Sulfur Recovery - 45 and 51, 53 and 54.

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

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

The above would require 37 to 38 more streams to be analyzed than the 23 listed in Table 35.

As indicated under Gasification (in 3.19.8), it may be necessary in some cases to make heat and material (including potential pollutants) balances around a particular unit. An example might be Oil Filtration (Section 4.7). Although no streams are indicated to be analyzed to make a pollutant material balance around the plant, it may be desirable to compare the pollution load of filtration with, for example, distillation. All streams of figure 23, together with any other streams of the particular unit of interest, would be sampled and analyzed according to the analytical sections of this plan and these analyses, together with utility requirements, would allow this unit to be compared with other units from the viewpoint of environmental impact.

5. TYPICAL AVAILABLE STREAM ANALYSES AND STANDARDS

Tables 36-39 list some stream analyses for existing commercial plants, proposed plants and pilot plants for those materials that have been suggested in the Analytical Test Plan. In some cases the rules were "bent" to include some data that shows approximate results. For example, results on benzene soluble tar from the Synthane process were included. Similarly, data from a biox unit at SASOL were included even though streams from other industries were mixed with the Sasol stream before the biox unit.

Also included in table 36 are data ranges for analysis of U.S. coals. To indicate ranges of interest, information has been included on existing or proposed state and Federal standards for air and water effluents.

It is obvious that data on most streams of interest are not available and even for those streams about which something is known, much of the data is lacking.

Table 40 presents some standards for water effluents and table 41 presents some air standards. These tables give some indication of what is or will be needed in the way of stream analyses and show something of the ranges of components to be analyzed.

Table 36

Stream Analyses for Existing Plants, Coal

Stream No. From Analytical Test Plan		5 (Gasification); 6 (Liquefaction)					
Stream Identification	Sized Coal to Gasifiers and Liquefaction, ppm						U.S. Coals From Ref. 42
	EPNG (Ref. 1) Navajo Coal	Synthane (Ref. 43) Illinois No. 6	Westfield (Ref. 44)	SASOL (Ref. 45)	SRC (Ref. 47) Illinois No. 6	COED (Ref. 39) Illinois No. 6	
<u>Stream Analyses</u>							
As	0.1-3	---	---	2-5	19	---	3-60
Ba	---	---	---	---	50	---	---
Be	---	---	---	2-3	<10	---	0.08-11
Ca	---	---	---	---	3400-4800	---	---
Cd	0.2-0.4	---	---	< 0.1	1.5- 33	---	---
Cr	---	---	---	---	---	---	2.7-20
F	200-780	---	---	100	300	---	10-100
Fe	---	---	---	---	20,000-24,000	---	---
Hg	0.2-0.35	---	---	< 0.1	0.05	---	0.01-1.2
Li	---	---	---	---	7.4	---	---
Mn	---	---	---	500	39-75	---	---
Na	---	---	---	---	166-320	---	---
Ni	3-30	---	---	30-50	29-120	---	1-50
Pb	1.4-4	---	---	10-20	8-<10	---	4-33
Sb	0.3-1.20	---	---	< 0.5	10.6	---	---
Se	0.08-0.21	---	---	---	7	---	0.5-4.0
V	---	---	---	300-500	200	---	2.3-190
Fixed C, %	---	43	---	---	51.70	51.1 (Dry)	---
Volatile Matter, %	---	37.5	---	---	38.47	37.2 (Dry)	---
Ash, %	17.3	11.2	13.24	31.6 (Dry)	7.13	11.6 (Dry)	---
Moisture, %	16.5	8.3	16.5	8	2.7(After drying)	12.6	---
C, % MAF	76.72	63	56.52	52.4	70.75	66.9	---
H, % MAF	5.71	5.3	3.73	2.6	4.69	4.9	---
N, % MAF	1.37	1.1	0.89	1.2	1.07	1.1	---
S, % MAF	0.95	3.5	1.13	0.43	3.38	4.1	---
O, % MAF	15.21	15.9	7.99	11.7	10.28	11.7	---
P, % MAF	---	---	---	---	---	---	---
Calorific Value, Btu/lb	7,500-10,250	---	9,810	8,890	12,821	12,420	---
Fusibility of Ash, °C							
Softening Point	---	---	---	1375	---	---	---
Melting Point	---	---	---	1475	---	---	---
Fluid Point	---	---	---	1500	---	---	---

Table 37

Stream Analyses for Existing Plants,
Liquid Organic Products

(ppm except as noted)

Stream No. from ATP	17 (Gasification)			24 (Gasification)		30 (Gasification)	
	Coal Tar			Tar Oil, ppm		Naphtha, ppm	
Stream Identification	Synthane (Ref. 43) (Benzene Soluble)	Westfield (Ref. 44)	SASOL (Ref. 45)	Westfield (Ref. 43)	SASOL (Ref. 45)	Westfield (Ref. 43)	SASOL (Ref. 45)
<u>Stream Analyses</u>							
As	0.7	---	3.1-5.0	---	23-30	---	---
Ba	---	---	---	---	---	---	---
Be	---	---	0.6-1.0	---	0.06	---	---
Ca	---	---	---	---	---	---	---
Cd	---	---	0.03- 0.05	---	0.3	---	---
Cr	---	---	---	---	---	---	---
Fe	---	---	---	---	---	---	---
Hg	---	---	0.3-0.5	---	0.1-0.15	---	---
Li	---	---	---	---	---	---	---
Mn	---	---	1.6-4.1	---	0.2-0.3	---	---
Na	---	---	---	---	---	---	---
Ni	---	---	1.6-4.1	---	1-1.4	---	---
Pb	---	---	50	---	0.5-1.2	---	---
Sb	---	---	0.8-1.0	---	0.5-0.6	---	---
Se	---	---	---	---	---	---	---
V	---	---	1.8-8.2	---	0.1-0.3	---	---
TOTAL S, %	2.8	0.77	0.3	0.29	0.25	0.078	0.34

Table 38

STREAM ANALYSIS FOR EXISTING PLANTS, ASH

<u>Stream No. from Analytical Test Plan</u>		<u>67 (Gasification)</u>	
		<u>Wet Ash (Dry Basis), ppm</u>	
<u>Stream Identification</u>	<u>Westfield (44)</u>	<u>SASOL (44)</u> <u>(Not Quenched)</u>	<u>Azot Sanayii (47)</u> <u>(Not Quenched)</u>
<u>Stream Analysis</u>			
As	---	1-2	---
Ba	---	---	---
Be	---	< 0.5	---
Ca	25,600	50,000	43,000-71,000
Cd	---	< 0.1	---
Cr	Trace	---	---
F	---	150	---
Fe	32,900	35,000	91,000-105,000
Hg	---	< 0.1	---
Li	---	---	---
Mn	Trace	2,000	---
Na	---	5,000	2,200-7400
Ni	Trace	150-200	---
Pb	---	50	---
Sb	---	< 0.5	---
Se	---	---	---
V	---	1000	---

Table 39

Stream Analyses for Existing Plants, Water Effluent	
Stream No. from Analytical Test Plan 39 (Gasification) and others	
Stream Identification	Biox Unit Treated Water Effluent From SASOL (45) mg/l where applicable
Stream Materials	
pH	8.5
Suspended solids	31.0
TDS	959
Free and saline ammonia (as N)	7.45
As	0.05
B	4.40
Hexavalent Cr	----
Total Cr	0.01
Cu	0.04
Phenols (Steam volatile)	0.03
Pb	0.02
CN ⁻	0.11
S ⁼	----
F ⁻	5.87
Zn	0.07
Na	158
Phosphates (as P)	0.29
COD	82
OA	11
Soap, Oil and Grease	0.13
Fe	----
Cd	----
Mn	----
Ag	----
Nitrates, total	----
, As NO ₂	----
, As NH ₃	----
Phosphates, Max.	----
, Average	----
Dissolved Oxygen	----
Max, T. °F	----
Max, ΔT, °F	----
Turbidity, Max Δ JV	----
EC ₅	----
TOC	----

Standards for Water Effluents

Stream Materials	States, Existing and New (Ref. 48) mg/l where applicable	Proposed New Standards for Petroleum Refining (Ref. 50) 1b/1000 bbl (\approx 1b/6,500 M Btu)	
		30 Day Max. Range	One Day Max Range
pH	(4.3-7.0)-(8.0-10.0)	6.0-9.0	6.0-9.0
Suspended	----	0.93-4.2	1.2-5.2
TDS	----	----	----
Total and saline ammonia (as N)	----	0.3-2.6	0.4-3.4
As	All toxics:	----	----
B	0.00-0.50	----	----
Hexavalent Cr	0.05-0.5	0.00046-0.0021	0.00058-0.0026
Total Cr	0.05-1.0	0.023-0.106	0.030-0.132
Cu	0.005-1.0	----	----
Phenols (Steam volatile)	----	0.0099-0.046	0.014-0.065
Pb	0.05-0.10	----	----
CN ⁻	----	----	----
S ⁼	----	0.0081-0.038	0.013-0.059
F ⁻	----	----	----
Zn	0.1-5.0	0.046-0.16	0.058-0.21
Na	----	----	----
Phosphates (as P)	----	----	----
COD	----	5.3-48.2	6.6-60.2
OA	----	----	----
Soap, Oil and Grease	----	0.46-2.1	0.58-2.6
Fe	0.1-1.5	----	----
Cd	0.1-0.5	----	----
Mn	0.05-1.0	----	----
Ag	0.0005-0.05	----	----
Nitrates, total	0.4-45.0	----	----
, As NO ₂	5.0-50.0	----	----
, As NH ₃	0.01-5.0	----	----
Phosphates, Max.	1.0-4.0	----	----
, Average	.025-0.1	----	----
Dissolved Oxygen	2.0-6.0	----	----
Max, T, °F	66-96.8	----	----
Max, ΔT, °F	0-20	----	----
Turbidity, Max Δ JTY	5-50	----	----
BOD ₅	----	1.5-6.6	1.85-8.2
TOC	----	1.3-9.2	1.6-11.4

Table 41
Air Standards

	Fuel Burning Equipment (Ref 48) States Ranges (Existing or All)	Industrial (Ref. 48) States Ranges (Existing or All)	Selected New Source Performance Standards for Specific Sources (Ref. 50,51)		State of New Mexico Emissions for Coal Gasification Plants (Ref. 49)	
			Steam Generators	Petroleum Refining Cat Cracker	Gas-Fired Power Plant for Gasification Plants	Gasification Plants
Particulates, lb/10 ⁶ Btu						
5,000 Btu/hr*	0.024-0.6	N.A.	0.10	0.027 gr/dscf	0.03	0.03 gr/dscf
10,000 Btu/hr*	0.02-0.6	N.A.	(Btu input)	+0.10 lb/10 ⁶ MM		
20,000 Btu/hr*	0.02-0.6	N.A.	(20% Opacity)	But aux. fuel		
				30% opacity except 3 min./hr.		
Process Rate, lb/hr.						H ₂ S - 10 ppm
200 tph	N.A.	21.20 - 142.7	N.A.	--		Total Sulfur - 0.008 lb/MM Btu
500 tph	N.A.	21.20 - 263.69	N.A.	--		H ₂ S + COS + CS ₂ - 100 ppm
1000 tph	N.A.	21.20 - 419.6	N.A.	--		HCN - 10 ppm
						HCl - 5 ppm
						NH ₃ - 25 ppm
Sulfur Oxides, lb/10 ⁶ Btu	(For Solid Fuel) 0.3 - 6.0	N.A.	(For Solid Fuel) 1.2	0.10 gr H ₂ S/dscf in fuel gas	0.16	
	(For Liquid Fuel) 0.3 - 1.5	N.A.	(For Liquid Fuel) 0.8	--		
Sulfur Oxides, ppm	N.A.	500 - 2000	N.A.	N.A.	N.A.	
Nitrogen Oxides, lb/10 ⁶ Btu	(Solid Fuel) 0.3 - 1.3	N.A.	(Solid Fuel) 0.7	--	0.20	
	(Liquid Fuel) 0.30 - 0.60	N.A.	(Liquid Fuel) 0.3	--		
	(Gaseous Fuel) 0.20 - 0.60	N.A.	(Gaseous Fuel) 0.2			
Carbon Monoxide	200 ppm (1 entry)	200 ppm (1 entry) 40 mg/m ³ - 1 hr Average Concentration		0.05 v% for cat cracker		

N.A. -- Not Applicable
* 1 MM Btu/hr ≈ 1 tpd of coal

6. BIBLIOGRAPHY

(Sections 1 through 5)

1. El Paso Natural Gas Company Burnham Coal Gasification Complex-Plant Description and Cost Estimate, Stearns-Roger Incorporated, Denver, Colorado, August 16, 1972.
2. Application of El Paso Natural Gas Company before U.S. Federal Power Commission, Docket No. CP 73-131, November 15, 1972 (Revised October 1973).
3. "El Paso Coal Gasification Project," Draft, Environmental Statement, U.S. Department of Interior, Bureau of Reclamation, July 16, 1974.
4. Shaw, H., and Magee, E.M., "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification, Section 1, Lurgi Process," EPA-650/2-74-009-c, July 1974.
5. Chemical Week, January 22, 1975, p. 36.
6. Eddinger, R. T., et al., "Char Oil Energy Development," Office of Coal Research R & D Report No. 11, Vol. I (PB-169 562) and Vol. II (PB-169 563), issued March 1966.
7. Jones, J. F., et al., "Char Oil Energy Development," Office of Coal Research R & D Report No. 11, Vol. I (PB-173 916) and Vol. II (PB-173 917), issued February 1967.
8. Jones, J. F., et al., "Char Oil Energy Development," Office of Coal Research R & D Report No. 56, Interim Report No. 1, GPO Cat. No. 163.10:56/Int. 1, issued May 1970.
9. Sacks, M. E., et al., "Char Oil Energy Development," Office of Coal Research Report 56, Interim Report No. 2, GPO Cat. No. 163.10:56/Int. 2, issued January 1971.
10. Jones, J.F., et al., "Char Oil Energy Development," Office of Coal Research R & D Report No. 56-Final Report, GPO Cat. No. 163.10:56, issued May 1972.
11. Jones, J. F., et al., "Char Oil Energy Development," Office of Coal Research R & D Report No. 73-Interim Report No. 1, GPO Cat. No. 163.10:73/Int. 1, issued December 1972.
12. Shearer, H. A., and Conn, A. L., "Economic Evaluation of Coed Process plus Char Gasification," Office of Coal Research R & D Report No. 72-Final, GPO Cat. No. 163.10:72, issued December 1972.
13. Eddinger, R. T., Proc. Fourth Synthetic Pipeline Gas Symposium, Chicago, Illinois, October 30, 1972, pp. 217-224.
14. Cochran, N. P., Proc. Fifth Synthetic Pipeline Gas Symposium, Chicago, Illinois, October 29, 1973, pp. 247-264.

15. Hamshar, J. A., et al., "Clean Fuels from Coal by the COED Process," EPA Symposium on Environmental Aspects of Fuel Conversion Technology, St. Louis, Missouri, May 1974, EPA-650/2-74-118, October 1974.
16. Kalfadelis, C. D., "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Liquefaction, Section 1. COED Process," EPA-650/2-74-009-e. January 1975.
17. Magee, E. M., Jahnig, C. E., and Shaw, H., "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification, Section 1. Koppers-Totzek Process," EPA-650/2-74-009a, January 1974.
18. Lowry, H. H., Chemistry of Coal Utilization, Supplementary Volume, John Wiley & Sons, Inc., 1963, pp. 892-1040.
19. Hottel, H. C., and Howard, J. B., New Energy Technology, The MIT Press, 1971.
20. Bodle, W.W., and Vyas, K. C., "Clean Fuels From Coal," The Oil and Gas Journal, August 26, 1974, pp. 73-88.
21. Rudolph, P.D.H., "The Lurgi Process - The Route to SNG from Coal," Proc. Fourth Synthetic Pipeline Gas Symposium, Chicago, Illinois, October 30, 1972, American Gas Association Cat. No. L11173, pp. 175-214.
22. Cameron, D. S., et al., "Environmental Aspects of El Paso's Burnham Coal Gasification Complex," EPA Symposium on Environmental Aspects of Fuel Conversion Technology, St. Louis, Missouri, May 1974, EPA-650/2-74-118.
23. Berty, T. E., and Moe, M. M., "Environmental Aspects of the Wesco Coal Gasification Plant," EPA Symposium on Environmental Aspects of Fuel Conversion Technology, St. Louis, Missouri, May 1974, EPA-650/2-74-118.
24. Kalfadelis, C. D., and Magee, E. M., "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification, Section 1, Synthane Process," EPA-650/2-74-009b, June 1974.
25. Jahnig, C. E., and Magee, E. M., "Evaluation of Pollution Control in Fossil Fuel Conversion, Gasification, Section 1, CO₂ Acceptor Process," EPA-650/2-74-009-d, 1975.
26. Flynn, J. V., Chemical Engineering, January 6, 1975, p. 61.
27. Chemical Week, January 8, 1975, p. 26.
28. Chemical Week, January 15, 1975, pp. 14-15
29. Chemical Engineering, January 20, 1975, pp. 56-58.
30. "Background Information for New Source Performance Standards," EPA, APTD-1352 a, June 1973.

31. Hartwell, I. L., Public Health Service Publication, No. 149, 1951.
32. Sarvicki, E., and Cassel, K., National Cancer Institute, Monograph No. 9, 1962.
33. "Coal Mining Industry - Effluent Limitation Guidelines," EPA, September 5, 1972.
34. "Demonstration Plant, Clean Boiler Fuels from Coal," OCR R&D Report No. 82, Interim Report No. 1, Vol. I and Vol. II, Ralph M. Parsons Co.
35. Phinney, J. A., "Coal Liquefaction at the Cresap, W. Va. Pilot Plant," presented at A.I.Ch.E. Coal Conversion Pilot Plant Symposium, Pittsburgh, Pennsylvania, June 2, 1974.
36. Frohning, C. D., and Cornils, B., "Chemical Feedstocks from Coal," Hydrocarbon Proc., November 1974, pp. 143-146.
37. U.S. Pat. No. 3,341,447, 1967.
38. Dierdoff, L. H., Jr., and Bloom, R., Jr., "The COGAS Project," SAE West Coast Meeting, Portland, Oregon, August 1973.
39. "Char Oil Energy Development," OCR R&D Report No. 73 - Int. Rept. No. 2, GPO Cat. No. I 63.10:73/Int. 2, July 1974.
40. Bulger, L., et.al., "Disposition of Power Plant Wastes," presented at American Power Conference, 36th Annual Meeting, Chicago, Illinois, May 1, 1974.
41. Ruch, R. R., Gulskoter, H. J., and Shimp, N. F., "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," EPA-650/2-74-054, July 1974.
42. Magee, E. M., Hall, H. J. and Varga, G. M. Jr., "Potential Pollutants in Fossil Fuels," EPA-R2-73-249, June 1973, NTIS PB No. 225 039.
43. Forney, A. J., et al., "Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology," St. Louis, Missouri, May 1974, EPA-650/2-74-118, p. 107, October 1974.
44. Communication from the Scottish Gas Board, Westfield Works, Cardenden Fife, Scotland November 1974.
45. Communication from the South African Coal, Oil and Gas Corporation, Ltd. (SASOL), Sasolburg, South Africa, November 1974.
46. Communication From Azot Sanayii, Kutahya, Turkey, (Koppers-Totzek and Winkler Plants), November 1974.
47. Jahnig, C. E., "Evaluation of Pollution Control in Fossil Fuel Conversion Processes - Liquefaction: Section 2 SRC Process," EPA-650/2-74-009f, March 1975.

48. Information collected from various sources.
49. Rubin, E. S. and McMichael, "Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology (May 1974, St. Louis, Missouri)", EPA-650/2-74-118, October 1974.
50. *ibid.*, (From Federal Register, Vol 38, No. 24, December 14, 1973; pp. 34541-34558).
51. *ibid.*, (From Federal Register, Vol. 39, No. 47, March 8, 1974).
52. Abstracts of Papers, 167th National Meeting of the American Chemical Society, I&EC Division, Los Angeles, April 1, 1974.

7. ANALYTICAL CONSIDERATIONS

7.1 Introduction

In selecting the possible pollutants for analysis in the selected plant streams, five factors were considered. These were 1) the potential impact of pollutant on the environment, 2) available data regarding the composition of commercial coal gasification and liquefaction plant streams,

3) the minor and trace constituents of coals, 4) various process considerations, and 5) lists supplied by the EPA of materials which are considered environmental hazards. Some of the literature which was consulted to arrive at the selection of possible pollutants is given in Table I.

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

Many analytical procedures are potentially applicable for the analysis of the potential pollutants and other required measurements, listed in Tables II and III, in the various streams of the liquefaction and gasification plants. In selecting the suggested procedures, which are given later, consideration was given to 1) procedures which are widely used for analysis of the pollutants in a given matrix, 2) procedures which have been demonstrated to be applicable for determinations of certain components of a given matrix, 3) procedures which are potentially applicable for the analysis of a matrix component but have not been extensively tested,

4) procedures for multicomponent analysis, and 5) the concentration ranges at which the procedures are applicable.

It must be stressed that since the detailed compositions of the plant streams are unknown, components may be present which will interfere with the suggested procedures. If interferences are suspected during the course of analysis for a pollutant or if a small quantity of a pollutant is to be measured in the presence of a large quantity of another component, the applicability of the procedure should be determined.

It is to be noted that the literature is frequently contradictory as to the applicability of procedures to various components and procedures other than the suggested procedures are available for measurement of pollutants. If an alternative procedure is selected, its applicability should be evaluated.

It is convenient to broadly classify the types of samples to be obtained from plant streams into 1) aqueous samples, 2) coal and coal-related solid samples, 3) gas and ambient air samples, and 4) coal liquid samples. The analytical methods which are suggested for samples

TABLE I

LITERATURE SURVEYED FOR SELECTION OF POSSIBLE POLLUTANTS

"Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," R. R. Ruch, H. J. Gluskoter and N. F. Shimp, Illinois State Geological Survey, EPA-650/2-74-054, July 1974.

"Potential Pollutants in Fossil Fuels," E. M. Magee, H. J. Hall, and G. M. Varga, Jr, EPA-R2-73-249, June 1973.

"Liquid Coal Compositional Analysis by Mass Spectrometry," J. T. Swansiger, F. E. Dickson, and H. T. Best, Anal. Chem., 46, 730 (1974).

"Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification, Section 3, Lurgi Process," H. Shaw and E. M. Magee, EPA-650/2-74-009-c, July 1974.

"Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Liquefaction, Section 1, COED Process," C. D. Kalfadelis and E. M. Magee, EPA-650/2-74-009-e, February 1975.

TABLE II

POSSIBLE POLLUTANTS FROM COAL PROCESSING

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

Other Organic Materials

Thiophene
CS₂
phenols
benzene
toluene
xylene
oil
acids
aldehydes

Inorganic Ions

CN⁻
SCN⁻
F⁻
S⁼
CO₃⁼
Cl⁻
Phosphates

Particulates

TABLE III

OTHER ANALYSIS

Coal Analysis

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

Water Quality Indicators

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

are discussed separately, as are sampling and preservation of samples, for each sample type. Before these specific discussions, a general discussion on the analysis samples for metals is presented because of the rapidly developing technology in this area and the fact that many different analytical techniques are potentially applicable for metals analysis.

7.2 Analysis of Metals

Much attention has recently been given to the analysis of metals in aqueous, oil, coal, and particulate samples. Flame atomic adsorption and heated vaporization atomic absorption have been widely used for analysis of samples containing small quantities of metals due to the selectivity and high sensitivity of the techniques and to the relatively low cost of the instrumentation involved. Neutron activation, spark source mass spectrographic, and emission spectrographic techniques have been applied for multielement trace analysis. X-ray fluorescence has been widely applied for metal analysis at somewhat higher levels than the aforementioned techniques.

The accurate analysis of trace quantities of metals in coal, coal ash, petroleum, and petroleum products has been the subject of much investigation recently. The National Bureau of Standards supplied samples of coal, fly ash, fuel oil, and gasoline to cooperating laboratories for analysis of trace metals as part of a program to 1) assess the need for standard reference materials of these substances, and 2) to determine comparability of various analytical techniques. The results obtained on these samples (1,2) indicated that there is definitely a need for standard reference materials of these substances because of the scatter in the results which were reported.

The Illinois Geological Survey recently published the results of a study of the determination of trace elements in coal using a variety of analytical techniques and found that certain techniques were better suited than others for the analysis of certain elements in coal.

The need for methods to obtain accurate, reliable data on trace metals content on oils is reflected in the fact that a project involving five petroleum companies was formed to develop and evaluate the precision and accuracy of methods for the analysis of petroleum oils for metals at the 10 ng/g level. The undertaking was deemed to be of such significance that when the first publication from the project appeared in Analytical Chemistry, an editorial regarding the project appeared in the same issue (3).

The point of this discussion is that perhaps the greatest difficulty and uncertainty in the analysis of the liquefaction and gasification plant streams will probably be with regard to their metals content. Therefore particular attention should be given to the implementation of the suggested procedure in the laboratory. Experiments should be performed to validate and develop the techniques that are needed for the use of the procedures before the analysis of the plant streams commences.

7.3 Alternative Analytical Techniques

References have been provided, when applicable, for alternative analytical techniques. For example, three sources have been cited for analysis of aqueous samples (Section 6.1). What is believed to be the best techniques have been selected for use in this analytical test plan. These selections were made on the basis of (1) use experience in a number of laboratories, (2) validation by independent workers, (3) methods used by EPA, and (4) use experience in analyses of related materials. As indicated above, the use of an alternative procedure found in the references should be validated.

7.4 Results Analysis

Since the overall objective of the test plan is to provide a material balance of all possible pollutants from a given plant, it is necessary that the analyses be sufficiently accurate to give the desired accuracy in the balance. The references cited indicate the number of samples to be analyzed in each case. This should provide sufficient accuracy for the desired result. In cases where a material balance is not obtained, a detailed search must be made as to the cause of the imbalance. This cause may not be related to the sampling and analysis but may be caused by other factors such as errors in the estimate of the delay time between process changes and attainment of steady state conditions down stream. Another factor may be reactions of a stream component between the unit where it is formed to the unit where the sampling is made. (Bacterial action in cooling towers was previously pointed out as an example of this problem.) Another problem source is the possibility of adsorption or absorption and desorption of trace materials when process conditions are changed. For instance, in acid gas treatment, if a trace component concentration is increased due to changes in a gasification reactor variable, the effluent from the acid gas absorbers will not contain the steady state concentration of that component until the absorption solution is saturated with that component at its new partial pressure. Changes in temperature of operating units can have similar effects. The age of absorber or catalysts can also produce these anomalous results.

Unless otherwise indicated, the following procedure is recommended to check sampling and analysis techniques: When a stream is to be analyzed for the first time, five samples should be taken. Three of these should be submitted for analysis as is. The other two should be spiked with two different levels of the component(s) of interest. In this way, if the final analyses correctly show the effects of spiking as well as agreement of the unspiked analyses, then additional validity of the results is indicated.

A final word of caution should be injected as to the analysis of the results. This has to do with sampling streams where the act of sampling can change the concentration of the stream components. This is often the case when sampling high temperature streams. Unless the sample is cooled extremely rapidly, a shift in equilibrium of the components can take place and reactions can take place on the sampler walls.

In most cases of interest, samples can be taken from two or more cool streams to give the desired information (e.g., a cool gas sample and a condensed water sample may take the place of a hot sample containing water vapor). Again, in all cases, experience and technical judgement are necessary to produce reliable results.

8. ANALYSIS OF AQUEOUS SAMPLES

8.1 Introduction

There are three collections of procedures for the analysis of aqueous samples for pollutants which are in general use in this country. These are "Methods for Chemical Analysis of Water and Wastes," EPA-625-/6-74-003, Environmental Protection Agency, Washington, D.C., 1974; "Standards Methods for the Examination of Water and Waste Water," 13th Ed., American Public Health Association, Washington, D.C. 1971; and "Annual Book of ASTM Standards, Part 31, Water," American Society for Testing and Materials, Philadelphia, Pa., 1974. These are abbreviated EPA/74, W & WW/13, and ASTM/31, respectively in this section. In addition to these collections, the chemical literature was surveyed for methods which are applicable for the analysis of pollutants in waters.

In selecting the suggested procedures which are given in Table IV, primary consideration was given to the methods in EPA/74 since the procedures in this collection will be used by the agency in determining compliance with water and effluent standards established by the agency. Where these methods were not thought to be applicable or where methods did not exist for potential pollutants of interest, other procedures were chosen.

For the analysis of metals as a group, neutron activation, spark source mass spectrographic and emission spectrographic techniques have been used. If a simultaneous determination of metals is desired, consideration should be given to the technique of LeRoy and Lincoln (4) which was shown to be applicable to the simultaneous determination of 36 elements, including all of those listed in Table II, except Ba, Li, and Se.

The methods in Table IV may be used to measure both total and dissolved constituents of samples. If the dissolved concentration is to be determined, the sample is filtered through a 0.45 μ m membrane filter and the filtrate analyzed by the suggested procedure. Filtration in the field is recommended; if that is not feasible, the sample should be filtered as soon as it is returned to the laboratory.

8.2 Sampling

Sampling methods which are generally applicable to industrial waters are discussed in detail in ASTM D-510 and the use of one of these procedures is recommended. Apparatus, frequency, and duration of sampling, composite samples, sampling points, and preparation of sample bottles are discussed in ASTM D-510.

8.3 Preservation of Samples

The amount of sample that should be collected for the analysis of each component, the method of preservation and the holding time before analysis, where these factors have been reported, are given in Table V. More information regarding these factors is discussed in many of the suggested methods.

TABLE IVa

SUGGESTED ANALYTICAL METHODS FOR AQUEOUS SAMPLES

<u>Component or Measurement</u>	<u>Method</u>	<u>Suggested Range* of Method</u>
Phenol	EPA/74, 32730	5 - 1000 µg/l
Ammonia	EPA/74, 00610	0.05 - 1.0 mg/l
Sulfide	EPA/74, 00745 (W&WW/13, 228)	>1 mg/l
Oil and grease	EPA/74, 00550, 00556 or 00560	>0.2 mg/l
Cyanide, total	EPA/74, 00720	>0.02 mg/l
Carbon dioxide	W&WW/13, 111	see method
Acids, volatile	W&WW/13, 233	up to 5,000 mg/l
Conductance, specific	EPA/74, 00095 (W&WW/13, 154)	see method
pH	EPA/74, 00400	
Fluoride, total	EPA/74, 00951	oil - 100 mg/l
Oxygen demand, chemical	EPA/74, 00335	5 - 50 mg/l
Chloride	EPA/74, 00940	"all ranges"
	(ASTM/31 D-512 Ref. Method A)	
Residue, total filterable	EPA/74, 70300	10 - 20,000 mg/l
Residue, total nonfilterable	EPA/74, 00530	10 - 20,000 mg/l
Phosphorus, total	EPA/74, 00665	0.01 - 0.5 mg P/l
Oxygen, dissolved	EPA/74, 00299	>0.05 mg/l
Metals by Atomic Absorption		
Antimony	EPA/74, 01097	1 - 40 mg/l
Arsenic	EPA/74, 01002	>2 µg/l
Barium	EPA/74, 01007	1-2 mg/l
Beryllium	EPA/74, 01012	0.05 - 2 mg/l
Cadmium	EPA/74, 01027	0.05 - 2 mg/l
Calcium	EPA/74, 00916	0.2 - 20 mg/l
Chromium	EPA/74, 01034	0.2 - 10 mg/l
Iron	EPA/74, 01045	0.3 - 10 mg/l
Lead	EPA/74, 01051	1 - 20 mg/l
Lithium	← applicability to be determined →	
Manganese	EPA/74, 01055	0.1 - 10 mg/l
Mercury	EPA/74, 71900	>0.2 µg Hg/l
Nickel	EPA/74, 01067	0.3 - 10 mg/l
Selenium	EPA/74, 01147	2 - 20 µg/l
Sodium	EPA/74, 00929	0.03 - 1.0 mg/l
Vanadium	EPA/74, 01087	1 - 100 mg/l
Organic Carbon, total	EPA/74, 00680	>1 mg/l
Oxygen Demand, Biochemical	EPA/74, 00310 (W&WW/13)	see method
Thiocyanate	J. M. Kruse and M. G. Mellon Anal. Chem., 25, 446 (1953)	0.5 - 20 mg/l
Nitrate	EPA/74, 00620	0.1 - 2 mg NO ₃ (as N)/l
Sulfite	EPA/74, 00740 (W&WW/13, 158)	detection limit is 3 mg SO ₃ ⁻ /l

* Range may be extended upward by appropriate dilutions in many instances; refer to the method.

TABLE IVb

PRINCIPLES OF THE SUGGESTED ANALYTICAL METHODS

Phenol EPA/74, 32730, p. 241

Distillation of the sample and reaction of the phenolic compounds in the distillate with 4-aminoantipyrine to form a colored dye. The intensity of the color produced in a function of the phenolic content of the sample.

Ammonia EPA/74, 00610, p. 159

Distillation from a buffer and colorimetric or titrimetric determination of ammonia in the distillate.

Sulfide EPA/74, 00745, p. 284 (W&WW, p. 551)

Distillation of sulfide and titration of distillate with iodine/thiosulfate. Sulfite, thiosulfite, and hyphosulfite interfere.

Cyanide, Total EPA/74, 00720, p. 40

Distillation of hydrogen cyanide from the sample and measurement of cyanide in the distillate titrimetrically or colorimetrically.

pH EPA/74, 00400, p. 239

Electrometric measurement.

Fluoride, Total EPA/74, 00951, p. 65

Distillation of the sample and determination of fluoride in the distillate using a selective ion fluoride electrode.

Chemical Oxygen Demand EPA/74, 00335, p. 21

Oxidation of the sample with potassium dichromate and titration of the excess dichromate with standard ferrous ammonium sulfate solution. For chloride contents above 1000 mg/l use EPA/74, 00340, p. 25; minimum accepted COD level for this method is 250 mg/l COD.

Chloride EPA/74, 00940, p. 29 (ASTM/31 D-512, Referee Method A)

Titration with mercuric nitrate.

Residue, Total Filterable EPA/74, 70300, p. 266

Filtration of the sample and evaporation of the filtrate.

TABLE IVb (Cont'd.)

Residue, Total Nonfilterable EPA/74, 00530, p. 268

Filtration of the sample and determination of the residue when dried at 105°C.

Phosphorous, Total EPA/74, 00665, p. 249

Treatment of the sample to convert phosphorus compounds to orthophosphate and determination of orthophosphate by formation of an antimony-phosphomolybdate complex. For determination of orthophosphate in sample use EPA/74, 70507; from determination of total hydrolyzable phosphorus use EPA/74, 00669; and for determination of total organic phosphorus use EPA/74, 00666.

Oxygen, Dissolved EPA/74, 00299, p. 56

Instrumental probes which depend on electrochemical reactions are used.

Carbon Dioxide W&WW/13, 111, p. 86

Nomographic and titrimetric methods are discussed.

Acids, Volatile W&WW/13, 233, p. 577

Column chromatography of the sample to separate organic acids and titration of the acids.

Conductance, Specific EPA/74, 00095, p. 275 (W&WW/13, 154, p. 323)

Conductance cell is used.

Metals by Atomic Absorption

Refer to the general discussion on these analyses given in EPA/74 pp. 78-93.

Antimony EPA/74, 01097, p. 94

Lean air-acetylene flame is used.

Arsenic EPA/74, 01002, p. 95

Oxidation of sample followed by arsine generation. Argon/hydrogen/entrained-air flame is used.

Barium EPA/74, 01007, p. 97

Rich nitrous oxide-acetylene flame is used.

TABLE IVb (Cont'd.)

Beryllium EPA/74, 01012, p. 99

Rich nitrous oxide-acetylene flame is used.

Cadmium EPA/74, 01027, p. 101

Oxidizing air-acetylene flame is used.

Calcium EPA/74, 00916, p. 103

Reducing air-acetylene flame is used.

Chromium EPA/74, 01034, p. 107

Slightly rich air-acetylene flame is used.

Iron EPA/74, 01045, p. 110

Oxidizing air-acetylene flame is used.

Lead EPA/74, 01051, p. 112

Slightly oxidizing air-acetylene flame is used.

Lithium

Applicability of atomic absorption to be determined.

Manganese EPA/74, 01055, p. 116

Oxidizing air-acetylene flame is used.

Mercury EPA/74, 71900, p. 118

Sample is oxidized to convert all mercury to the divalent state then divalent mercury is reduced to elemental mercury which is measured by cold-vapor atomic absorption.

Nickel EPA/74, 01067, p. 141

Oxidizing air-acetylene flame is used.

Selenium EPA/74, 01147, p. 145

Sample is oxidized, selenium is reduced to tetravalent state and then converted to hydrogen selenide and measured using an argon/hydrogen/entrained-air flame. Details are given by J. S. Caldwell, R. J. Lishka, and E. F. McFarren, J. Am. Water Works Assoc., 65, 731 (1973).

TABLE IVb (Cont'd.)

Sodium EPA/74, 00929, p. 147

An oxidizing air-acetylene flame is used.

Vanadium EPA/74, 01087, p. 153

A fuel rich nitrous oxide-acetylene flame is used.

Organic Carbon, Total EPA/74, 00680, p. 236

Organic carbon is converted to CO_2 which is measured using an IR detector or is converted to CH_4 and measured using a flame ionization detector.

Oxygen Demand, Biochemical EPA/74, 00310, p. 11 (W&WW/13, 219, p. 489)

The 5-day BOD is an biassay procedure which measures the dissolved oxygen consumed by microbes during assimilation and oxidation of organic material.

Nitrate EPA/74, 00620, p. 197

Reaction of nitrate ion with brucine in sulfuric acid to form a colored complex. The complex is measured colorimetrically and related to the nitrate concentration. See the method for interferences.

Sulfite EPA/74, 00740, p. 285 (W&WW/13, 158, p. 337)

The sample is titrated with standard potassium iodide-iodate solution. Oxidizable material interferes. See method for a discussion of interferences.

Thiocyanate J. M. Kruse and M. G. Mellon, Anal. Chem., 25, 446 (1953)

The sample is treated with copper sulfate and pyridine and the dipyridine - Copper (II) - thiocyanate complex which is formed is extracted into chloroform and measured colorimetrically.

Oil and Grease EPA/74, 00550, 00556 or 00560, pp. 226-235

Extraction with Freon and measurement of the Freon extractable material gravimetrically or by IR spectroscopy. Refer to methods.

TABLE V

RECOMMENDATION FOR SAMPLING AND PRESERVATION
OF SAMPLES ACCORDING TO MEASUREMENT(1)

(Primary Reference: EPA/74)

Measurement	Volume Required (ml)	Container(2)	Preservative	Maximum Holding Time(6)
Acids, volatile	50	← unknown →		
Arsenic	100	P, G	HNO ₃ to pH <2	6 Mos
BOD	1 000	P, G	Cool, 4°C	6 Hrs (3)
Carbon dioxide	100	G only		
COD	50	P, G	H ₂ SO ₄ to pH <2	7 Days
Chloride	50	P, G	None Req.	7 Days
Cyanides	500	P, G	Cool, 4°C NaOH to pH 12	24 Hrs
Dissolved Oxygen				
Probe	300	G only	Det. on site	No Holding
Winkler	300	G only	Fix on site	No Holding
Fluoride	300	P, G	Cool, 4°C	7 Days
Metals				
Dissolved	200	P, G	Filter on site HNO ₃ to pH <2	6 Mos
Suspended			Filter on site	6 Mos
Total	100		HNO ₃ to pH <2	6 Mos
Mercury				
Dissolved	100	P, G	Filter HNO ₃ to pH <2	38 Days (Glass) 13 Days (Hard Plastic)
Total	100	P, G	HNO ₃ to pH <2	38 Days (Glass) 13 Days (Hard Plastic)
Nitrogen				
Ammonia	400	P, G	Cool, 4°C	24 Hrs (4)
Nitrate	100	P, G	Cool, 4°C	24 Hrs (4)
Oil and Grease	1000	G only	Cool, 4°C	24 Hrs
Organic Carbon	25	P, G	H ₂ SO ₄ to pH <2 Cool, 4°C	24 Hrs
pH	25	P, G	H ₂ SO ₄ to pH <2 Cool, 4°C	24 Hrs
Phenolics	500	G only	Det. on site Cool, 4°C H ₃ PO ₄ to pH <4 1.0 g CuSO ₄ /l	24 Hrs

TABLE V (Cont'd.)

<u>Measurement</u>	<u>Volume Required (ml)</u>	<u>Container⁽²⁾</u>	<u>Preservative</u>	<u>Holding Time⁽⁶⁾</u>
Phosphorus				
Orthophosphate, Dissolved	50	P, G	Filter on site	24 Hrs (4)
Hydrolyzable	50	P, G	Cool, 4°C	24 Hrs (4)
Total	50	P, G	H ₂ SO ₄ to pH <2 Cool, 4°C	24 Hrs (4)
Residue				
Filterable	100	P, G	Cool, 4°C	7 Days
Nonfilterable	100	P, G	Cool, 4°C	7 Days
Specific Conductance	100	P, G	Cool, 4°C	24 Hrs (5)
Sulfide	50	P, G	2 ml zinc acetate	24 Hrs
Sulfite	50	P, G	Cool, 4°C	24 Hrs
Thiocyanate	100		← unknown →	

-
- (1) More specific instructions for preservation and sampling are found with each procedure.
 - (2) Plastic or Glass.
 - (3) If samples cannot be returned to the laboratory in less than 6 hours and holding time exceeds this limit, the final reported data should indicate the actual holding time.
 - (4) Mercuric chloride may be used as an alternate preservative at a concentration of 40 mg/l, especially if a longer holding time is required. However, the use of mercuric chloride is discouraged whenever possible.
 - (5) If the sample is stabilized by cooling, it should be warmed to 25°C for reading, or temperature correction made and results reported at 25°C.
 - (6) It has been shown that samples properly preserved may be held for extended periods beyond the recommended holding time.

Where possible, analyses should be performed as soon after sample collection as possible because as stated in EPA/74:

"Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural water, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. Biological changes taking place in a sample may change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell analysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition."

9. COAL AND COAL RELATED SOLID ANALYSIS

9.1 Introduction

Much attention has recently been focused on the analysis of coal, coal ash, fly ash, and airborne particulate matter for elemental composition. Atomic absorption spectroscopy, X-ray fluorescence, spark-source mass spectrometry, optical emission spectroscopy, and neutron activation have been applied for the analysis of these materials for trace elements (5-12). There is some disagreement in the literature as to which technique is best suited for the determination of a particular element.

A recent comprehensive study involving the analysis of 101 coals for trace elements, which was conducted by the Illinois Geological Survey, has appeared (15). Because of the extensive study of sample preparation techniques and methods of analysis given in this report, the methods described in it have been selected as the suggested procedures for the analysis of the coal and coal solids for trace elements where applicable. The measurement techniques which are used in the methods are given in Table VI. Some of the methods given in references 5-12 could be substituted for these as they have been also demonstrated to be valid. Perhaps the most important factor, besides the inherent detection limit in the selection of a method, is that experience with a method specifically for analysis of coal and coal related solids for a particular element is required before accurate, reliable results can be obtained.

In addition to the analysis of the solids for potential pollutants, it is desirable to analyze coal and related samples for ultimate and proximate compositions and to determine the ash fusion temperature. The results of these analyses may lend insight into the influence of various types of coals on pollutants in various plant streams. The suggested procedures for determining the values are given in Table VII.

9.2 Sampling

A gross coal sample should be collected as indicated in ASTM D-2234. ASTM D-2013 and D-271 describe the preparation of coal samples for analysis, and one of these methods should be used.

It is suggested that the collection of samples of coal ash and dump pit solids be performed as indicated in the "Proposed Method for Sampling Iron Ores," ASTM 1974, Part 12, p. 799.

9.3 Preservation

The literature does not contain recommendations for the preservation of coal or coal ash samples. Therefore, it is suggested that these samples are stored in clean glass bottles equipped with polyethylene lined caps until analyses are performed.

TABLE VI

MEASUREMENT TECHNIQUES USED IN THE SUGGESTED
METHODS FOR ANALYSIS OF COAL AND COAL
RELATED SOLIDS FOR TRACE ELEMENTS

(Details are given in reference 5)
(except for Ba and Li)

<u>Element</u>	<u>Technique(1)</u>	<u>Detection Limit $\mu\text{g/g}$</u>
As	NAA	1.2 in ash
Ba(2)	Emission Spectroscopy	Unknown
Be	OE-DR	1 in ash
Ca	XRF	12 in whole coal
Cd	AA	2.5 in ash
Cr	OE-DR	1.5 in ash
F	ISE	10 in whole coal
Fe	XRF	36 in whole coal
Hg	NAA	0.01 in whole coal
Li(2)	AA	Unknown
Mn	NAA	2 in whole coal
Na	NAA	0.5 in whole coal
Ni	OE-DR, AA, OE-P, XRF	1 in ash
Pb	AA, OE-DR	5 in ash
Se	NAA	1.8 in ash
V	OE-DR, OE-P, XRF	5 in ash

- - - - -
- (1) NAA signifies neutron activation analysis.
OE-DR signifies optical emission, direct reading.
XRF signifies X-ray fluorescence.
AA signifies atomic absorption
OE-P signifies optical emission photographic.
ISE signifies ion-selective electrode.
- (2) Experiments must be performed to validate these techniques.

TABLE VII

SUGGESTED METHODS FOR GROSS COAL ANALYSIS

<u>Component</u>	<u>Method</u>
Moisture	ASTM D-271
Ash	ASTM D-271
Volatile Matter	ASTM D-271
Fixed C	ASTM D-271
S	ASTM D-271
P	ASTM D-271
C	ASTM D-271
H	ASTM D-271
N	ASTM D-271
Calorific Value	ASTM D-271 or D-3286
Fusibility of Coal Ash	ASTM D-1857

10. ANALYSIS OF COAL LIQUIDS

10.1 Introduction

As was stated earlier, much attention has been focused recently on the analysis of oils for trace quantities of metals (1-3). As the result of studies performed in conjunction with the Trace Metals Project involving the Atlantic Richfield Company, Chevron Research Company, Exxon Research and Engineering Company, Mobil Research and Development Corporation, and Phillips Petroleum Company and a study performed for the American Petroleum Institute (13) much insight has recently been gained on the analysis of oils for metals. These studies indicate that neutron activation analysis is applicable for the determination Sb, As, Co, Mn, Hg, Mo, Ni, Se, and V if they are present in oils in amounts greater than 5-50 ng/g, depending on the element, and that emission spectroscopy is applicable for the determination of Sb, Cd, Be, Cr, Co, Mn, Mo, Ni, and V if they are present in amounts greater than 20-50 ng/g. In addition to these techniques which give multielement analysis of samples, the members of the Trace Metals Project developed specific methods for the analysis of oils for Sb, Cd, As, Be, Cr, Co, Mn, Se, Mo, Ni, Se, and V to 10 ng/g. The methods developed during the course of the project have appeared in Analytical Chemistry and were the topic of an American Chemical Society Symposium held in conjunction with the National ACS Meeting in Philadelphia in April, 1975. The determination of trace quantities of metals in oils, other than those listed, has not been exhaustively studied, but other metals probably could be determined by modification of the techniques studied by the Trace Metals Project.

The selected methods for the analysis of oils for the elements listed in Table VIII are those developed by the Trace Metals Project for the individual elements, where available; and where unavailable, suggested methods for investigation to determine their applicability to oils are given. In some instances the multielement techniques may be preferable.

In addition to the analysis of coal liquids for metals, the analysis of these materials for polynuclear aromatic hydrocarbons, PNA's, is important because of the carcinogenic activity of some of these compounds.

The PNA analysis of the coal liquids is carried out by a gas chromatographic-ultraviolet spectrographic (GC/UV) technique. If the level is high with few interfering substances the ISM method 11104-03 73T "Tentative Method of Analysis for Polynuclear Aromatics in Coke Oven Effluents" is employed. A 1-10 microliter sample of the liquid would be injected into the GC and the appropriate peaks trapped and measured by UV.

If other high boiling organics are present, it is necessary to isolate an aromatic concentrate before the GC/UV step. The technique employed is presented in the LSM method 11104-04 73T. 0.5 grams of the liquid would be taken in a 100 ml beaker and spiked with radioactive B(a)A and B(a)P as directed in paragraph 7.1 of the procedure. The spiked sample would then be chromatographed on alumina as directed in paragraph 7.6.1. The procedure would then be followed as written.

10.2 Sampling

The collection of coal liquids samples over a period of time, and the preparation of composite samples for analysis is recommended.

10.3 Preservation

The storage of composite samples in Teflon bottles is recommended.

TABLE VIII

SUGGESTED METHODS FOR DETERMINATION OF
METALS IN COAL LIQUIDS

<u>Metal</u>	<u>Technique (1)</u>	<u>Reference (4)</u>
As	Wet Digest/ AsH_3 generation/AA	TMP
Ba	Wet Ash/ES	(2)
Be	Direct/HVAA	TMP
Ca	Wet Ash/AA	(2)
Cd	Wet Ash/HVAA or AA	TMP
Cr	Direct/HVAA	TMP
Fe	Wet Ash/AA	(2)
Hg	Wet Digest/CVAA	(2)
Li	Wet Ash/AA	(2)
Mn	Direct/HVAA	14
Na	Wet Ash/AA	(2)
Ni	Wet Ash/HVAA	TMP
Pb	Wet Ash/HVAA (3)	(2)
Se	Wet Digest/ H_2Se generation/AA	TMP
V	Wet Ash/HVAA	TMP

-
- (1) AA signifies flame atomic absorption.
 HVAA signifies heated vaporization atomic absorption
 CVAA signifies cold vapor atomic absorption
 ES signifies emission spectroscopic.
- (2) Methods have not been thoroughly investigated; in these instances, suggested techniques are given by the TMP which must be validated.
- (3) Contamination from ambient sources of Pb will be a problem.
- (4) TMP signifies method developed by the Trace Metals Project. Method has appeared in Analytical Chemistry.

TABLE IX

POLYNUCLEAR AROMATIC HYDROCARBONS WHICH ARE DETERMINED IN
COAL LIQUIDS USING THE ISM METHODS

Benzo(k)fluoranthene
Benzo(b)fluoranthene
Benzo(a)pyrene
Benzo(e)pyrene
Perylene
Benzo(ghi)perylene
Coronene
Chrysene
Fluoranthene
Pyrene
Benzo(ghi)fluoranthene
Benz (a) anthracene
Triphenylene
Benzo(f)fluoranthene

TABLE X

OTHER ANALYSES

Total Sulfur

ASTM D-129, D-2622, or D-2784

11. ANALYSIS OF ATMOSPHERIC AND GASEOUS SAMPLES

11.1 Introduction

A variety of materials may be emitted to the air from coal gasification or liquefaction plants. Provision must be made to collect and analyze all components of interest, from heavy particulates to the most volatile gases and vapors. A great variety of sampling devices is needed for a complete sampling. Methods for collecting, measuring, and characterizing particulate matter are presented in Table XI. The best techniques for gases and vapors are in Table XII. Table XIII lists a number of direct reading indicator tubes. These are portable and convenient to use but at present many are only rangefinding and approximate in nature.

11.2 Particulates

The particulates in ambient air of the plant will be determined by the EPA specified method, "Reference Method for the Determination of Suspended Particles in the Atmosphere, High Volume Method, (High Vol.)." In this method, air is drawn into a covered housing and through a filter by means of a high-flow-rate blower at a flow rate (1.13 to 1.70 m³/min; 40 to 60 ft³/min) that allows suspended particles having diameters of less than 100 μ m (Stokes equivalent diameter) to pass to the filter surface. Particles within the size range of 100 to 0.1 μ m diameter are ordinarily collected on glass fiber filters. The mass concentration of suspended particulates in the ambient air (mg/m³) is computed by measuring the mass of collected particulates and the volume of air sampled.

The particulates in the stack of the plant will be collected and measured by the EPA Method No.5, "Determination of Particulate Emissions from Stationary Sources." Where desirable, Monitaire samplers will be used to monitor the actual exposure of individual workers.

Total Particulate - In all cases total particulate will be determined gravimetrically by conditioning the filter, before and after use, in a constant humidity room and by weighing. This value will include both the inorganic and organic portions of the sample.

Particulate Size - Particulates are to be sized according to ASTM 2009.

Benzene Solubles - The benzene soluble components will be determined by extracting the particulates in a Soxhlet extractor using benzene. After extraction, the benzene will be removed and the solubles determined gravimetrically.

Characterization of Benzene Solubles - One of the objectives is to measure the concentration of individual PNA hydrocarbons, such as benzanthracene (BaA), Benzo(a)pyrene (BaP), and 12 others. In addition, it is desirable to obtain some overall compositional information. The methods to be employed are briefly described below.

Polynuclear Aromatic Hydrocarbons - Up to 14 polynuclear aromatic hydrocarbons will be measured by either the Intersociety Methods No. 11104-03 73T or ISM 11104-04-0473T depending on the complexity of the material. In the latter after the Soxhlet extraction, a sample to be analyzed is spiked with known quantities of carbon-14 labeled BaA and BaP. The sample is then transferred to a 100-ml beaker and evaporated, on a steam bath under nitrogen, to dryness as described earlier for the measurement of benzene solubles. This residue is dissolved in cyclohexane and caustic treated to remove some acidic compounds. Then a PNA hydrocarbon concentrate is obtained by solvent elution off a column of partially deactivated alumina. The solvents are cyclohexane, cyclohexane-benzene, benzene, and benzene-methanol. The fraction containing the PNA's is reduced to a small volume by evaporation on a steam bath. An aliquot of this sample is injected into a gas chromatograph and fractions are collected for measurement by UV and, in the case of BaA and BaP peaks, also for carbon-14 activity. These activities, compared with known concentrations originally added, give factors by which to relate the concentrations of each PNA to its total weight in the sample.

Other information on the nature of the benzene solubles will be obtained by gas chromatography, mass spectrometry, and UV and IR spectrophotometry. Elemental analysis for carbon, hydrogen, nitrogen, etc. will be done if necessary.

11.3 Gases and Vapors

C₁-C₅ Hydrocarbons - ASTM D-2820-72, page 950

G.C. analysis of a grab sample on a packed column operated isothermally at 0°C.

Benzene, Other Volatile Organics - NIOSH No.: 127

Adsorption on charcoal, desorption with carbon disulfide, G.C.

Carbon Monoxide - NIOSH No.: 112

Infrared analysis of a grab sample using a 10-meter-path-length gas cell.

Volatile Sulfur Compounds - (Hydrogen Sulfide, Carbonyl Sulfide, Carbon Disulfide, Mercaptans, Thiophenes, Sulfur Dioxide).

J. E. Chaney, J. of Gas Chromatograph 4, 42, (1966).

A grab sample is taken in a 250-ml glass sampling tube through a Perma Dry tube to remove water. The compounds are separated by G.C. on a Triton X-305 or other suitable column and detected by a flame photometer or microcoulometer sulfur detector. Details on the detector are given in ASTM D-3246.

Total Sulfur - ASTM D-3246

Burning of sample oxygen in special tube to SO₂ followed by detections with microcoulometer.

Sulfur Dioxide - NIOSH No.: 163

Sulfur dioxide is absorbed and oxidized in 0.3N hydrogen peroxide, then titrated with barium perchlorate using Thorin as indicator.

Sulfuric Acid Mist - EPA Method 8 R-490

Sulfur trioxide is separated from the sulfur dioxide in a special collection apparatus and determined by the barium-thorin titration method.

Nitrogen Dioxide - 0.5-50 ppm - NIOSH No.: 108

Nitrogen dioxide is absorbed in an impinger containing an azo dye forming a stable pink color read at 550 nm on a spectrophotometer.

Nitrogen Dioxide - 5-1000+ ppm - EPA No.: 487

Grab sample collected in flask with oxidant, nitrogen oxide measured colorimetrically using the phenoldisulfonic acid procedure.

Aldehydes - MBTH Procedure

Aliphatic aldehydes are absorbed in impingers containing 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH). The azine is oxidized by a ferric chloride-sulfamic acid solution and measured at 628 nm. Procedure of Hauser, T. R. et. al., Anal. Chem. 36 679 (1964).

Ammonia - ASTM D-1426

Ammonia absorbed in acid in impinger, distilled from alkaline solution and determined volumetrically or colorimetrically.

Phenols - ASTM D-1783

Phenol absorbed in alkaline solutions in impinger, distilled, reacted with 4-aminoantipyrine, and determined colorimetrically.

Cyanide - NIOSH No.: 116

The samples are taken using an impinger containing 0.1N NaOH. The samples are then analyzed using a cyanide ion specific electrode.

Arsine - ACGIH Method No.: 40

Arsine is collected in an impinger containing silver diethyldithiocarbamate. After sampling, the concentration is determined colorimetrically at 560 nm.

Mercury - EPA Method No.: 101 or 102, pages 512 and 521

The first method is used on samples that are primarily air, while the second is employed for hydrogen and other reducing gas streams. The mercury is collected in impingers containing acidic iodine monochloride solution. It is reduced to elemental mercury, aerated from the solution, and determined in a gas cell at 253.7 nm.

Beryllium Referee Procedure - EPA No.: 104, page 532

Sample is collected on Millipore filters and impingers containing distilled water. It is digested with acid and analyzed by atomic absorption spectrophotometry.

Beryllium Screening Procedure - EPA No.: 102, page 530

Sample is collected on a Millipore filter and analyzed by any acceptable method such as atomic absorption, spectrographic, fluorometric, etc.

Fluorides and Hydrogen Fluoride - NIOSH No.: 117

Samples are taken through impingers containing 0.1N NaOH, diluted with a buffer and analyzed using the fluoride specific ion electrode.

Nickel and Iron Carbonyls - Denshaw, et al., J. Appl. Chem., 13, 576, (1963).

Method could probably be extended to cobalt carbonyl.

Hydrogen Selenide - Collection in impingers containing Na_2CO_3 and measurement according to W. H. Allaway and E. E. Cary, Anal. Chem., 38, 1359 (1964).

Total selenium would be determined.

11.4 Direct Reading Colorimetric Indicator Tubes

Direct reading color indicator tubes have been used for the measurement of hydrogen sulfide and carbon monoxide for a number of years, and now there are more than a hundred different types in use. They are rapid, inexpensive, and are especially convenient for evaluation of toxic materials in industrial surroundings. At present, however, results may

be regarded as only approximate. The best accuracy that can be expected from indicator tubes of the better types is plus and minus 20 percent. Table XIII presents some of the tubes that may be applicable in coal conversion plants.

TABLE XI

SAMPLING AND ANALYTICAL METHODS FOR
PARTICULATES IN ATMOSPHERIC AND OTHER GASEOUS SAMPLES

Component	Method of Analysis
Particulates in Air (High Volume Sampler)	Code of Federal Regulations, Title 40, Appendix B. Environmental Protection Agency, U.S. Federal Register Office, "Reference Method for the Determination of Suspended Particles in the Atmosphere (High Volume Method)." ASTM D-2009-65.
Particulates in Stack Gases	ASTM D-2928; EPA Method No.: 5
Dust Fall	ASTM D-1739 - Collection and Analysis of Dustfall (Settleable Particles)
Benzene Soluble in Particulates	E. C. Tabor and D. H. Fair, <u>J. Air Pollution Control Assoc.</u> , <u>11</u> , 403 (1961).
Analysis of Benzene Soluble Portion of Particulate	
Polynuclear Aromatic Hydrocarbons 14 compounds including Benzanthracene and Benzo(a)pyrene	Intersociety Method 11104-03 73T "Tentative Method of Analysis for Polynuclear Aromatics in Coke Oven Effluents and ISM 11104-04 73T "Tentative Method of Analysis for Polynuclear Aromatic Hydrocarbons in Automobile Exhaust. Sensitivity is 1 $\mu\text{g}/\text{m}^3$ for each PNA.
Gas Chromatographic Analysis for Boiling Range	ASTM D-2887-72T "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography."
Mass Spectrometric Method	M. E. Fitzgerald, V. A. Cirillo, and F. J. Galbraith, <u>Anal. Chem.</u> <u>34</u> , 1276 (1962).
Infrared and Ultraviolet Spectra	
Carbon, Hydrogen, Nitrogen	R. D. Condon, <u>Microchem. J.</u> <u>10</u> , 408, 1966.
Sulfur	ASTM D-1552

SAMPLING AND ANALYTICAL METHOD FOR ATMOSPHERIC AND OTHER GASEOUS SAMPLES

Component	Sample Collection	Method of Analysis	Sensitivity
Volatile Hydrocarbons (C ₁ -C ₅)	Aluminized Bag	ASTM D-2820-72 "C ₁ through C ₅ Hydrocarbons in the atmosphere by Gas Chromatography"	0.01 ppm
Benzene, Toluene & Other Volatile Organics	Charcoal Adsorption	NIOSH Method No.: 127 "Organic Solvents in Air"	0.01 mg/sample
Carbon Monoxide	5-liter bomb or bag	NIOSH Method No.: 112	5 ppm
Volatile Sulfur Compounds: H ₂ S, SO ₂ , COS, RSH CS ₂ thiophene	250 ml glass sample tubes	D. F. Adams and R. K. Koppe, Tappi, 42, 601 (1959); S. S. Brody and J. E. Chaney, J. of Gas Chromatography, 4, 42, (1966); F. V. Wilby, Am. Gas Assoc. Oper. Sect. Proc., Year 1965, pgs. 65-136.	1 ppm
SO ₂ Only	Impinger	EPA Method No.: 6, NIOSH No.: 163	.25 ppm
Sulfuric Acid Mist and SO ₂ emissions	Special EPA Train	EPA Method No.: 8	
Total Sulfur	250-ml glass tube	ASTM D-3246-73 "Sulfur in Petroleum Gas by Oxidative Microcoulometry"	
Nitrogen Dioxide High Levels	Special Flask	EPA Method No.: 8	5 ppm
Low Levels	Impinger	NIOSH Method No.: 108, ASTM D-1607-69, "Standard Method of Test for Nitrogen Dioxide Content of Atmosphere (Griess-Saltzman Reaction)."	.01 µg/litre
Aldehydes	Impinger	EPA MBTH Procedure, Hauser, T.R. Cummins R. L., <u>AnaI. Chem.</u> (36) 679 1964	0.1 ppm
Ammonia	Impinger	ASTM D-1426, after collecting in acid in impinger.	1 ppm
Phenols	Impinger	ASTM D-1783 after collecting in NaOH in impinger	1 ppm

TABLE XII (Continued)

<u>Component</u>	<u>Sample Collection</u>	<u>Method of Analysis</u>	<u>Sensitivity</u>
Cyanide	Impinger	NIOSH Method No.: 116	0.13 mg/m ³
Arsine	Silver Diethyldi- thiocarbamate in impinger	Manual of A.C.G.I.H. "Determination of Arsenic in Air," NIOSH Method No.: 140	1 µg/sample
Mercury	Impingers with iodine monochloride	EPA Method No.: 10	
Beryllium	Filter (screening) Impinger (reference)	EPA Method No.: 103 EPA Method No.: 104	.03 µg/ml
Hydrogen Fluoride	NaOH in Impinger	NIOSH Method No.: 117 Fluorides and Hydrogen Fluoride in Air	.01 mg/m ³
Nickel and Iron Carbonyls	Impinger with iodine monochloride	A.B. Densham, et al. <u>J. Appl. Chem.</u> 13, 576 (1963)	.01 ppm
Hydrogen Selenide	--	--	--

TABLE 11.11

Some MSA Direct Reading Colorimetric Indicators

<u>Substance</u>	<u>Measurable Range</u>	<u>Interference</u>	<u>Catalog Number</u>
Arsine	0.025 - 1.0 ppm	Stibine, phosphine	81101
Carbon Disulfide	5 - 500 ppm	--	95297
Carbon Monoxide	10 - 3000 ppm	Hydrogen	91229
Formaldehyde	1 - 100 ppm	Turpentine, other aldehydes	93963
Hydrogen Chloride	2 - 500 ppm	HNO ₃	91636
Hydrogen Cyanide	1 - 65 ppm	Ammonia, H ₂ S	93262
Hydrogen Fluoride	0.5 - 5 ppm	--	81213
Hydrogen Sulfide	1 - 800 ppm	SO ₂	87414
Nitrogen Dioxide	0.1 - 50 ppm	H ₂ S; Halides	83099
Sulfur Dioxide	1 - 400 ppm	Acetic Acid	92623

12. SAMPLE FORMAT FOR STREAM SAMPLING AND ANALYSIS

Sample formats to be completed for sampling and analyses are shown in Figures I and II.

FIGURE I
SAMPLE SHEET FOR GROSS SAMPLE

Gross Sample No. _____

Date Taken: _____

Sample Size: _____

Time Taken: _____

Container: _____

Stream No.: _____ Location of Sample in Stream: _____

Flow Rate of Stream: _____

Pressure of Stream: _____

Temperature of Stream: _____

Sampling Procedure: _____

Disposition of Gross Sample: _____

Interfering Substances: _____

Comments: _____

Name of Person Taking Sample

FIGURE II
SAMPLE SHEET FOR DETAILED SAMPLE

TO BE FILLED IN BY SAMPLER

Detailed Sample No. _____

(Use Gross Sample Number Followed by
a Dash and Number for Specific Sample)

Sample Size: _____

Date Taken: _____

Container: _____

Time Taken: _____

Preservative: _____

Analyze For: _____

To Be Filled in By Analyst

Date Analyzed: _____

Time Analyzed: _____

Analysis Method: _____

Method of Preparation: _____

Component Concentration: _____

Comments: _____

Analyst: _____

Date: _____

13. BIBLIOGRAPHY

(Sections 7 through 11)

1. van Lehmden, D. J., Jungers, R. H., and Lee, R. E., Jr., Anal. Chem., 46, 239 (1974).
2. Symposium on the EPA-NBS Round Robin Analysis Results for Trace Elements in Coal, Fly Ash, Fuel Oil and Gasoline, Research Triangle Park, North Carolina, July 19, 1973.
3. Laitinen, H. C., Anal. Chem., 46, 2073 (1974).
4. LeRoy, V. M., and Lincoln, A. J., Anal. Chem., 46, 369 (1974).
5. Ruch, R. R., Gluskoter, H. J., and Shimp, N. F., "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," EPA-650/2-74-054, July 1974.
6. Davison, R. L., Natusch, D. F. S., Wallace, J. R., and Evans, Jr., C. A., Environ. Sci. Tech., 8, 1107 (1974).
7. Guidoboni, R. J., Anal. Chem., 45, 1275 (1973).
8. Sugimae, A., Anal. Chem., 46, 1123 (1974).
9. Vijou, P. N. and Wood, G. R., At. Absorption Newslett., 13, 33 (1974).
10. Janssens, M., and Davis, R., Anal. Chem. Acta, 70, 25 (1974).
11. O'Gorman, J. V., Sahr, N. H., and Walker, Jr., P. L., App. Spectros., 26, 44 (1972).
12. Kuhn, J. K., Norelco Reporter, 20, 7 (1973).
13. "Validation of Neutron Activation Technique for Trace Element Determination in Petroleum Products," API Publication Number 4188, August 1973.
14. Robbins, W. K., Anal. Chem., 46, 2177 (1974).

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)			
1. REPORT NO. EPA-650/2-74-009-1		3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Evaluation of Pollution Control in Fossil Fuel Conversion Processes (Analytical Test Plan)		5. REPORT DATE October 1975	
7. AUTHOR(S) C.D. Kalfadelis, E.M. Magee, G.E. Milliman, and T.D. Searl		6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Exxon Research and Engineering Company P.O. Box 8 Linden, New Jersey 07036		8. PERFORMING ORGANIZATION REPORT NO. Exxon/GRU.13DJ.75	
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO. IAB013; ROAP 2IADD-023	
		11. CONTRACT/GRANT NO. 68-02-0629	
15. SUPPLEMENTARY NOTES		13. TYPE OF REPORT AND PERIOD COVERED Task Final	
		14. SPONSORING AGENCY CODE	
16. ABSTRACT The report gives results of a preliminary definition of those streams which require analysis to permit an assessment of the pollution potential of the processes in the light of current environmental standards, using a coal gasification process (Lurgi) and a coal liquefaction process (COED) as a basis. It defines methods for sampling indicated streams and analytical procedures which are required to obtain the data. These summaries may be readily modified or adapted to other processes, and expanded to include additional polluting constituents or improvements in analytical procedures.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Coal Conversion Testing Sampling Analyzing		Air Pollution Control Stationary Sources Pollution Potential Lurgi Process COED Process	13B 13H 21D 07D 14B
19. DISTRIBUTION STATEMENT Unlimited		19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 184
		20. SECURITY CLASS (This page) Unclassified	22. PRICE

SATISFACTION GUARANTEED

NTIS strives to provide quality products, reliable service, and fast delivery. Please contact us for a replacement within 30 days if the item you receive is defective or if we have made an error in filling your order.

▲ **E-mail: info@ntis.gov**

▲ **Phone: 1-888-584-8332 or (703)605-6050**

Reproduced by NTIS

National Technical Information Service
Springfield, VA 22161

***This report was printed specifically for your order
from nearly 3 million titles available in our collection.***

For economy and efficiency, NTIS does not maintain stock of its vast collection of technical reports. Rather, most documents are custom reproduced for each order. Documents that are not in electronic format are reproduced from master archival copies and are the best possible reproductions available.

Occasionally, older master materials may reproduce portions of documents that are not fully legible. If you have questions concerning this document or any order you have placed with NTIS, please call our Customer Service Department at (703) 605-6050.

About NTIS

NTIS collects scientific, technical, engineering, and related business information – then organizes, maintains, and disseminates that information in a variety of formats – including electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

The NTIS collection of nearly 3 million titles includes reports describing research conducted or sponsored by federal agencies and their contractors; statistical and business information; U.S. military publications; multimedia training products; computer software and electronic databases developed by federal agencies; and technical reports prepared by research organizations worldwide.

For more information about NTIS, visit our Web site at
<http://www.ntis.gov>.

NTIS

**Ensuring Permanent, Easy Access to
U.S. Government Information Assets**



U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161 (703) 605-6000
