APPENDIX A

Process Descriptions - Gasification

APPENDIX A

PROCESS DESCRIPTIONS - GASIFICATION

In this appendix a general description is presented of the gasification processes studied. The reader is referred to the individual process reports for details.

A.1 Koppers-Totzek Process

A.1.1 General

The gasifier operates at about 2700°F and atmospheric pressure with oxygen, a small amount of steam, and a dilute suspension of powdered coal to produce synthesis gas. The product gas is high in CO and hydrogen, with negligible methane. The process is described generally in the Koppers brochures. Additional information has been obtained from the literature and by discussions with the Koppers Company. A discussion of the processing steps follows.

A.1.2 Main Gasification Stream

Figure A.1.1 is a block flow diagram of the process and auxiliary facilities. This design, based on the design supplied by the Koppers Company, feeds 6,750 T/D of bituminous coal containing 16.5% moisture, 17.3% ash, and 0.63% sulfur with a HHV of 8830 Btu/lb. The product gas, after acid gas removal, is 290 MM cfd with a HHV of 303 Btu/cf and 300 ppm sulfur. This sulfur content meets requirements but could be reduced by the use of more equipment. Most commercial applications are for making ammonia or methanol, but the gas can also be used as a clean fuel for firing ceramics, glass manufacture, etc., or for steam generation and combined cycle power plants or for upgrading to high Btu SNG; in other words the gas can be used whenever synthesis gas, fuel gas or reducing gas can be used. The process can also be used to gasify coal fines, char, hydrocarbons, or tar.

A.1.2.1 Coal Preparation

The first unit to be considered is the coal storage pile and handling facilities. This particular design does not require beneficiation of coals of 30% ash content or lower. For 30 days storage, the coal piles are about 200 feet wide, 20 feet high, and 1,000 feet long. There are two of these, with loading, unloading, and conveying equipment. These will generally be tamped down, but there can still be dusting and wind loss. Covered conveyors should be used, and other precautions included in the design to minimize dusting from stacking etc. Thorough planning is necessary to avoid possible combustion in coal storage piles etc., and to provide for extinguishing any fires that may start.

Coal drying uses a rotary drum drier fired with part of the product gas, giving a sulfur level in the off gas well below that allowable for liquid or solid fuel firing. Use of feed coal as fuel would be more

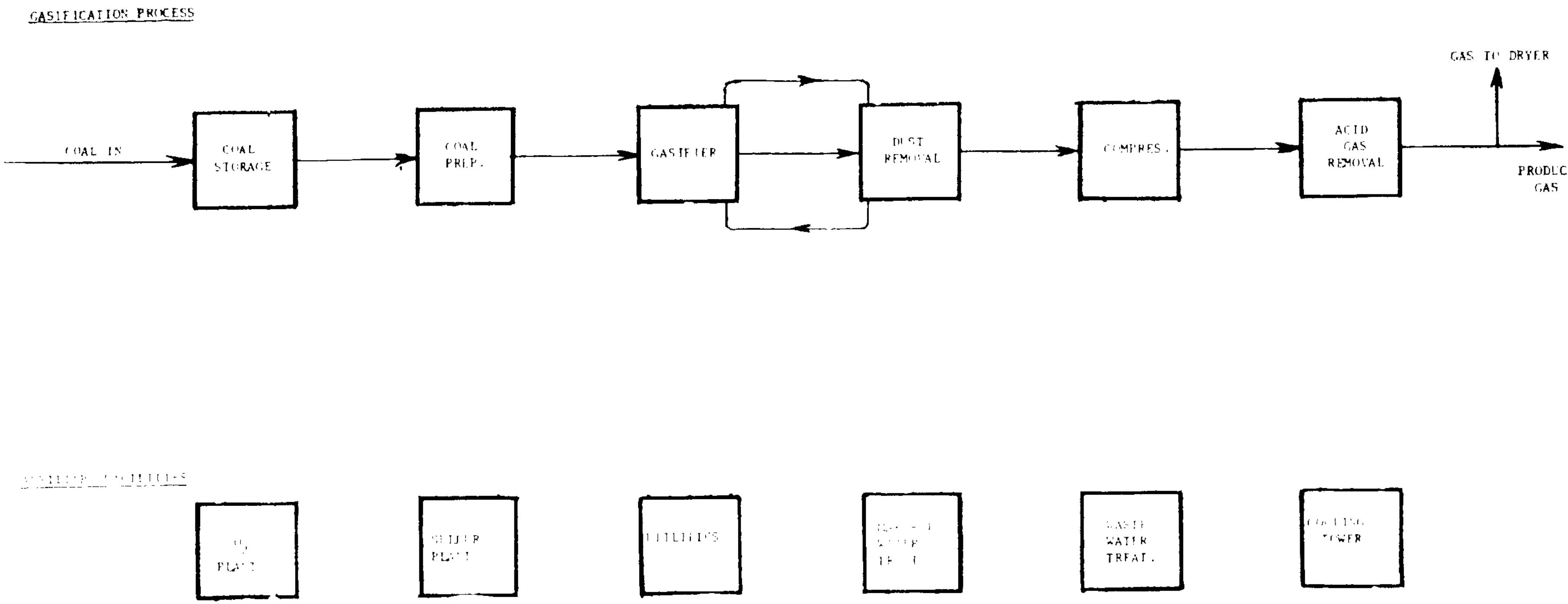

Figure A.1.1

Koppers-Totzek Gasification Process

efficient than the use of product gas but would give 1.4 lb SO_2/MM Btu compared to the allowable 1.2 lb SO_2/MM Btu. However, the major part of the fuel could be coal, supplemented by some product gas to meet sulfur emission limits. A large volume of excess air is used to bring the drying gas temperature down to less than 1000°F in order to avoid overheating the coal. Also, flue gas is recycled on the drier to hold a maximum of about 10% oxygen in the gas. The coal is not oxidized in the drying step and no tar, sulfur, or volatiles should be evolved, since the coal temperature is not over 200°F. It may be that a fluid bed drier would be more effective than the preceeding because it would allow a higher gas inlet temperature without overheating the coal. This would reduce the volume of dusty effluent gas since less excess air is needed, and the fuel efficiency would increase correspondingly. As an alternative, it might be possible to dry the coal using heat in the flue gas from the utility boiler.

The drier vent gas must be cleaned up and for this purpose an electrostatic precipitator was added to the base design. Bag filters might be used instead, but they must be kept hot enough to avoid water condensation. A water scrubber could be used, and may be preferred if odors in this vent gas are objectionable. The degree of odor control needed will depend on the type of coal and the plant location. It may be more of a problem for example on lignite, and this information should be obtained from plant or experimental operations. Even so, the gas will have a high moisture content and may form a water fog under certain atmospheric conditions. In locations where this is not acceptable, one solution is to make sure that the vent gas is above the critical temperature for fog formation.

Grinding and pneumatic transport with nitrogen are designed for completely closed gas recycle. The gas balance lines from this system (e.g. coal feed hoppers) should be vented into the dust removal system. Great care should be taken to avoid spills, overflow, leaks on seals, and the like. As a further precaution to control pollution, this entire system could be housed in a building, with positive ventilation control tied into bag filters.

Noise control may also be needed. While the building may shield the process area from undue noise of the grinding and handling operations, additional precautions may be needed from the standpoint of personnel inside the building.

A.1.2.2 Gasifier

The gasifier uses an entrained flow of coal, oxygen and steam. Coal is fed by screw feeders and is intimately mixed with steam and oxygen. The high temperature of operation causes slagging of the ash. Part of the slag exits at the bottom of the reactor and part passes overhead with the gas. The very hot gases are quenched above the reactor by a water spray before entering a waste heat boiler. Low pressure steam is produced in the gasifier jacket and high pressure steam is produced in the waste heat boiler. The gas then passes to the gas cleaning section.

A.1.2.3 Gas Cleaning

The raw product gas is cooled in a waste heat boiler and then scrubbed with water. Water from the scrubber, containing approximately half of the slag as well as dissolved H_2S etc., goes to a clarifier to remove solids and then to a cooling tower in which the air will strip out dissolved gases. If all the dissolved H_2S is stripped into the air, it will give a concentration of 1-2 vppm. While this is below the Maximum Allowable Concentration, it is far above the odor threshold and would be unacceptable. It is common to find an appreciable Biox action in the cooling water circuit, and Koppers Company experience shows that there is no odor problem, but this area needs better definition, particularly on higher sulfur coals. The problem can be avoided by using indirect cooling by cooling water or air-fins. The calculated amount of H_2S is less than 100 lbs/hr and it should be relatively easy to inactivate it by adding lime slurry, or by passing the circulating water through a bed of lump limestone. There might be sufficient alkalinity from the fraction of the slag that is carried over to do the task.

A.1.2.4 Acid Gas Removal

After compression, the gas is scrubbed with amine to remove H_2S. It is understood that Koppers Company is planning to use MDEA (methyl diethanolamine) for selective removal of H_2S; thus, a concentration of 22% H_2S passes to the Claus plant.

The final product gas after scrubbing contains 200 vppm of H_2S, as well as an estimated 100 vppm of COS. This gas is considered a relatively clean low Btu fuel. The sulfur level is too high, however, for methanation etc., to make a high Btu fuel. However, if methanation is desired other systems can be used to reduce sulfur to acceptable limits.

A.1.3 Auxiliary Facilities

In addition to the basic process, a number of auxiliary facilities are required which will now be discussed with regard to effluents to the air.

A.1.3.1 Oxygen Plant

The oxygen plant provides 4,000 tons per day of oxygen. It should pose no pollution problems since the only major effluent is a nitrogen stream, but there is a large consumption of utilities which affects overall thermal efficiency of the process.

A.1.3.2 Sulfur Plant

The H_2S stream from acid gas removal goes to a Claus plant. Sulfur recovery of about 97% can be achieved with three stages in "straight-through" flow. The tail gas still contains about 1 ton per day of sulfur and must be cleaned up, although this gas volume of 7 MM cfd is small relative to the other effluents. A number of processes are available now for tail gas clean up and several of these will be in commercial use soon (e.g. Shell's SCOT process, Wellman-Lord process, Beavon Process, etc.). In some, the tail gas is first reduced to convert all sulfur compounds to H_2S which can then be removed; in others, the tail gas is incinerated and the SO_2 is then scrubbed out. Limestone scrubbing of the incinerated tail gas may be used, with disposal of spent limestone along with the coal ash being returned to the mine. The amount of spent limestone is relatively small.

No specific preference is indicated for Claus tail gas clean-up since by the time that coal gasification finds much commercial application in this country, there will be considerable commercial experience to draw on. It is reasonably certain that there will be at least one demonstrated, satisfactory process available.

A.1.3.3 Utilities

In the utilities area, the main cooling tower has by far the largest volume of discharge, 48,000 MM cfd of air. It is therefore critical from the standpoint of pollution. In this particular case it is not expected to contain significant amounts of undesirable contaminants. The cooling water circuit is clean and does not contain ash or objectionable materials such as H_2S. Normally a certain amount of leakage can be expected on exchangers using cooling water. Since the process operates at low pressure, this should not be a major item. Also, most of this cooling water is from steam condensers of drivers on compressors, rather than on oil, sour water, etc. Cooling towers will always have the problem of mist as well as fog formation, as discussed under the area of gas scrubbing.

The utility power plant is a major item from the standpoint of pollution as well as thermal efficiency of the over all process, and is sized to make the plant self-sufficient in steam and power. It is desirable to burn coal as fuel, which means that sulfur and ash removal are required on the flue gas. This particular coal contains 0.63 wt. % sulfur corresponding to 1.4 lb SO_2/MM btu, whereas the allowable is 1.2. Therefore, some sulfur control is required. There are many ways to do this. As one example, a water scrubber can be used to remove ash and if some limestone is added it should be feasible to remove, for example, 20% of the SO_2, and thereby conform to regulations. The amount of limestone to dispose of is moderate, amounting to about 40 tons per day for complete SO_2 removal, compared to the ash production of 235 tons per day from the utility boiler.

An alternative is to burn part of the product gas along with coal to meet the allowable quantity of SO_2 in the flue gas discharged to the atmosphere. It would be possible to burn only product gas in this utility boiler to supply all the fuel required. This may not be a practical case but does set a limit. It would result in minimum pollution from the utility boiler, with regard to sulfur and particulates, in cases where this is justified or necessary. The volume of flue gas from the power plant is 320 MM cfd, or about the same as the volume of clean product fuel gas.

In view of the intensive effort underway on flue gas clean-up, it is expected that there will be techniques in wide spread use by the time that coal gasification finds extensive application. When flue gas desulfurization is used on a boiler with coal firing, it may be desirable to add the Claus tail gas to the boiler so that it is incinerated and passes through the sulfur cleanup. This would avoid the need for separate facilities for tail gas cleanup, but it does assume that the Claus plant would be near the boiler house. Location of the boiler might also be dictated by the practicality of using the flue gas for coal drying.

A.2 Synthane Process

A.2.1 General

The Synthane Process being developed by the Bureau of Mines is an intrinsically high efficiency fluidized bed coal gasification system operating at commercial pipeline pressure and designed to produce high-Btu content product gas. Gasification is accomplished in the presence of steam/oxygen, whereby heat required for the gasification reactions is supplied by the reaction of oxygen with a portion of the coal. High pressure favors methane yield, minimizes gasifier volume, reduces oxygen requirement and reduces product gas compression. A good fluidized bed operation insures the homogeneous reaction system required to avoid damage by locally high oxygen concentrations.

It was found possible to pretreat any caking coal by the proper combination of oxygen content of the fluidizing gas, temperature, and residence time, using a single vessel system wherein the operations of coal pretreatment, carbonization, and gasification are combined.

An engineering evaluation of the Synthane Process, which by this time incorporated Bureau of Mines methanation developments, was prepared by The M.W. Kellogg Company in 1970. Notwithstanding the substantial extension of high-pressure technology required to commercialize the process, there was found sufficient incentive in the economies projected in terms of overall simplicity, high gasifier methane yield, and small reaction volumes to proceed with design of a prototype large pilot plant. The prototype pilot plant was designed by The Lummus Company, and is now being operated.

A block flow diagram of the process and auxiliary facilities is shown in Figure A.2.1. This design feeds 14,250 tpd of a Pittsburgh seam coal containing 2.5% moisture, 7.4% ash, and 1.6% sulfur to the gasifiers. 250MM scfd of product gas is produced, with a HHV of 927 Btu/scf.

A.2.2 Main Gasification Stream

A.2.2.1 Coal Preparation and Storage

On-site coal storage will be required for all gasification plants to provide back-up for continuous gasification operations. For

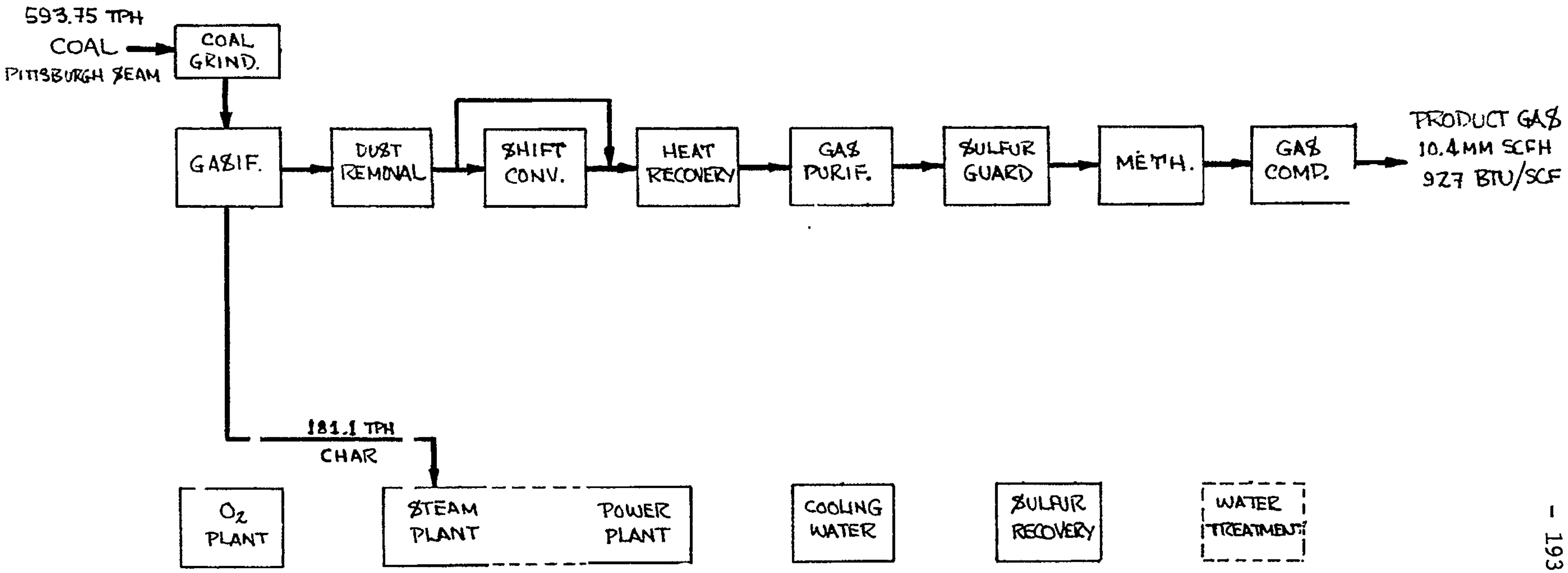

Figure A.2.1

SYNTHANE Coal Gasification - 250 million SCFD High - BTU Gas thirty days storage, there might be four piles, each about 200 feet wide, 20 feet high, and 1000 feet long. Careful management and planning will minimize dusting and wind loss and the hazard of combustion in storage facilities.

The feed coal employed in this design has low inherent moisture content, such that a special coal drying step is not provided. It may be possible to operate the system without such a facility with coal from particular seams, but this indicates enclosed on-site storage. Coal of the type and size range (-3/4 inch) indicated to be held in stockpiles in this design might be expected to acquire and retain 6-8 weight per cent surface moisture on exposure to rain.

A.2.2.2 Coal Grinding

Approximately 53 MM cfd of atmospheric air is aspirated into the ball-mill grinding operation, which reduces coal size to 70 percent through 200 mesh. The air stream is heated in a circulation system and passed through the mills, where it serves both to control moisture in the pulverizing process and as transport medium for the pulverized material.

The coal/air mixture passes through cyclones, where separation occurs, and the air stream is discharged to the atmosphere through bag filters. Such arrangement is commercially proven, with acceptable particulate emission, though load on the filters may amount to some 60 tpd in this case. Only trace quantities of hydrocarbons have been detected in such commercial streams, and odor is not considered a problem. Collected fines from the filters are recycled to mill product.

A.2.2.3 Gasification

A.2.2.3.1 Coal Feed System

Coal is charged to the gasifiers in the Bureau of Mines design through pressurized lock hoppers. A number of alternatives regarding the mechanical arrangement, the pressurizing medium, and the consequent net energy requirement and pollution potential of lock hopper operation appear feasible.

In this design, each gasifier is provided with one lock hopper, which discharges alternately into two feed hoppers from which coal is passed to the gasifier using a steam/oxygen mix as transport medium. Oxygen reacts with coal in the transfer line, liberating heat which prevents steam condensation that might otherwise interfere with coal transport. Hence, in this case, some pretreatment of coal occurs in the transfer line.

The gasifier charging sequence involves filling the vented lock hopper from pulverized coal storage bins, pressurizing the filled lock hopper, and discharging its load into a feed hopper. In this configuration, it is presumed that a feed hopper is maintained slightly above gasifier operating pressure while on line to the gasifier, and that pressure is allowed to drop to the gasifier pressure level as the hopper empties. At this point, the feed hopper is ready to accept another charge from the filled, pressurized lock hopper.

The pressurized lock hopper must be vented to essentially atmospheric pressure when empty of coal in order to be refilled. In a multiple gasifier system, operation may be sequenced such that initial venting may be to a lock hopper awaiting pressurization, or to a succession of these, such that some of the energy represented by the compressed gas may be recovered directly, while simultaneously reducing the quantity of residual gas to be vented ultimately. Alternatively, two or more lock hoppers might be provided each gasifier specifically to permit such sequencing, since there may be practical operating limitations to the degree to which gasifier operation may be scheduled.

The choice of pressurizing medium may directly affect the main gasification processing sequence, as well as the design and operation of the lock hopper system. The use of steam alone as this medium is considered mechanically unacceptable due to interference expected with coal transport from condensation, which may not be controllable.

Since some fraction of the pressurizing medium will travel with the coal into the gasifier, the use of a nitrogen-containing inert gas for such medium is considered unacceptable from a process viewpoint, since it dilutes the product gas, reducing its heating value, and occupies volume in the reaction sequence otherwise.

It is believed that CO_2, which is separated from the main process gas stream following shift conversion, is the preferred pressurization medium. Such CO_2 must be superheated to prevent liquefaction at 1000 psia, and the rate of heat loss from the pressurized feed system must be controlled to prevent condensation. Depending on the mode of operation of the feed system, the volume of raw gas issuing from the gasifier may be increased some 3-5 percent as a consequence of admission of pressurization gas with coal. This increased volume must be handled through the acid gas removal step, but it is presumed otherwise not to affect process operation.

In the method of operation of the coal feed system described above for this design, there should be no opportunity for gasifier gas to back through the lock hopper. Hence, trace quantities only of coal-originated materials, other than coal dust, should appear in vent gas. However, the use of a heated hopper system, as will be required if CO_2 is the pressurization medium, may subject coal in contact with heated surfaces to sufficiently high temperature to cause stripping of volatiles or of sulfurous gas. Formation of carbon- or carbonyl sulfides is also possible.

We have assumed an alternative to continuous atmospheric venting which involves containment of lock hopper vent gas, as in gas holders from which it could be recompressed, limiting the requirement for fresh make-up gas to the losses (largely back into the system) from the coal feed system. In this arrangement, it will probably be necessary to treat or filter gas entering the holder to remove dust.

A.2.2.3.2 Char Letdown

Ash must be removed from the Synthane gasifier, as in most gasification processes, in a more or less continuous fashion, to maintain carbon concentrations in the gasification zone sufficiently high for desired reactions to proceed. Experimental work indicates incentive for limiting the degree of carbon gasification, and a proposed feature of the Synthane process involves setting the carbon content of the ash (char) removed from the gasifier such that combustion of the char will balance the total steam and energy requirements for the process.

The high operating pressure of the Synthane gasifier imposes special problems on the system used to extract char. At the point of discharge from the gasifier bed, char is indicated to be at temperatures in excess of 1700° F.

The char in this design represents a significant sensible heat discharge from the gasifier. From thermal and process points of view, perhaps the ideal system would transfer hot char directly to the boiler in which it is to be combusted along with any associated gas, preserving most of this heat and avoiding use of cooling media, water or steam, that would require additional energy to subsequently separate or treat. The mechanical design of a throttling arrangement that would permit such operation, however, will require substantial development.

Consideration of a variety of alternatives led the designers of the large pilot plant to a system wherein char is cooled in situ prior to the point at which it must be passed through valves. Hot char is caused to flow into a separate fluidized bed cooler by regulating the pressure differential between the gasifier bed and the cooler. Steam is used to fluidize the bed, and water is injected into the system for cooling. High-pressure steam is generated in the cooler, and this steam may be used in the process (specifically in the carbon monoxide shift converter) after it has been filtered to remove char fines. The designers point out that this steam might be directed to the gasifier in its contaminated state if the gasifier distributor were designed to introduce contaminated steam and oxygen separately.

Cooled char may be fluidized out of the cooler bed into lock hoppers, avoiding throttling valves, or may be passed from the bottom of the cooler bed through valves into lock hoppers. Agglomerates which may come from the gasifier could present problems with either method of cooler operation.

The preferred alternative is a "dry" system, in which a filled char lock hopper is isolated with valves which are arranged to be blown clean before closing. Steam is vented to atmosphere via filters arranged within the lock hopper, ahead of the pressure-reducing valves. Char flows out of the bottom of the lock hopper into a conveying line in which steam is used as transport medium. The empty lock hopper is repressurized with steam before being put on line to again receive char.

A second alternative directs a char/steam mix from the cooler through a slide valve into a char slurry quench tank, where water sprays cool the char and a slurry is formed. The quench tank is vented to the char cooler. Char slurry is depressured through orifice valve arrangements, the char slurry is filtered to recover water, and water is recycled to the slurry quench tank through coolers. The char filter cake is estimated to contain 40-50 percent water in this case.

Gas from the gasifier will be carried into the char cooler along with char. It is presumed that most of this gas will issue from the char cooler along with the generated steam and be directed back into the main gasification stream, either directly into the gasifiers or at the shift converters. It is not possible to estimate the degree of gas contamination that may persist through the char depressurizing system into the steam which is indicated to be vented ultimately from a "dry char" process. Some 3000 pounds per hour of steam is estimated to be so vented if this scheme be applied to the Bureau of Mines design. Depending on its composition, some of this vent steam may be employed in the scrubber water treating system, or may serve to transport char to the utility boiler, in an integrated commercial plant. Although there would probably be least atmospheric pollution associated with a "wet char" or slurry letdown system, the water pollution generated and the energy associated with water treatment and wet char combustion would indicate that the slurry technique would be used only if an operable dry char arrangement cannot be developed.

To summarize, the design basis does not specify the method by which char will be removed from the gasifiers, except to provide lock hoppers to receive char. The lock hopper volume provided is not consistent with estimates of char density, so that lock hopper cycle rate may be higher than indicated.

With the preferred dry char process, we have assumed that about 100,000 pounds per hour of high pressure steam will be generated by direct water injection in the char cooler, and that this steam, along with associated gasifier gas, will be reintroduced into the process at the shift converters. Some 3000 to 6000 pounds per hour of steam is estimated to be vented from the lock hoppers, depending on cycle rate. "Dry" char is assumed to be conveyed to the utility boiler using a steam transport system. Net atmospheric pollution associated with char let-down is therefore assumed minor.

A.2.2.4 Dust Removal

Raw gas issuing from the gasifiers must be treated to remove particulates and condensable matter that may interfere with subsequent gas processing. The precise nature of materials which must be separated from raw gas at this point is not known, except that coal or char fines and coal-tars or oils are assumed to be present.

In the design basis, gas from the gasifiers passes first through cyclones, where heavier particles (char) are removed, and then the gas is subjected to cold-water scrubbing. Scrubber liquor effluent is depressured into decanters, where tar separation occurs, and water is recirculated to the scrubbers through water-cooled heat exchangers by high-pressure pumps. This design does not further detail the operation, or provide for further handling of separated products or of scrubber liquid.

We believe it may be possible to adapt a "tar-scrubber" of the type developed for petroleum fluid coking reactors to the Synthane coal gasifier to avoid the mechanical problems associated with tar and solids deposition in the gas outlets. Moreover, it should be possible to extract high-level energy from the process.

In the fluid coker, the scrubber vessel is integral with the coker reactor. The cyclone is internal to the reactor, with its outlet gas discharge into the scrubber. Heavy tar condensed from the gas stream in the scrubber is pumped through external exchangers, where high-pressure steam is generated. The cooled tar stream separates, with the portion not used for scrubbing being returned to the coker feed line. It is of course necessary to control temperature of the tar pool in the bottom of the scrubber vessel and tar velocities in the external circuit to prevent coking and solids deposition.

In the Synthane design, gasifier outlet temperature is estimated to be 800-1400°F. A steam dew-point of about 440°F is estimated for the raw gas conditions. It is further estimated that up to 70 percent of the heavy tar in the gas stream may be condensed by operation of the tar scrubber at about 560°F, or sufficiently high in temperature to permit generation of 1000 psia steam in the external circuit. It is estimated that about 365,000 pounds per hour of 1000 psia steam could be generated in this manner, assuming gasifier output to be at 1000°F.

Removal of the bulk of the heavy tar in the gas stream at this point should greatly reduce the emulsification problem as water is condensed from the gas downstream. Similarly, the tar scrubber would serve to remove a major fraction of the char, ash, and coal fines contained in this gas, so that loads on the downstream tar-oil separation and water treatment systems should be reduced significantly.

From a thermal point of view, it would be desirable to return the separated tar stream to the gasifier, as is done in the petroleum coker. But if this is found to adversely affect gasification, such separated tar could instead be directed to the char utility boiler or may be further processed for sale.

In this design, we have assumed that scrubbing will be used following the tar scrubber, but that gas which separates from the scrubber effluents on depressuring will be recompressed back into the main gas stream at a point following shift conversion. Additional tar and hydrocarbons which condense along with water from the gas stream as the stream temperature is lowered may be directed to finishing facilities to be processed for sale, or could be burned in the utility boiler. Either or both water and light hydrocarbon might be recirculated to scrub the gas stream, and steam could be generated in the process of cooling the circulated fluids. Alternatively at some point, gas would be sufficiently clean to permit direct operation in a conventional waste heat boiler. On the assumption that gas temperature is reduced to about 300°F to effect clean-up, some 300,000 to 400,000 pounds per hour of low-pressure steam may be generated in the scrubbers.

A.2.2.5 Shift Conversion

Scrubbed raw gas from the dust removal process is separated into two equal streams, one of which by-passes the shift converters, since only half of the total stream must be shifted to adjust the total H_2:CO ratio to 3:1 for purposes of methanation. In this design, a significant quantity of high-pressure steam must be introduced to the catalytic shift converters to achieve desired equilibrium, however.

A.2.2.6 Waste Heat Recovery

The raw gas streams which are split ahead of shift conversion are recombined following the converters, and are cooled from an average temperature of about 500°F to 300°F ahead of the gas purification system. Low-pressure steam is generated, and there are no effluents to atmosphere.

A.2.2.7 Light Hydrocarbon Removal

For our design, we have assumed that the gas stream may be cooled in water exchangers to about 90°F after it has been used to reboil the Benfield regenerator and passed through light oil scrubbers to remove B-T-X components. The scrubbing fluid would be available from the upstream hydrocarbon separators. Gas which separates on depressurizing this scrubber effluent could be recycled to the vapor space of the upstream separators for recompression into the main gas stream. Downstream distillation facilities would be required to separate naphtha if it were to be sold. It is estimated that 20,000-25,000 GPD of B-T-X could be so separated, requiring an estimated equivalent of 25,000 pounds per hour of low-pressure steam.

Part of the heat removed in the cooling process could be returned to the gas stream after scrubbing by exchange with the heated water leaving the coolers, so that the net thermal loss might be held to the equivalent of about 60,000 pounds per hour of low-pressure steam. About 18,000 pounds per hour of water would be condensed from the gas stream on cooling, and this (equivalent) water would have to be reintroduced on reheating the gas to avoid depletion of the Benfield solution. This might best be accomplished by direct introduction of high-pressure steam, rather than by reintroduction of the contaminated separated water, which would be directed to the waste water treatment facility.

A.2.2.8 Gas Purification

The gas purification or acid gas removal process which is used is the "Benfield" hot potassium carbonate system developed by the Bureau of Mines. This method of removing CO_2 and H_2S from the produced gas is indicated to have substantial thermal advantage over amine systems at the high process pressure employed.

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 the high-pressure absorber. The high solution temperature permits high concentrations of carbonate (alkalinity) to exist without incurring precipitation of bicarbonate according to:

$$K_2CO_3 + CO_2 + H_2O \longrightarrow 2KHCO_3$$

Partial regeneration of the rich carbonate solution is effected by flashing as the solution is depressured into the regenerators. In this design, sensible heat of the main gas stream is used to reboil the regenerators, so that the gas is cooled to about 260° F in the process. The gas is further cooled in cold-water exchangers to about 225° F before entering the absorbers.

It is necessary in this design to admit additional low-pressure steam into the regenerators to complete the regeneration process and to balance heat and water requirements. Regenerated solution is pumped back through the absorbers. The main process gas stream exits the absorbers at 230° F, and is cooled by cold-water exchange to about 100° F before undergoing residual sulfur cleanup. Stripped acid-gas flows to the sulfur recovery plant.

A.2.2.9 Residual Sulfur Cleanup

Methanation catalysts are adversely sensitive to very small quantities of sulfur in feed gas. The Benfield system is reported to be capable of operation such that sulfur present in process gas as hydrogen sulfide and carbonyl sulfide may be virtually completely removed. Less is known about the other forms of organic sulfur which may be present in process gas, especially thiophenes.

This design incorporates a sequence of iron oxide and char towers for residual sulfur cleanup ahead of the methanation reactors. It is estimated that total sulfur in gas may be reduced to less than 0.1 grain/100 ft^3 in this arrangement. Some provision will have to be made to permit change-out of the beds in this section. Hence, the high-pressure gas in the beds will have to be vented, and the beds will have to be inerted before being opened. It is assumed that the vented high-pressure gas will be directed to the utility boiler. Steam, which may be used for inerting, may be directed back to the Benfield regenerator.

Steaming, or other inerting, will also be required to purge the bed of oxygen when a new bed is to be put on line. It is assumed then that the only discharge to atmosphere from this section will be such inerting medium, and, further, that the quantity of this gas will be very small.

A.2.2.10 Methanation

The Bureau of Mines has developed two methanation processes for application in the Synthane system, and both will be tested in the prototype pilot plant being constructed at Bruceton.

This design incorporates the Tube Wall Reactor or TWR process, in which the methanation reactor is constructed in the form of a heat exchanger. Reaction occurs on a Raney nickel catalyst coating applied to the exterior of the exchanger tubes, and Dowtherm is vaporized through the tubes to remove reaction heat. High-pressure steam is generated in a separate boiler in the process of condensing and cooling the Dowtherm heat exchange fluid, which is then recycled to the methanator.

A.2.2.11 Final Methanation

The design basis does not include specific equipment for limiting CO content of product gas issuing from methanation. Depending on the ultimate use of product, CO content may be required to be held to less than 0.1 volume percent. The experimental data reported to date would indicate that a final treat will be required to limit CO content in methanator effluent to specification. In a commercial plant, some arrangement, possibly involving standby methanators, would probably be required in any event to handle sudden loss of activity or other malfunction in the process train at this point. In our design, we have assumed that specification CO levels will be achieved in the methanation plant proper.

A.2.2.12 Final Compression

Pressure drop through the Synthane train is indicated to amount to about 65 psi. Gas leaving the methanation plant is cooled to 100°F to remove water, and is then compressed to 1000 psig, the design product delivery pressure.

A.2.3 Auxiliary Facilities

We have elected in this study to treat the main gasification stream separately from all other facilities, which are thereby defined as auxiliary facilities. The functions of these auxiliary facilities are nonetheless required by the process, and, for economic and/or ecologic reasons, would be constructed along with the gasification system in an integrated plant.

A.2.3.1 Oxygen Plant

The oxygen plant provides a total of 3650 tons per day of oxygen. The only effluents to the air from this facility should be the components of air, principally nitrogen. About 330 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, as an inert stripping agent in regeneration or distillation, or to dilute other effluent gas streams.

It will be possible to generate about 900 KW of electricity by recovering the compression energy of the nitrogen through turbo-expanders.

About 425 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.

A.2.3.2 Sulfur Plant

The Stretford process has been assumed for sulfur removal. In the Stretford process, sour gas is washed with an aqueous solution containing sodium carbonate, sodium vanadate, anthraquinone disulfonic acid, and a trace of chelated iron. The solution reaches an equilibrium with respect to CO_2, such that only small amounts of CO_2 are removed from the gas undergoing treatment.

In this system, H_2S dissolves in the alkaline solution, and may be removed to any desired level. The hydrosulfide formed reacts with the 5-valent state vanadium, and is oxidized to elemental sulfur The wash liquor is regenerated by air blowing, wherein reduced vanadium is restored to the 5-valent state via an oxygen transfer involving the ADA. The sulfur is removed by froth flotation and filtration or centrifugation.

A.2.3.3 Utilities

A.2.3.3.1 Power and Steam Generation

The choice of fuel for the generation of the auxiliary electric power and steam required by coal gasification plants markedly affects the overall process thermal efficiency. It is generally least efficient to burn the clean product gas for this purpose. On the other hand, investment in power-plant facilities, including those required to handle the fuel and to treat the flue gas, is generally least when product gas is so used.

Synthane gasification is one of the class of coal gasification processes which generate a carbon-containing char. Research to date would indicate that it is not desirable to gasify more than about 90% of the carbon in feed coal, and that it may be preferable to limit gasification to about 60-70 per cent of carbon for most feeds. A particular feature of the Synthane process design, therefore, is that the carbon content of char leaving the gasifier may be adjusted such that the subsequent combustion of the char will balance the power and steam requirements for the system.

It may be assumed that combustion of Synthane chars will be possible in conventional fireboxes if product gas is used as supplemental fuel. This alternative might be preferred then on the basis of carrying the least developmental debits, and because it should be possible to adjust SO_2 concentration in flue gas from most chars such that subsequent flue gas treatment may be avoided. It has the disadvantage of adversely affecting overall thermal efficiency.

For this design, we have assumed that equipment will be developed to combust char alone with essentially complete carbon utilization. This may be possible, for example, in a fluidized bed boiler and, especially, in a fluidized bed system which incorporates combustion in the presence of limestone to remove sulfur. Otherwise, such char combustion will in general require that flue gases be treated to remove sulfur. And, as indicated above, the development of a large-scale char burning system, as with the development of any new commercial boiler concept, may involve appreciable effort, a long lead time, and considerable investment.

A.2.3.3.2 Cooling Water

A total of 260,000 gpm of cooling water is indicated to be required in this design. If cooling towers were used for this total plant, a minimum of 6600 gpm of water would be evaporated. Drift loss would be in excess of 500 gpm, and draw-off might be about 800 gpm. Air requirement would amount to some 48,000 MM scfd. Reheat of plumes would be required to avoid fogs in some cases.

A.2.3.3.3 Waste Water Treatment

Facilities required to treat water, including raw water, boiler feed water, and aqueous effluents, will include 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 run-offs and for flow equalization within the system will be required. Run-off from the paved process area could easily exceed 15,000 gpm during rainstorms. Run-off from the unpaved process and storage areas could exceed 60,000 gpm in a maximum one-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.

A.3 Lurgi Process

A.3.1 General

The Lurgi process has operations similar to other types of coal gasification processes, except for the gasification step itself. The gasification step in each case is peculiar to the process. In general, coal gasification involves getting coal from the mine, storing it, reducing its size to that necessary for gasification, and, possibly, pretreating the coal. The gasifier raw gas is generally processed through a shift reactor which converts carbon monoxide and steam to carbon dioxide and hydrogen. The hydrogen is necessary for a later step in methanation. This shift reaction is only applied to the raw gas if one desires to up-grade it to a synthetic natural gas (SNG) stream. For a low heating value gas, a water gas shift section is not required. In this Lurgi study, the assumption is that the gas will be up-graded to SNG. Following the shift there is a clean-up step to remove from the effluent gas all the H_2S and most of the CO_2. The acid gases are then taken for sulphur production through a Claus plant or other sulfur recovery process. The last traces of sulfur are then removed from the gas purification product stream in order not to poison the methanation catalyst.

The next step is methanation, where three moles of hydrogen react with each mole of carbon monoxide to produce a mole of methane and a mole of steam. Considerable quantities of CO_2 also react to produce methane. These are highly exothermic reactions which produce a fair amount of the steam required in the plant. Following methanation there is a drying step and the gas is compressed to pipeline pressure.

The plant is designed to produce 250 MM scfd of SNG with a heating value of 972 Btu/scf. A flow diagram for the plant is shown in Figure A.3.1.

A.3.2 Main Gasification Stream

A.3.2.1 Coal Storage and Pretreatment

The coal storage part of the plant does not involve coal cleaning, gangue removal or primary screening. All of these operations are assumed to have taken place at the mine. The coal from the mine is transported to the gasification plant by a continuous belt conveyor. The higher heating value (HHV) used in the design is 8872 Btu/lb of coal.

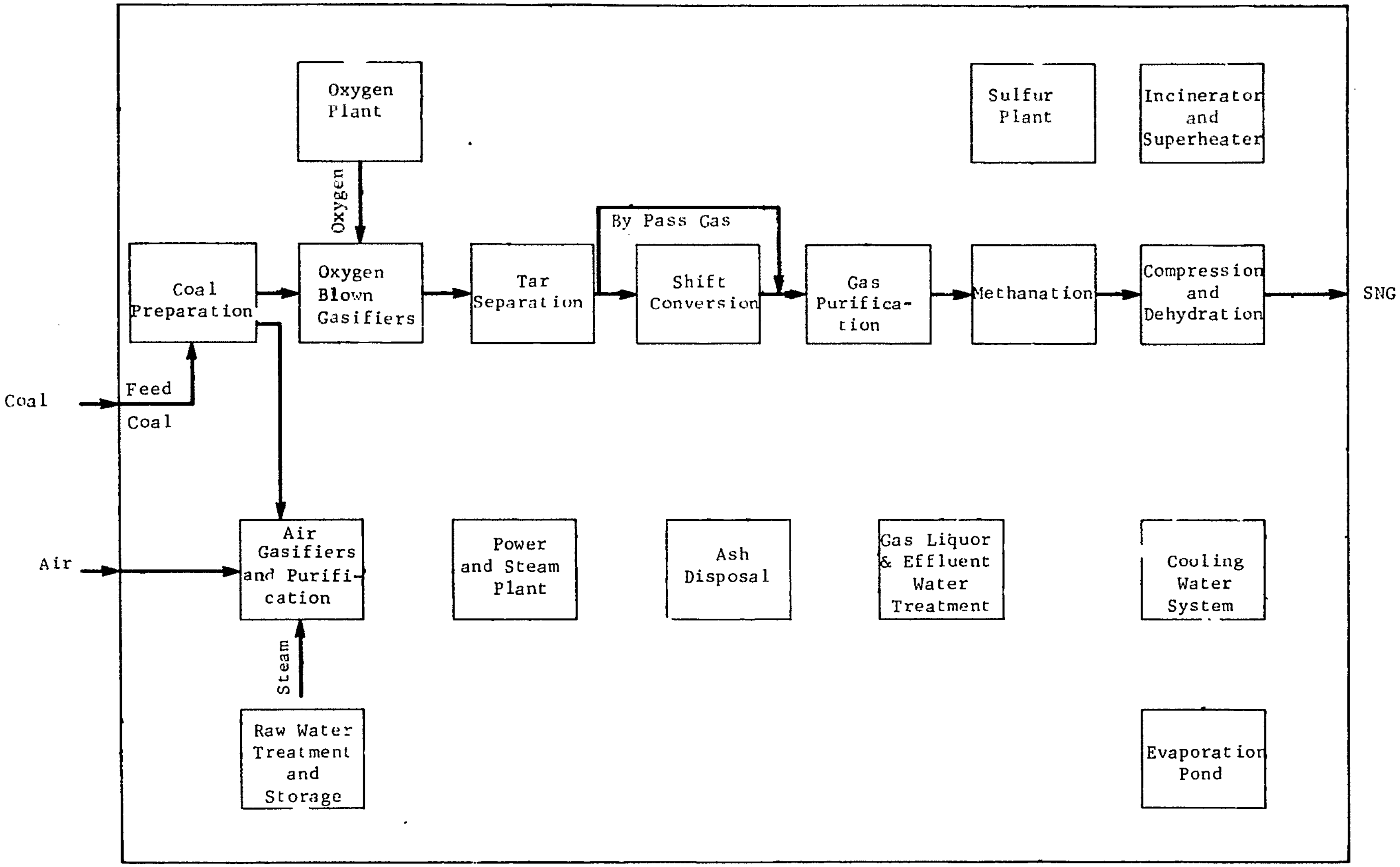

Figure A.3.1

LURGI Process

The sub-bituminous coal delivered to the gasification plant is crushed to 1-3/4" x 0. Six storage areas are used for stock piling. Each area is 1,750 ft. long x 124 ft. wide and contains roughly 120,000 tons of coal. Coal from the various storage piles is blended prior to feeding it to the gasifier in order to achieve proper heating value control (Btu control). An emergency stock pile and re-claiming facility are available to provide an additional 650,000 tons of coal. This will provide a 25 day supply of coal in cases of emergency.

A secondary screening facility is present at the gasification plant. The 1-3/4" x 0 coal is screened to produce two gasifier feed sizes (1-3/4" x 5/8" and 3/8" x 3/16"). Two sizes of coal are used as an economic measure to minimize size reduction and screening operations. All undersized material is conveyed at a rate of about 260 tons per hour to a briquetting plant. Briquettes are fabricated and sized to 1-3/4" x 5/8". The briquettes are mixed with the feed going to the gasifier. The briquetting plant contains mixers, coaters and compactors in order to mix the coal fines with a tar binder.

Wet scrubber dust collectors are installed in the screening and briquetting plant to eliminate dust and fuel emissions. Sprays are used at transfer points for dust suppression.

A.3.2.2 Gasification

In the Lurgi Process, gasification takes place in a counter-current moving bed of coal at 420 psig. A cyclic mode of operating using a pressurized hopper is used to feed coal. The pressurizing medium is a slip stream of raw gas which is later recompressed and put back into the raw gas stream going to purification. The gasifier has a water jacket to protect the vessel and provide steam for gasification. Approximately 10% of the gasification steam requirement is provided in this manner.

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

The top and middle zone temperatures are generally between 1100 and 1400°F, where the devolatilization and gasification take place. The gas leaves the bed between 700 and 1100°F depending on the rank of the coal. The effluent stream for the Navajo sub-bituminous coal will be approximately 850°F. The temperature of the ash is kept below the ash fusion temperature by introducing sufficient steam to avoid ash fusion.

The gas stream leaving the Lurgi gasifier contains coal dust, oil, naphtha, phenol, ammonia, tar oil, ash, char and other constituents. This mixture goes through a scrubbing and cooling tower to remove the tar.

The raw gas stream then goes through a waste heat boiler where the raw gas temperature is cooled to about 370°F. The boiler produces 112 psia steam for the Rectisol, Phenosolvan, and Stretford plants. The raw gas stream after cooling is split into roughly two equal parts. Half of it goes through shift conversion to produce additional hydrogen which will be needed for methanation. The other half goes directly to the gas purification system. Any liquid that is condensed in the waste heat boiler and gas cooling section is sent to the gas liquor separation unit.

The coal lock hopper gas is compressed and mixed with the stream that goes directly to purification. This lock hopper gas stream is mixed with other vent streams which contain sufficient quantities of carbon monoxide and methane to warrant its re-introduction into the raw gas stream.

A.3.2 3 Tar Separation

The water that was used to initially quench the gas as it comes out of the gasifier becomes a gas liquor. The gas liquor cools the crude gas mixture to a temperature at which it is saturated with water. This gas liquor is then flashed, and the tar is removed out of the bottom. The top phase is then sent to water purification. The gas liquor flash tanks will also receive the aqueous effluent from the cooling area prior to the shift reactor. In the gas liquor purification system,dissolved phenol and ammonia are removed for subsequent by-product recovery value.

A.3.2.4 Shift Conversion

Slightly less than half of the total crude gas is sent to the shift conversion section. The crude gas will be cooled in a waste heat boiler generating steam at about 76 psia. This is the gas that goes to the shift reactor section. The shift reactors are designed to produce hydrogen by the "water-gas shift" reaction. The shift gas feed is quenched and washed in a countercurrent water tower. The washed gas is heated and passed through a pre-reactor to remove carbon containing residues. The heated gas will be shifted in a series of reactors resulting in 77.2% conversion of carbon monoxide. The equilibrium temperature at which the 77.2% of the CO would be converted in this system is 800°F. Shift reactors generally operate between 700 and 1000°F. The shift section is designed to produce a ratio of over three moles of hydrogen to each mole of carbon monoxide in the total gas stream for methanation. In this design the ratio of H_2:CO going to methanation is 3.7.

The hot gas liquor and tar which are condensed during cooling in the wast heat boiler are sent to the tar separation units. The product stream from shift conversion is then mixed with the by-pass gas stream from the gasification unit and is cooled and sent to gas purification. Since the shift reaction is fairly exothermic, a fair quantity of heat is recovered prior to the low temperature gas purification step. Heat is also recovered from the crude gas stream that does not go through the shift reactors.

A.3.2.5 Gas Purification

The effluent stream from the shift reactor section is combined with the other half of the raw gas and the recompressed lock hopper gas, and is then sent to the purification system. The mixed gas stream is cooled to low temperature in order to go into the Rectisol system. The Rectisol process is a low temperature methanol wash process which removes acid gases such as H_2S, COS and CO_2 down to a level of about 0.1 vppm. The gas purification system is also used for drying and reducing the CO_2 level prior to final pipeline compression. The efficiency of methanol absorption increases considerably with decreasing temperature. The lowest temperature used in the process is on the order of -75°F. The first vessel in the Rectisol unit is a prewash tower which strips out naptha and cools the raw gas. The absorber then removes H_2S and COS down to about 0.1 vppm. Roughly 88% of the CO_2 is also absorbed at this time. The effluent raw gas from the methanol refrigerated absorption column is used to cool the incoming acid gas stream. This sulfur free gas stream is then sent to the methanation area.

All the acid gas streams are combined into a single stream and delivered to the sulfur recovery plant. The sulfur plant stream also includes the carbon dioxide that is removed after methanation. The acid gases from the cold methanol are recovered in a multi-stage operation. The acid gas containing stream is regenerated by step-wise expansion. The last step is a vacuum distillation. The stream to the sulfur plant contains, in addition to the acid gases, a fair amount of product hydrocarbons and carbon monoxide which will ultimately be burned in the incinerator. A mechanical compression refrigeration cycle is used which provides refrigeration at two temperatures: high level refrigeration at 32°F and -50°F which is used for the acid gas treatment. The 32°F methanol stream is used mostly for removing water vapor.

A.3.2.6 Methanation

The feed gas leaving the acid gas purification system is preheated with product gas leaving the methanation reaction section. Methanation catalysts are known to be extremely sensitive to poisoning by sulfur. The fresh feed is therefore treated with zinc oxide beds prior to exposure to the catalyst. A fraction of the methanated product is recycled and mixed with the feed to dilute the concentration of reactants in the feed. The heat of reaction that is generated by the synthesis of methane is removed by converting boiler feed water to process steam. This steam is used for gasification and in other parts of the plant.

A.3.2.7 Compression and Dehydration

The product gas from the methanation reaction section leaves at approximately 225 psia and 800°F. The stream is cooled and is sent to a final product condensate separator. The water is recovered and is sent to the raw water treatment plant. The gas is cooled to 90°F and is then recompressed from 225 to 500 psia. This stream is then sent back to acid gas removal systems for CO_2 and water removal. The effluent from the gas purification system is then sent to the second stage of the compressor where the pressure is boosted to 915 psia to meet pipeline requirements. Air cooling is used to cool the compressor effluent gas prior to delivery to the pipeline.

A.3.3 Auxiliary Facilities

In addition to the basic process facilities described above a number of auxiliary facilities are required to make the plant run efficiently and to remove pollutants. These will be described in this section.

A.3.3.1 Oxygen Plant

Three oxygen plants are required in this process to produce 6,000 tons per day of 98% pure oxygen. Approximately 444,000 scfm of air are compressed to 90 psia with three parallel centrifugal compressors. In so doing, the moisture content of the air is condensed and is available for process use.

A.3.3.2 Sulfur Plant

The H_2S effluent stream from the acid gas purification system and the H_2S from the acid gas treatment plant (hot potassium carbonate) from fuel gas production are sent to a Stretford sulfur recovery plant. The Stretford process was chosen for sulfur recovery in this plant because the total percentage of sulfur in the input stream is only 1%. It is not practical to use a Claus Plant for less than 10% H_2S; capital and operating costs increase drastically as throughput volume increases. Roughly, 94% of the sulfur that comes into this unit is removed and high quality elemental sulfur is produced. The effluent stream contains 741 ppm of sulfur as H_2S and COS. This stream is combined with fuel gas and is incinerated in the superheater fire box.

The acid gas entering the Stretford unit is treated with a water solution containing sodium carbonate, sodium vanadate, anthraquinone disulfonic acid (ADA), citric acid, and traces of chelated iron at 80°F and a pH of 8.5. The H_2S is oxidized by the vanadate to form elemental sulfur. The vanadium, which is reduced by the sulfur reaction, is then reoxidized by the ADA to the pentavalant state. This reaction occurs in the absorber using air as the oxidizing medium. The liquid containing elemental sulfur passes to an oxidizer where ADA is reoxidized by air. The elemental sulfur/air froth overflows to a holding tank. The reoxidized solution is recycled back to the absorber. The sulfur is recovered from the sulfur froth by filtration, centrifugation or floatation. A typical Stretford solution purge contains sodium salts of anthraquinone disulfonate, metavanadate, citrate, thiosulfate and thiocyanate for which acceptable disposal must be arranged.

A.3.3.3 Incineration

The effluent stream from the Stretford sulfur plant is sent to incineration. The incinerator superheater fire box consumes about 13.7% of the product gas from the air gasification section. This corresponds to 44.9 MM scfd. This stream which consists essentially of 96% carbon dioxide will have a total flow of 367 MM scfd on a dry basis, and a higher heating value of 29 Btu/scf. Approximately 321 M lb/hr of air will be required to completely burn the Stretford effluent stream. The combined effluents from incineration and superheating come out of a common stack. The flue gas composition will be 62.5% CO_2, 7.4% H_2O,295 ppm SO_2, 76.5 ppm COS, 57.5 ppm NO_x, 0.3% O_2, and 29.8% N_2. The total amount of heat input into the incinerator/superheater is approximately 872 million Btu/hr.

A.3.3.4 Power and Steam Production

The power requirements for the gasification complex are met with a boiler-gas turbine combined cycle fired with a low Btu gas produced in a Lurgi gasifier using air. The Navajo coal is gasified at about 285 psig. The method of operating the 10 gasifiers (9 on stream and 1 on stand-by) is similar to that previously described for the oxygen gasifiers. The raw gas produced goes through a tar separation unit and then through an acid gas treatment section. The raw gas is desulfurized using a hot potassium carbonate system. The H_2S and CO_2 from the hot potassium carbonate system is sent to the Stretford unit and combined with the Rectisol effluent in order to produce elemental sulfur.

The same type of coal preparation mentioned previously is used for this gasification. The lock hopper vent gas is compressed and combined with the raw gas prior to acid gas treatment. In this system, hot compressed air and steam are mixed and introduced through the bottom grate. The ash is removed and combined with the ash from the oxygen gasifier in the ash quench pond. The ash slurry is transported back to the mine for ultimate disposal. Approximately 327 MM scfd of dry fuel gas is thus produced with a higher heating value of 230 Btu/scf.

The flue gas is used in a combined cycle operation. Approximately 1/4 of the total gas is sent to gas turbines to operate the oxygen plant compressors. The rest of the fuel gas stream is heated in a fuel gas fired heater prior to going through a fuel gas expander. The effluent stream from the expander is used to fire the fuel gas heater, steam superheater, incinerator, and the power boiler. The fuel gas distribution is given in Table 5.

A.3.3.5 Raw Water Treatment

Raw water is supplied to a 21-day hold up storage reservoir from a major source such as a lake or river. The capacity of the reservoir is 185 million gallons, and it occupies a site of 28 acres by 30 feet deep. The reservoir serves various functions which include a place to settle silt and provide water for fire control. The reservoir is lined to avoid seepage. The rate of evaporation from the reservoir is 145 gpm. Raw water strainers are placed on the inlet to the pumps going to the raw water treatment section.

Approximately 4900 gpm of raw water are pumped out of the reservoir to the treatment section. An additional 600 gpm are recycled from the methanation reaction and condensate from the oxygen plant. After the water is strained to remove silt, it is pumped to a lime treater where it is treated and clarified. The water in the clarifier is treated with alum and polymers. The effluents from the clarifier are drained to a clear-well where they are temporarily stored. The water from the clear-well is pumped through anthracite pressure filters. Approximately 4500 gpm are sent to demineralization. Of this amount 3900 gpm go in to become feed water for steam production. The demineralization section blowdown consisting of 551 gpm is sent to the ash quench area. Roughly 1/3 of the latter amount of water is taken back to the mine as part of the ash slurry for ultimate disposal. The process condensate aerator is used to remove hydrocarbons as well as carbon dioxide which might be dissolved in the water. The effluent from the condensate aerating vessel is mixed with the demineralizer effluent. The total demineralizer effluent flow rate is therefore approximately 4500 gpm. The pressure filter requires roughly 300 gpm of back wash which is sent back into the reservoir. The reservoir capacity is sized so that all the silt can be collected over the life of the project which is roughly 25 years.

Approximately 2 tons per hour of water treating chemicals will have to be disposed of from the raw water treatment section. Most of these chemicals are sent to the evaporation pond and stored there for the life of the project. Roughly 1000 lb per hour of water treating chemical wastes are chemicals associated with the demineralization section. The demineralization waste stream contains caustic, sulfuric acid and resins. The internal water cooling system also requires chemical treatment.

The plant is designed to use 130,000 gpm of cooling water. This system removes 1170 MM Btu/hr. Water is designed to leave the cooling water system at 75°F and is returned at 93°F. The cooling water make-up requirement is approximately 2.2% of the circulation or 2810 gpm. Most of this make-up is supplied from the effluent water treatment area. The cooling water is supplied by three 5-cell cross-flow cooling towers. The cooling water is treated with chemicals in order to control corrosion, scale formation, plant growth and pH. The cooling towers are designed for a wet bulb temperature of 67°F, allowing an 8°F approach to the designed condition. The cooling tower blowdown, consisting of only 210 gpm, is sent to the evaporation pond. Drift loss from the cooling towers is 260 gpm. The chemicals that are added to the cooling tower include an antifoam package, a biological control package, a scale and corrosion control package, and sulfuric acid for pH control.

A.3.3.6 Gas Liquor Treatment and Effluent Water Treatment

The aqueous streams condensed from the coal gasification and gas processing areas by scrubbing and cooling the crude gas stream are called the gas liquor. Gas liquor is collected in one central area coming from gasification, shift, gas purification, and fuel gas synthesis. Before all of these aqueous streams are collected,all of the tar, the tar oil naphtha, and naphtha will have been collected and stored for by-product value. Gas liquor streams will contain all of the ammonia and phenols that are produced in gasification. In addition to these by-products, the gas liquor will also contain carbon dioxide, hydrogen sulfide, trace quantities of hydrogen cvanide, and other trace components.

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

The effluent stream from the steam stripper is air cooled and sent to the deacidifier reboiler. The carbon dioxide and hydrogen sulfide coming off the reboiler are recompressed and treated in the Rectisol process. The ammonia is collected as a 24.1 wt % aqueous solution. Some of the vent gas associated with collecting the ammonia in solution is sent to incineration. The bottoms from the steam heated ammonia stripper go to the effluent water treatment section after air cooling.

The effluent water treatment system, biological treatment (biox), is used to reduce the phenol and ammonia concentrations in the effluent from the gas liquor so that the water can be reused as cooling tower make-up. The biox system is also used to treat sanitary sewage discharge and discharge from the API separator. Approximately 2900 gpm of effluent come from the gas liquor treatment area,and 110 gpm come from all the other feed streams. These two streams are treated in series. The first section treats the gas liquor effluent in an aeration basin followed by a settling basin. The second section treats the effluent from the first section,as well as the 110 gpm from all other streams in the same way. Thus, the second treatment area acts as a polishing section for the effluent water treatment plant. The purified liquid from the polishing settling basin is filtered and sent to the cooling tower sump.

A.3.3.7 Ash Disposal

Dry ash produced from both the oxygen blown gasifier and the air blown gasifier is quenched with demineralizer blowdown water. The water is used to reduce the ash temperature and to avoid dust problems in transporting the ash. Quenched wet ash is sent from the ash hopper through a drag conveyor to the belt conveyor for ultimate disposal to the mine. Additional ash slurry that is carried with the steam produced in the quench goes to a bin lock condensor as well as to a cyclone separator, followed by a droplet separator, and finally through an ash slurry thickener. The de-watered ash is then conveyed back to the mine on the belt conveyor together with the ash from the ash hopper. A total of 466,700 lb/hr of wet ash is transferred. Of that amount roughly 73,000 lb/hr is water, 20,000 lb/hr is the equivalent of dry ash free coal, and 374,000 lb/hr is ash. The sulfur content of this material is approximately 0.05%. In addition to the ash, some spent chemicals and sludge from the water effluent treatment plant are also sent to the mine for burial. The total quantity of additional material will not add more than 0.5 wt % to the mass going back to the mine.

A.4 CO_2 Acceptor Process

A.4.1 General

This process makes synthetic natural gas (SNG) from lignite by gasifying it with steam at 1500°F and 150 psig. Heat is supplied indirectly by circulating dolomite which also takes up CO_2 and sulfur. After clean-up to remove dust and sulfur, the gas is methanated, giving a heating value of 952 Btu/cf HHV. Since the gas fed to methanation has a high hydrogen content, it requires no shifting or CO_2 removal ahead of the methanator. It is compressed and dried to meet pipeline requirements. Figure A.4.1 shows the general flow diagram of the CO_2 acceptor process.

A.4.2 Main Gasification Stream

The plant is sized to make 250 x 10^9 Btu/day of synthetic natural gas having a higher heating value of 952 Btu per cubic foot (262.6 MM scfd). Total consumption of lignite is 28,517 tpd of 33.67% moisture content. The preheated lignite fed to the gasifier contains .90% sulfur, 11.45% ash, and has a higher heating value of 11,120 Btu per pound.

A.4.2.1 Coal Preparation

Large storage piles are needed in view of the high lignite consumption rate. Tamping down of the storage pile as it is being formed is one customary precaution to prevent dusting and fires, but facilities and plans are also needed for extinguishing fires if they occur.

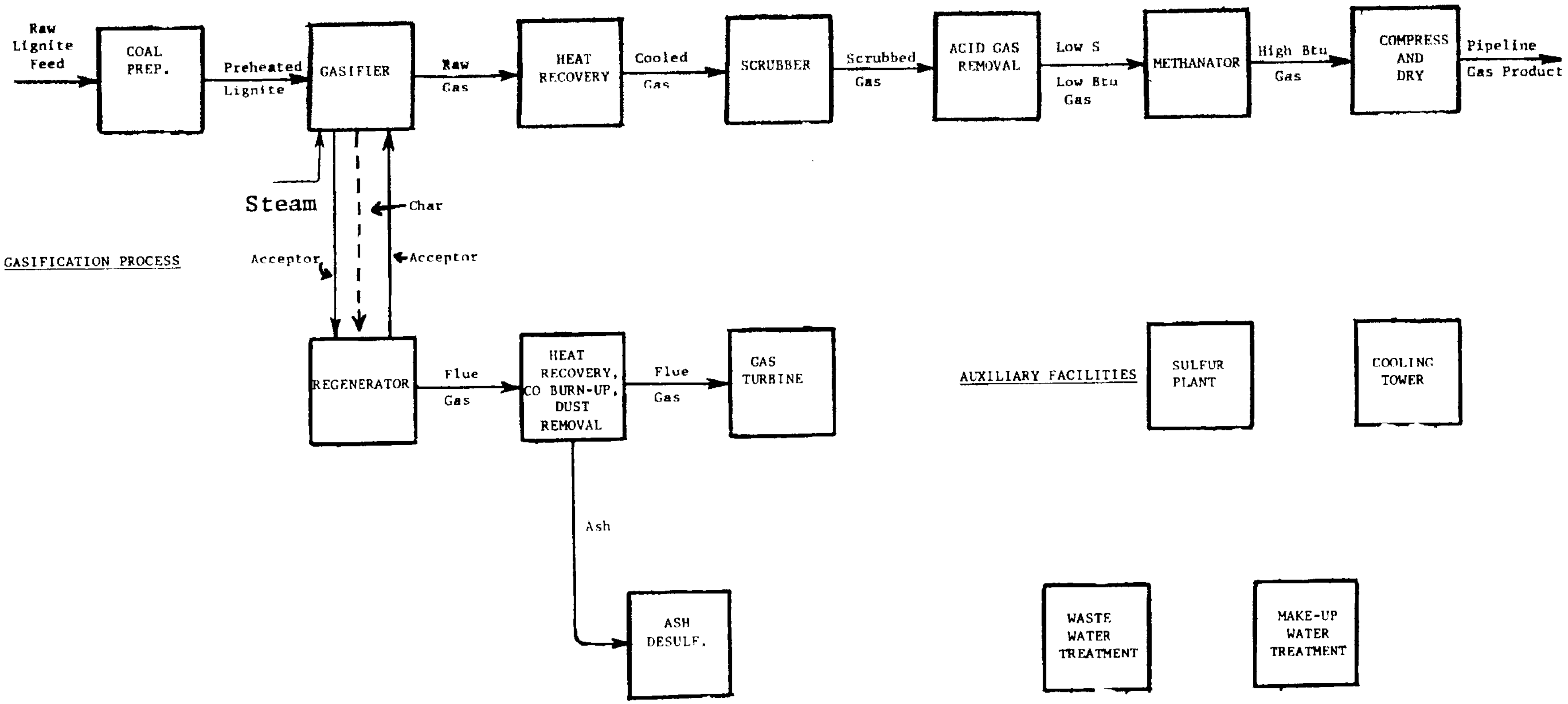

Figure A.4.1

CO_2 Acceptor Process

In the coal drying system, hot combustion gas is contacted with the lignite feed. General requirements are that the hot gas must be introduced at less than 1000°F so that local over-heating does not occur and release a large amount of volatile material from the lignite. Also, oxygen content of the gas is held down to about 11% or less by recycling flue gas in order to meet safety requirements.

Sulfur emission from the coal preparation section is decreased primarily by using some desulfurized low Btu gas from the gasification section as fuel to the furnaces. This gas is not methanated but rather is drawn off after acid gas removal.

. To bring total sulfur emission down to the target 1.2 lbs SO_2 per MM Btu requires replacing 25% of the lignite fuel with gas, corresponding to 1.0 MM scfh or about 2.6% of the total gas made by gasification. For simplicity, flue gas from the regenerator has not been added to the coal preparation system. Instead, flue gas from the dryer is recycled through the furnaces to lower flame temperature and thereby reduce NO_x formation.

Cyclones are used to separate ash from the hot gas after the furnace. The hot gas of course picks up lignite fines in passing through the drying and grinding operation, therefore, bag filters are provided on the vent gas streams in order to recover all dust.

Separate bag filters are provided on the preheater. This operation consumes only 12% of the total fuel for coal preparation, and only gas fuel is fired to it. Consequently, all of the fines recovered from the gas leaving the preheater are pure lignite and can be used as fuel for the furnaces if desired.

To minimize loss of fines in the dryer, it can be operated on a relatively coarse crushed lignite of say 1/2" size. Then the fine grinding can be carried out after the dryer and before the preheater. With this arrangement the very fine lignite is exposed to a smaller volume of gas so that the problem of dust recovery is minimized.

A.4.2.2 Gasifier

A stream of reject acceptor leaves the gasifier at 1500°F, cooled by a fluid bed cooler that allows generating steam for use in the gasifier. Final cooling uses a small amount of water that is evaporated to dryness so that the material is not wetted.

A.4.2.3 Gas Cleaning

Raw gas leaves the gasifier through cyclones which remove most of the solids. It is cooled in a waste heat boiler to make steam, and then scrubbed with water to remove essentially all of the dust using Venturi type scrubbers operating at the dew point and evaporating a small amount of water. The gas is further cooled to 150°F in air-fins so as recover condensate and conserve cooling water.

A.4.2.4 Acid Gas Removal

The raw gas contains 330 ppm of sulfur, mainly as H_2S. Sulfur removal is required before methanating, but it is undesirable to remove much CO_2 because it is needed to consume the available hydrogen during methanation. Various processes have been reported that remove concentrated streams of H_2S while allowing most of the CO_2 to pass through the absorber system. A major problem in most gasification systems is obtaining a CO_2 stream free from sulfur that can be vented. In the present case the sulfur only has to be removed to a level sufficiently low to prevent overloading the zinc oxide guard boxes.

Consideration should be given to using an absorption/oxidation process, such as Stretford, Takahax, IFP etc., on the raw gas directly. This would remove H_2S only and convert it to sulfur product without removing CO_2.

As an alternative, it may be possible to take low sulfur ash from the ash desulfurizing system and add it to the scrubber water so as to pick up sulfur. Sulfur-containing ash could then be returned to the ash desulfurizing system for regeneration.

A.4.2.5 Methanation and Compression

Final clean-up of the gas is accomplished in a bed of zinc oxide before methanation, to remove traces of sulfur and dust which could foul the catalyst. There may be traces of tar fog, naphthalene, etc. present in the gas, in which case it would be desirable to include a guard bed of activated carbon. Methanation itself generates no effluents to the air. After methanation the gas is compressed to 1000 psig and dried, for example with glycol, before being sent to the pipeline.

A.4.2.6 Regenerator

The circulating dolomite is calcined at 1850°F to remove CO_2. Make up dolomite is also added and calcined. Heat is supplied by burning the required amount of char with air in a fluid bed regenerator operating at 150 psig. A small content of carbon monoxide is maintained in the outlet gas in order to avoid forming oxidation compounds of calcium which were found to cause deposits. The flue gas is removed through cyclone separators to take out most of the dust, consisting of ash residue from all of the lignite fed to the gasifier. This ash is removed from the system by way of a fluid bed cooler, and sent to the ash desulfurizing unit.

Gas from the cyclones passes to heat exchangers where steam is super-heated to 1200°F. Additional steam is then generated in a waste heat boiler. At an appropriate point in this system additional air can be added to burn up residual carbon monoxide (e.g. before the waste heat boiler). This is necessary to avoid releasing carbon monoxide to the atmosphere, and at the same time it provides a convenient way to recover high level heat by burning the carbon monoxide. It is known that this reaction is reasonably fast at temperatures above 1300°F.

The reaction raises the gas temperature by about 300°F, which still leaves it lower than the regenerator temperature of 1850°F, consequently, deposits should not be a problem.

Flue gas then goes to an expansion turbine to recover power. For a turbine inlet temperature of 1000°F or higher, enough power can be generated to drive both the air compressor and the product gas compressor. In fact, there may be excess power available. Noise control for this area needs careful attention in a final plant design.

The flue gas contains 470 ppm of total sulfur, and can be discharged to the atmosphere, assuming that the dust content, nitrogen oxides, and odor are acceptable. Further information is needed on these critical items. The NO_x content may be low, in view of the relatively low combustion temperature in the regenerator, but specific data should be obtained on this in the pilot operations. For treating the ash to remove sulfur, a stream of CO_2 is needed, which might be provided by scrubbing part of the flue gas.

A.4.2.7 Ash Desulfurizer

Ash produced from the coal is processed to give 98% sulfur removal by reacting it in a water slurry with CO_2 at 190°F. Off-gas containing a calculated 27% H_2S, 7% CO_2 and 66% H_2O is sent to a sulfur recovery plant such as a Claus, Stretford, or other type unit. All of the gas streams in this system are contained and should not cause environmental problems. The carbonated ash is withdrawn as a 50% slurry in water and is not expected to create odors, although this should be checked out. CO_2 required for this operation is 1530 moles/hr, including 25% excess over theoretical and can be provided from the regenerator flue gas.

A.4.3 Auxiliary Facilities

In addition to the basic process, auxiliary facilities are required which will now be discussed.

A.4.3.1 Sulfur Plant

H_2S streams from acid gas removal and from the ash desulfurizer go to a sulfur recovery plant. If a Claus plant is used, sulfur recovery of about 97% can be achieved with three stages in "straight-through" flow. The tail gas still contains about 3 tons per day of sulfur and might be cleaned up, although this gas volume of 20 MM cfd is small relative to the other effluents. In fact, in this process as opposed to others, the sulfur in the Claus tail gas represents such a small percentage of emitted sulfur that investments or costs for sulfur removal could best be spent cleaning the regenerator flue gas or dryer vent gas. Thus, the Claus tail gas could be incinerated and vented to the dryer stack and a small additional quantity of clean product gas added as fuel to decrease total sulfur emissions to acceptable levels. No specific preference is indicated for sulfur recovery.

A.4.3.2 Utilities

Net utility requirements are low because considerable power is recovered by passing the regeneration flue gas through an expander turbine. Also a large amount of heat is recovered in waste heat boilers to generate steam, and on the methanator where the heat released by reaction amounts to about 19% of the heating value in the entering gas. Most of this can be converted to steam by recirculating gas from the reactor through waste heat boilers. Under development are alternative techniques using a fluid bed or liquid slurry reactor that should be more efficient.

A utilities balance for the process indicates that the process is self-sufficient in steam and power, so that no utility boiler is required for normal operation. It is likely that a more definitive and optimized utility balance will show that it is possible to make more steam and power than consumed by the gasification plant, so that these could be used for shops, mining operations, offices and general off-sites. For example, 1.65 million pounds per hour of steam at 150 psig is used in the gasifier. This could be generated at a higher pressure such as 600 psig and run through bleeder turbines down to 150 psig, while generating by-product power at the rate of about 40,000 kW.

In the utilities area, the main cooling tower has by far the largest volume of discharge. It is, therefore, critical from the standpoint of pollution. In this particular case it is not expected to contain significant amounts of undesirable contaminants. The cooling water circuit is clean and should not contain ash or objectionable materials such as phenols, oil, or H_2S. Normally a certain amount of leakage can be expected on exchangers using cooling water. Since the process operates mainly at 150 psig pressure, this should not be a major item. Also, most of the cooling water is from steam condensers on drivers rather than on oil, sour water, etc.

Total cooling water requirement is modest considering the plant size. Effluents to the air from this cooling tower amount to 457,000 lbs/hr of water evaporated, plus 43,000 lbs/hr of estimated drift loss or mist. Flow of air through the tower is 15,000 MM cfd.

The drift loss or mist will contain dissolved solids which can result in deposits on the ground and on nearby equipment, and in some cases drift loss has caused icing problems on equipment and public roads in the winter. With any cooling tower, the problem of fog formation must be assessed, since under certain conditions the moisture condenses and the resulting plume can be a problem if it affects public highways. Reheat of the stack gas is one way to reduce fog formation, but is inefficient. In planning the layout of the plant facilities, these aspects should be given careful consideration, and every effort made to avoid potential problems by proper placement of the equipment.

There will also be evaporation and the possibility of odor from ponds and water treating facilities. While most of the ammonia will be recovered as a by-product, the waste water still will contain traces of ammonia and probably also some phenols, hydrocarbons, etc. particularly during start-up or during upsets. These must be controlled and a biological oxidation (biox) pond for waste water treating is needed. Depending upon pilot plant results with regard to tar and hydrocarbons produced, it may be necessary to provide an oil separator ahead of the biox unit, and possibly a froth flotation separator.

A.5 BIGAS Process

A.5.1 General

The plant is sized to make 250 million scfd of pipeline gas by gasifying coal with steam and oxygen. The design includes shift conversion and methanation to give a gas with a heating value of 943 Btu per cubic foot, available at 1,075 psia. Western Kentucky coal is used, and after cleaning and washing, the amount if 14,535 tons per day (at a nominal 8.4% moisture) which provides all of the fuel for coal drying and utilities production in addition to the gasification requirements.

A flow plan of the process is shown in Figure A.5.1. It is convenient to subdivide the process into the following operations, each of which will be described in the following subsections: (1) Coal Preparation, (2) Gasification, (e) Quench and Dust Removal, (4) Shift Conversion, (5) Acid Gas Removal, (6) Methanation, and (7) Auxiliary Facilities.

A.5.2 Main Gasification Stream

A.5.2.1 Coal Preparation and Drying

This process section includes crushing, cleaning and drying as well as a storage pile with 30 days capacity. Run of mine coal feed amounts to 23,243 tons per day. This is crushed and coarse refuse is rejected amounting to 4,804 tons per day. The coal can then be sent to storage, or to the washing operation which rejects an additional 3,904 tons per day. Drained coal from washing, containing 8.4% moisture, is used partly as fuel to the utilities plant supplying steam for the process, while the remainder goes to the grinding and drying facilities. Here it is ground to 70% smaller than 200 mesh, dried to 1.3% moisture, and sent to storage silos. Some of the dried coal is used as fuel in the dryer, amounting to 11,137 pounds per hour or about 134 tons per day.

Since the gasifier operates at 80 atmospheres, it is necessary to pressurize the coal feed. The original design used piston feeders to push the coal into a high pressure feed hopper and is the system used in the present environmental evaluation. Subsequent work has indicated that other methods such as lock hoppers or slurry feeding may be preferable; however, the change would make only minor modifications in effluents to the environment, although thermal efficiency would be lower than for the case using piston feeders.

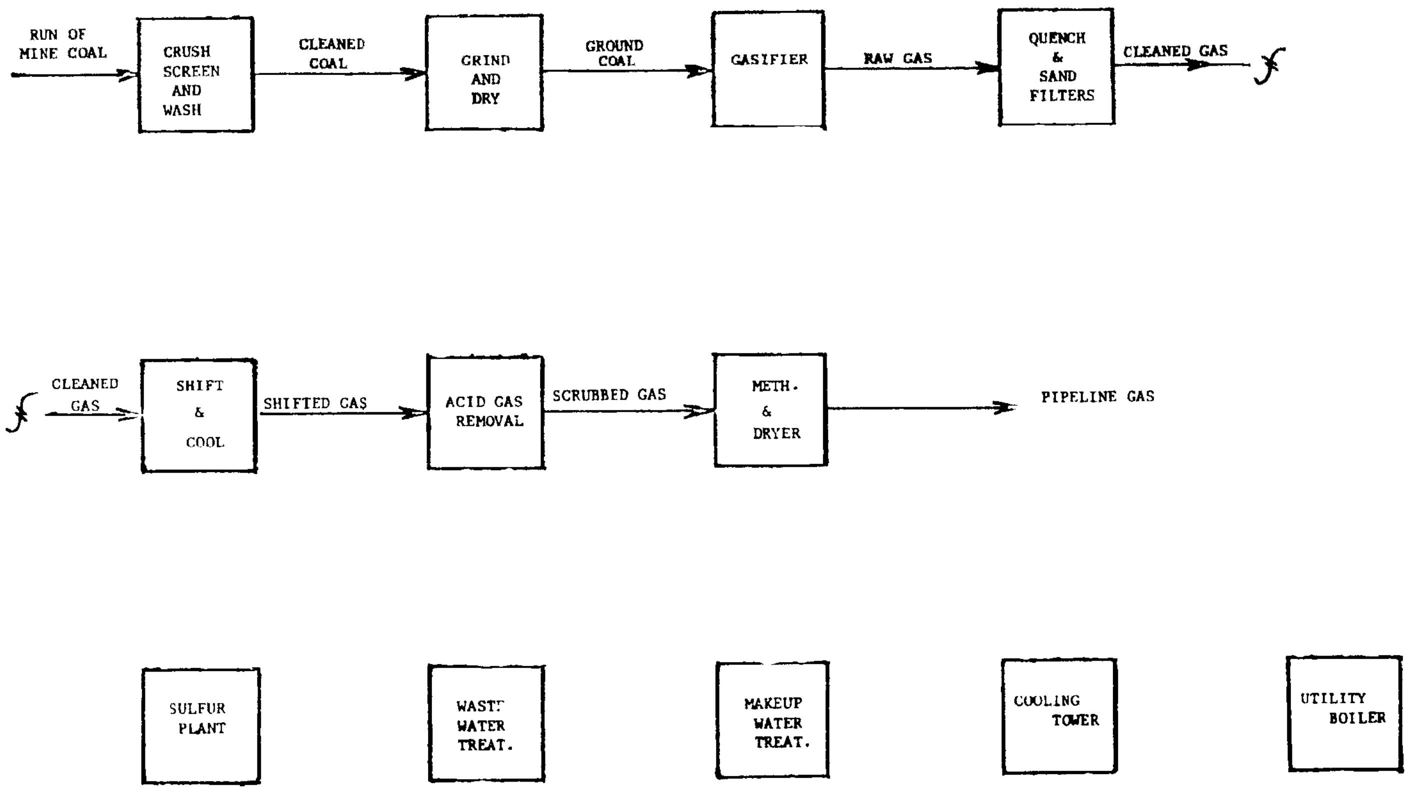

Figure A.5.1

BIGAS Process

A.5.2.2 Gasification

The coal is gasified using steam and oxygen in a two zone reactor at 80 atmospheres. Operation of the reactor is based on entrained flow rather than using a fluidized bed or fixed bed reactor. Coal is fed to the top 1700°F zone where it mixes with steam and hot synthesis gas entering from the lower zone. Conditions in this upper zone favor high formation of methane, with negligible amounts of tar or oil. Although the volatile content of the coal feed is completely consumed, there is considerable unreacted char remaining which is carried out with the gas and recovered by cyclones following the reactor.

The char is recycled by means of lock hoppers to the lower gasification zone where it is reacted with steam and oxygen at 3000°F. A special char feeding system is provided, since it is indicated that a reliable and very uniform feed rate must be maintained, so as to avoid conditions that could give excessive flame temperatures. Synthesis gas is formed and passes to the upper reactor as described earlier. Slag is withdrawn from the bottom, quenched with water, and removed by way of lock hoppers. Since it has little or no combustible content, it can be discarded (from an energy viewpoint).

A.5.2.3 Quench and Dust Removal

Hot raw gas from the gasifier passes to cyclone separators which remove most of the char and solid particles in the gas. Quench water is added to the cyclone in order to moderate the temperature, and additional quench water is added in a quench vessel after the cyclone separator.

The quenched gas still contains some dust that was not removed by the cyclones, but must be removed so as not to plug the fixed bed of shift conversion catalyst. Rather than scrub the dust out with water, which would require considerable cooling, the dust is filtered out at high temperature using sand beds. These operate in parallel in a cyclic manner. Pressure drop will build-up during the onstream cycle, and the bed is cleaned when necessary by back flushing with clean gas so as to lift and agitate the sand particles. Entrained dust from back flushing is then returned to the gasifier where it leaves with the slag.

A.5.2.4 Shift Conversion

After dust removal, the gas next goes to a shift converter where carbon monoxide reacts with steam to form hydrogen and carbon dioxide, incre- the ratio of H_2 to CO to three to one as required in the final methanation. A sulfur resistant shift catalyst must be used, resulting in relatively low activity compared to those used on sulfur free gases. A large excess of steam is maintained to give 50 mol. % steam in order to facilitate the desired reaction and to prevent catalyst degradation or carbonaceous deposits. Steam conversion in this shift reactor is about 27%.

After shift conversion, the gas is cooled to remove most of the remaining moisture. This, of course, produces sour water containing H_2S

and ammonia and possibly traces of cyanides, phenols, etc. It is conveniently disposed of by using it as part of the quench water, and thereby provides steam required for shift conversion. One advantage of this specific design is that a very large quantity of sour water can be disposed of by injecting it into the hot gas for quenching. A further advantage is that no facilities are then needed for generating steam used in shift conversion, and neither are exchangers needed for cooling the hot raw gas from the gasifier.

A.5.2.5 Acid Gas Removal

Removal of all sulfur compounds is needed to meet pipeline gas specifications and to protect the methanation catalyst. The bulk of the sulfur, as well as CO_2, is removed using the proprietary Benfield process based on hot carbonate scrubbing. Two separate absorber towers are used in series. The first of these produces a gas relatively high in sulfur content, about 8% H_2S, to facilitate sulfur recovery in the Claus plant. The second absorber is for final cleanup of sulfur from the gas and for CO_2 removal.

Most of the CO_2 is removed in this second absorber and vented to the air; however, this CO_2 vent stream contains excessive amounts of H_2S, namely 3400 ppm, and further processing is needed to clean it up. Therefore, adsorption using molecular sieves has been provided to recover the H_2S content and send it to the Claus sulfur plant. Gas leaving the hot carbonate scrubbing system used in the present design contains moisture, most of which is removed by cooling the gas ahead of methanation. This is a clean condensate which can be used for boiler feed water make-up.

Gasification can produce many compounds in addition to H_2S, such as cyanides and thiocyanates as well as large amounts of ammonia. There are also various sulfur compounds, particularly carbonyl sulfide and some carbon disulfide. It is essential to completely remove all of these before methanation in order to protect catalyst activity. Most of the ammonia and compounds that are highly soluble in water will be removed in the condensation after shift conversion. Hot carbonate systems for acid gas removal have the important advantage that they do remove carbonyl sulfide. Amine systems, in general, do not remove carbonyl sulfide, and moreover react irreversibly with cyanides thus requiring purge of the chemical solution.

A.5.2.6 Methanation and Drying

Clean synthesis gas is methanated in this section to increase the heating value of the gas up to pipeline quality. The reaction of CO with 3 volumes of H_2 to make methane and water can be carried out in a fixed bed of nickel catalyst. A guard bed of zinc oxide ahead of the reactor removes traces of sulfur compounds in order to protect the methanation catalyst. Methanation is a highly exothermic reaction, releasing about 20% of the heating value in the reacting gases. Reactor temperatures of 500°F at the inlet and 850°F at the outlet are maintained by recirculating some of the gas leaving the reactor through exchangers to generate high pressure steam. Methanation is carried out to a high conversion so that the residual CO content is no more than the 0.1 Vol. % specified for pipeline quality gas. Residual hydrogen content is 5.1 Vol. %. Since methanation generates a considerable amount of water, this is recovered as clean condensate upon cooling. More complete drying of the gas is then carried out using a glycol system to meet the requirement of 7 lb water maximum per MM scf in gas.

A.5.3 Auxiliary Facilities

In addition to the gasification system, auxiliary facilities are needed to make the plant complete and self-sufficient. A Claus plant is included to make by-product sulfur from the H_2S that is recovered in acid gas removal. The basic Claus plant will not give adequate sulfur recovery or clean-up, since the feed gas will contain no more than 15% H_2S, therefore tail gas clean-up was added.

A conventional air separation plant is included in the base design to provide oxygen needed for gasification. It does not generate contaminated waste streams, but it is a large consumer of utilities and therefore has an important effect on thermal efficiency.

As would be expected, the process uses large amounts of steam and electricity. All utilities needed to make the plant self-sufficient are provided in the design, including high pressure and low pressure steam, electric power generation, water make-up treating, circulating cooling water, and waste water treating. Fuel requirement for these has been been included on the basis that coal would be used for fuel. Since the coal has a high sulfur content, pollution control will be needed on these fuel consumers. The simplest approach is to add flue gas clean-up so that coal can still be used as fuel, and a number of processes are available. An alternative would be to use low sulfur, low Btu gas made in the process for fuel in utilities generation and in coal drying.

The particular study includes utilities requirements for offices, shops, laboratories, and cafeteria (e.g. 50,000 lb/hr of steam for heating buildings). These are not always included in similar studies of other processes; therefore, caution is required in making comparisons with other studies.

A.6 HYGAS Process

A.6.1 General

The process makes 250 MM scfd of pipeline gas (SNG) from Illinois No. 6 coal by gasifying it with medium Btu gas (mainly CO plus H_2 and steam) in a series of countercurrent fluidized zones. Residual char is then gasified with oxygen and steam in a bottom zone to provide gas for gasification in the upper zones. Carbon content of the rejected char may be 10-30 wt. %.

Raw gas is cleaned-up, shifted, and methanated. Operating pressure is sufficiently high so that compression of the product gas is avoided. The method of pressurizing coal feed involves slurrying it with light oil by-product, pumping to high pressure, and evaporating the slurry to dryness by direct contact with hot raw gas in a fluidized bed.

A block flow diagram of the processing steps is shown in Figure A.6.1. The process can conveniently be sub-divided into a sequence of operations, each of which will be described in the following sub-sections: (1) Coal Preparation, (2) Gasification, (3) Quench and Dust Removal, (4) Shift Conversion and Cooling, (5) Acid Gas Removal, (6) Methanation and (7) Auxiliary Facilities.

A.6.2 Main Gasification Stream

A.6.2.1 Coal Preparation

These facilities include storage and handling, crushing, and drying. It is assumed that cleaned coal is delivered, the separation of refuse and washing having been done at the mine or elsewhere with suitable disposal of waste, and environmental controls. Coal feed, amounting to 17,517 tons/day (6.48% moisture), is received and 30 days storage is provided. Since the storage pile is very large, roughly 15 acres at 25 ft high, protection will be needed to control dust nuisance due to wind, while rain run off should be collected and cleaned up to supply makeup water for the plant.

Crushing is the next step in coal preparation, to reduce the coal feed to minus 8 mesh. Crushed coal is then dried to negligible moisture content in a fluid bed drier fired with part of the low Btu gas produced by the U-Gas system. The latter also supplies clean gas fuel for generating utilities, and consumes 22.5% of the total coal used by the plant.

Dried coal going to gasification is pressurized by mixing with oil to form a slurry which is pumped to about 1200 psia. Theoretical power for pumping is about 4500 horsepower. Oil is vaporized and recovered when the slurry is subsequently dried. Sufficient oil is thereby recycled to give a slurry containing 35% coal/65% oil, and cooling is provided so that temperature of the recycle oil is 400°F.

It should be emphasized again that this specific study case does not include pretreating to destroy caking properties of the coal feed.

A.6.2.2 Gasification

The HYGAS reactor has four zones, through which the coal passes. These include an initial drying zone, followed by gasification zones at increasing temperature and severity. Slurry feed is dried in the first zone at 600°F using heat in the raw gas. Vaporized oil is condensed and most of it is recycled to slurry preparation, but part of it is withdrawn as net product.

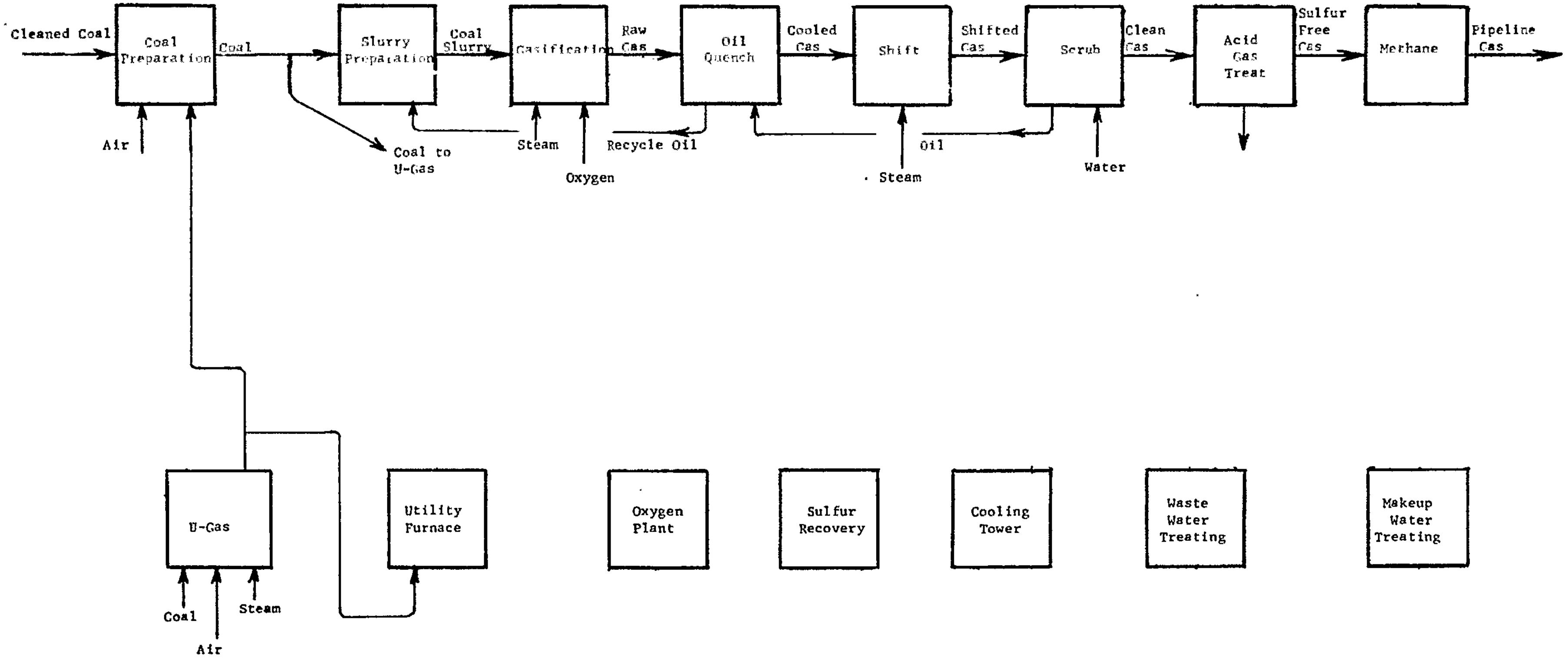

Figure A.6.1

HYGAS Process

Dry coal then flows to the next bed at 1250° where partial gasification occurs, then to a bed at 1750°. Finally the char passes to the bottom zone where steam and oxygen are added for final gasification. Residual char rejected from this lower zone may contain 10-30% carbon, corresponding to 2-7% of the original carbon contained in the coal feed. The char is slurried in water, depressured, and discharged through lock hoppers.

The countercurrent contacting between gas and char provided by this multibed arrangement results in a considerable saving in oxygen. Of the total methane in the product, 58% is formed in the gasifier by the favorable effects of high pressure, temperature gradient, and the contribution from volatile matter in the coal feed.

A.6.2.3 Quench and Dust Removal

Raw gas leaving the drying bed of the gasifier at 600°F, is cooled to 400°F by contact with a recirculating oil stream, whereby most of the oil is condensed out and returned to slurry preparation. Temperature is maintained high enough to avoid condensing water which could cause emulsion problems; moreover, the steam is needed for the subsequent shift reaction. Heat removed in this cooling operating can be used to generate low pressure steam by recirculating the 400°F oil through waste heat boilers.

When the oil is condensed upon cooling, most of the dust in the raw gas leaving the drying bed will also be removed. Since the condensed oil is recycled and used for slurrying coal feed, the fines will also be recycled and buildup in concentration, unless some provision is made to purge them from the system.

A.6.2.4 Shift Conversion and Cooling

The next step in gas handling is shift conversion, to react part of the CO with steam and thereby increase the H_2/CO ratio to 3/1 as needed for methanation. A sulfur resistant shift catalyst such as cobalt-molybdenum is used, and one-third of the raw gas bypasses the catalytic reactor. The catalyst is also exposed to oil vapors contained in the gas, and operates at about 700°F.

After shift conversion, the gas is cooled to condense most of the moisture. This sour water is cleaned up for reuse by extraction and stripping, which operations will be described later.

A.6.2.5 Acid Gas Treatment

At this point, the gas still contains various contaminants that must be removed, such as: H_2S, COS, CO_2, and condensable hydrocarbons. The required cleanup is accomplished by scrubbing with refrigerated methanol, using the Rectisol process. Gases containing the sulfur compounds removed in the Rectisol unit are sent to a Claus plant for sulfur recovery. The Claus plant also provides incineration of COS and combustibles on this stream.

Most of the CO_2 is removed as a separate stream in the Rectisol regeneration, and indicated to be discharged to the atmosphere. However, this vent stream is shown as containing over 2.0 vol. % of combustibles, most of which is ethane; consequently, it will require further cleanup or incineration. While sulfur content is indicated to be low, nil H_2S and 30 ppm COS, other detailed evaluations of similar Rectisol applications show that additional controls will be needed.

It is not clear that any one simple process for acid gas treatment available today can simultaneously meet the targets of a highly concentrated stream to the sulfur plant, together with a CO_2 waste stream that is clean enough to discharge directly to the atmosphere, without further treatment such as sulfur cleanup or incineration. Therefore it appears that additional facilities will be needed, such as adsorption by molecular sieves or activated carbon.

A guard bed, for example of zinc oxide, is used to remove remaining traces of sulfur in the clean gas, so as to protect the methanation catalyst, which is extremely sensitive to sulfur poisoning. Reheating is needed since the guard bed operates at about 600°F, and can be provided by heat exchange with gas leaving the methanator. Such preheat is also needed to initiate the methanation reaction when this is carried out in a fixed bed of catalyst.

A.6.2.6 Methanation and Drying

Fixed bed catalytic reactors with conventional nickel base catalyst are used to react CO and H_2 to form methane and water. Operating temperature is 550-900°F. Outlet gas at 900°F is recycled to the inlet through waste heat boilers which generate steam, thereby recovering the large exothermic heat of reaction. Heat release amounts to 954 MM Btu/hr, which can generate about 1 million lb/hr of high pressure steam.

Water formed by the methanation reaction is condensed and recovered when the product gas is cooled, providing 200,000 lb/hr of clean condensate suitable for boiler feed water makeup. Final drying of the gas is effected by scrubbing with glycol, to meet pipeline specifications of 7 lb/MM scf. The product specification of 0.10 vol. % CO maximum is met by providing effective control of methanation and excess hydrogen, leaving 6.5 vol. % hydrogen in the product gas. High heating value is then 960 Btu/cf.

A.6.3 Auxiliary Facilities

To make the plant complete and self-sufficient, various utilities and auxiliary facilities are needed in addition to the main gasification process. A Claus plant is used for sulfur recovery on a concentrated stream from acid gas removal, with tail gas cleanup by incineration followed by scrubbing with sulfite to remove SO_2, using the Wellman-Lord process. The Rectisol design basis provided shows 29.8 vol. % H_2S in the feed to the Claus plant, while at the same time the CO_2 vent gas contains no H_2S and 300 ppm of carbonyl sulfide. This would represent a very desirable high concentration of feed to the sulfur plant together with complete removal of H_2S from the CO_2 vent gas, although the latter contains an excessive amount of COS plus 2 vol. % combustibles, so it would require further treatment. However, other data on similar designs do not support the excellent separation assumed in the HYGAS design; consequently further investigation and evaluation are called for.

Oxygen for gasification is supplied by a conventional air separation plant. While it does not generate contaminated waste streams, it is a large consumer of utilities, with a correspondingly large impact on thermal efficiency for the overall process.

Large amounts of steam and power are needed in the process. These are supplied by a utilities system fired with clean gas fuel manufactured by the U-Gas process being developed by The Institute of Gas Technology.

In the U-Gas process, coal feed goes first to a pretreating reactor to destroy caking properties. Here it is contacted with air at 750-800°F in a fluid bed to give partial oxidation, accompanied by a decrease in volatiles. A very large amount of heat is released, which is used to generate steam. Hot char then goes to a second reactor where it is gasified with steam and air at 1800°F and 300 psia in a fluid bed. Off gas from pretreating, with a high heating value of only 39 Btu/CF, contains tar and sulfur, so it is mixed with hot gases from the gasifier in order to destroy the tar.

Sulfur removal is provided at high temperature by contacting the gas with a "molten metal," which is regenerated in a separate zone by reacting with air to form a concentrated SO_2 stream that is sent to the sulfur plant.

After further clean up by cooling to condense water and by scrubbing, the gas is used as clean fuel for coal drying, furnaces, and gas turbines.

A combined cycle system is used to maximize efficiency by first burning the high pressure fuel gas from the U-Gas unit for use in a gas turbine, and then discharging the hot exhaust to a boiler furnace which supplies process steam. Combined cycle systems are a very effective way to supply by-product power for the oxygen plant compressors and for generating electricity.

Water treatment is an important part of the process. A Phenosolvan unit is used in water treatment. Treated water from the Phenosolvan unit then passes to a sour water stripper which removes ammonia as a by-product, and H_2S which is sent to the sulfur plant.

Other auxiliary facilities include treatment of makeup water, boiler feed water preparation, storage of by-product oil, phenol, ammonia, and sulfur, as well as ash disposal, and a cooling water circuit with cooling tower. The waste water is treated in a biox unit before sending it to cooling tower makeup.

A.7 U-Gas Process

A.7.1 General

In the U-Gas process, pretreated coal is gasified with steam and air in a fluidized solids system, at 1900°F and 350 psig to make 840 MM scfd of low Btu clean gas fuel (158 Btu/scf) suitable for use in a combined cycle power plant. Coal feed amounts to 7346 tons/day containing 6% moisture.

A.7.2 Main Gasification Stream

As shown in Figure A.7.1, dry coal crushed to 1/4 inch and smaller is fed to the pretreater by means of lock hoppers. Gases from the pretreater flow into the gasifier at a point above the fluid bed, for the purpose of reacting and destroying all tar and oil vapors that are evolved in pretreating. A residence time of 10-15 seconds is provided on the vapors.

In the fluid bed gasifier operating at about 2 ft/sec, char is reacted to give a carbon level of about 20% in the ash. Agglomeration of ash particles is accomplished in a "spouting" zone or venturi throat at the bottom of the gasifier maintained at sintering temperature by adding air and steam. Ash agglomerates of perhaps 1/8 inch diameter pass down through this throat, to be quenched and removed from the system. Dust recovered by cyclones from the raw gas product is also passed through the agglomerating zone.

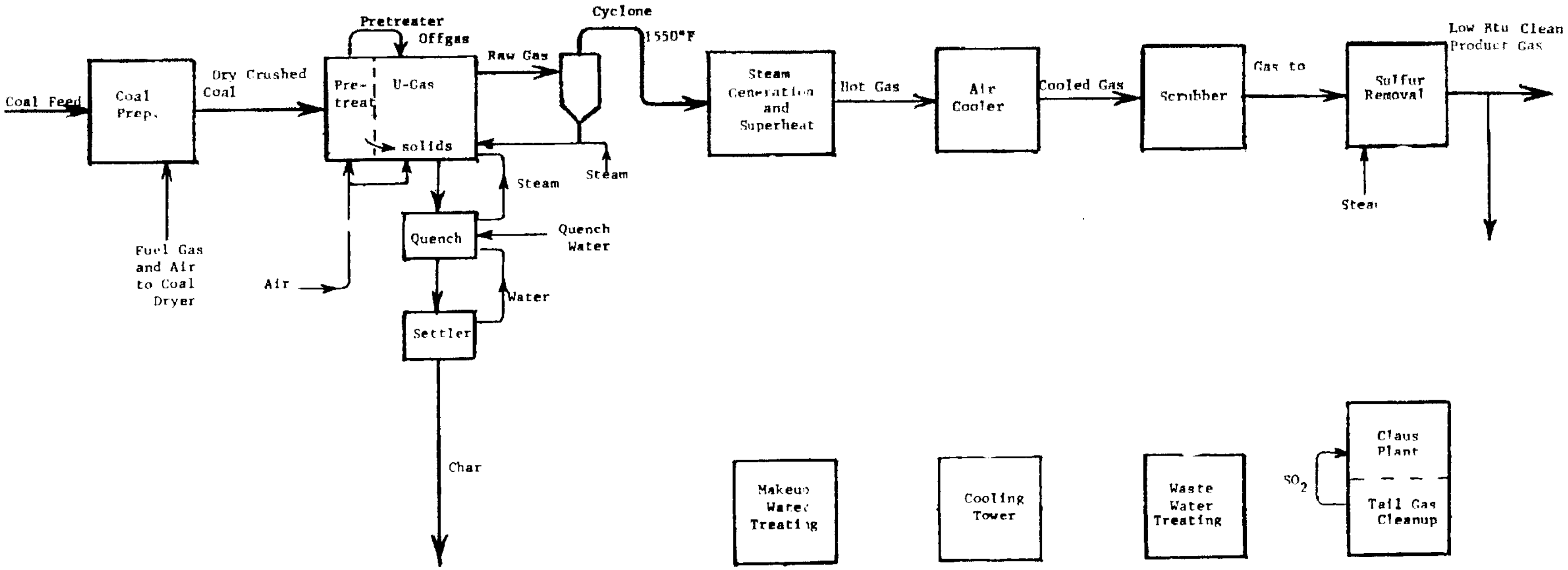

Figure A.7.1

U-Gas Process

Raw gas is cooled in a waste heat boiler to make high pressure steam, following by additional heat recovery to preheat boiler feed water. Air cooling is then used to bring the gas down to scrubbing temperature. The water scrubber removes dust and ammonia primarily, together with unreacted steam. Gas liquor from the scrubber is processed in a sour water stripper to recover ammonia and remove H_2S. The treated water is recycled to the cooling tower or used to slurry the ash being returned to the mine for disposal.

In this particular design, water is indicated to be recycled to extinction within the process, in which case there would be no net water discharge that might cause environmental concern. However, there will be soluble salts (e.g., sodium chloride and sulfate) introduced with the makeup water, plus volatile elements from gasification (chlorine, fluorine, boron, etc.) that will accumulate and must be purged from the system. It is obvious that some water must be discharged.

Sulfur is removed from the cooled gas using the Selexol process based on a glycol type solvent, which can remove H_2S and COS from the gas. About 60% of the CO_2 is left in the gas, but the solvent does dehydrate the gas.

Clean, low Btu gas from the Selexol unit is available to use as fuel, or in a combined cycle system. The H_2S stream from solvent regeneration is indicated to contain 16.6% H_2S, and is sent to a Claus unit for sulfur recovery. Tail gas cleanup by the Wellman-Lord process is included to give 250 ppm SO_2 in the final gas released to the atmosphere.

High heating value of the total gas produced is 5533 MM Btu/hr, but part of the gas is needed to supply requirements of the process. Net gas available from the process is 5060 MM Btu/hr, equivalent to a potential power generation of 593,000 KW at a nominal 40% efficiency. Of the total gas produced, 6.7% is consumed in the process to supply fuel to the coal dryer and tail gas incinerator on the sulfur plant, plus a combined cycle system supplying plant electricty and power for air compression. In addition, steam is generated from waste heat in the process, but all of this is used within the plant, partly to drive the air compressor.

A.7.3 Auxiliary Facilities

Auxiliary facilities are required in addition to the basic process, such as coal handling and storage. Coal preparation will include drying and crushing, as well as coal cleaning unless this is provided elsewhere. Ash handling and disposal are also needed, with means to drain the ash slurry, recover the water for reuse, and transport the drained ash to the mine or to a landfill area. The Claus plant for sulfur recovery includes tail gas cleanup by scrubbing with sodium sulfite using the Wellman-Lord process, but sulfur storage and shipping facilities are also needed.

Waste water treatment employs the Chevron process to recover by-product ammonia, and makes it feasible to reuse the water. While not included in the original design, a biological oxidation system (biox) is needed to give adequate cleanup of the water for return to the cooling water circuit. In addition, to prevent buildup of sodium salts etc., some water will have to be discharged from the plant.

The plant may be self sufficient in steam and power during normal operation, but in order to start it up a furnace or other method for heating is required, together with startup steam and power. Fuel for startup probably should be oil rather than gas or coal, so as to avoid the storage problem with gas, or the environmental problems with coal due to sulfur and ash.

Makeup water must be brought in and treated to make it suitable for use in the cooling water circuit, while further treatment and demineralization are required to supply boiler feedwater makeup. Cooling towers are used, and are a major area of environmental concern.

Other facilities required are maintenance shops, fire protection, warehouses, control laboratory, offices, cafeteria, roads, trucks, etc., all of which must be taken into account in assessing total environmental impact.

A.8 Winkler Process

A.8.1 General

Lignite type coal is gasified at about 1700°F and 2 atmospheres in a turbulent bed of particles using oxygen and steam, to make medium Btu gas for fuel or synthesis. Some of the residual char is withdrawn from the bottom of the gasification reactor, but most of it is blown overhead as a result of the high gas velocity of 5-10ft/sec. Most of the entrained char is collected in cyclones for disposal, and the gas is then cooled and cleaned up to remove residual dust and sulfur.

An overall flowplan of the process is shown in Figure A.8.1 The process can be subdivided into a sequence of steps, each of which will be described in the following sub-sections: (1) Coal Preparation, (2) Gasification, (3) Cooling and Scrubbing, (4) Sulfur Removal, and (5) Auxiliary facilities.

A.8.2 Main Gasification Stream

A.8.2.1 Coal Preparation

This section of the plant includes storage and handling, drying, and crushing. It is assumed that coal cleaning is not required, or that it is carried out elsewhere. Storage requirements will depend upon the specific situation but may provide for example 30 days reserve.

Drying may not always be needed, since it is only necessary to avoid surface moisture which would cause problems in handling and crushing.

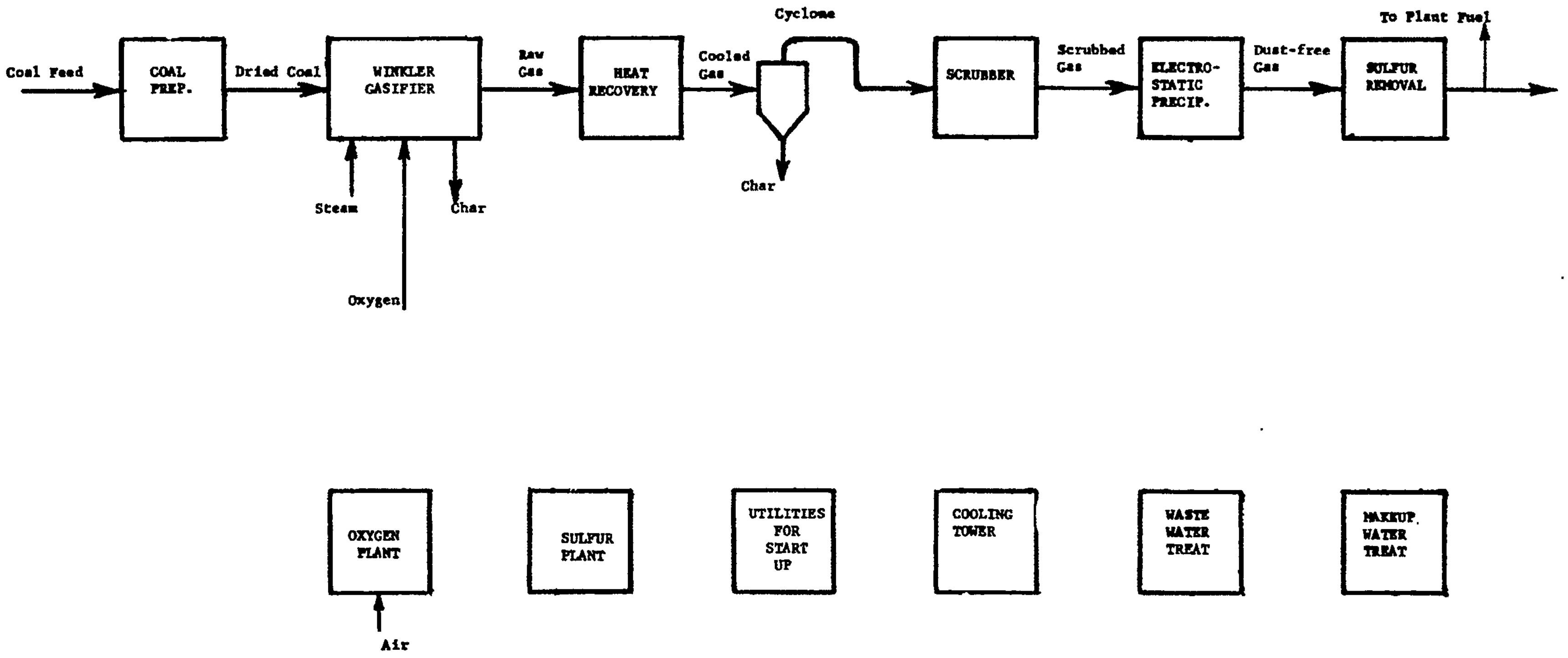

FIGURE A.8.1

WINKLER PROCESS

Rotating tray dryers are used, and for this study a moisture removal of 5% on feed has been taken. Cool gas is recycled to control gas inlet temperature so as not to drive off volatiles. Stack temperature is 350-400°F, resulting in good fuel efficiency. Coal can be used as fuel if flue gas desulfurization is provided, but instead of this we have used part of the clean product gas as fuel to the dryer, with bag filters on the vent gas to control dust emissions. Coal is crushed to 0-8mm, all of which is sent to the gaisifer feed hopper.

A.8.2.2 Gasification

Coal from the feed hopper is fed to the gasifier by means of screw feeders which give the necessary pressure seal. Steam and oxygen are added near the bottom of the reactor, maintaining the particles in a turbulent bed where reaction takes place without reaching temperatures that would fuse the ash. Typically, the bed may be at about 1700°F so that tar and heavy hydrocarbons are destroyed by gasification reactions.

Considerable fines are entrained from the bed, consequently supplemental oxygen and steam are added just above the bed to help consume them. Heat exchange surface in the dilute phase above the bed removes heat for temperature control and generates useful steam. Additional cooling of the raw gas to about 1300°F is accomplished by injecting condensate just before the gas leaves the reactor, in order to prevent fused deposits in the downstream waste heat boiler.

With high reactivity coal, conversion of carbon in the coal feed may be 90%. The remainder is in the char by-product, and represents a significant loss of heating value unless it is used. Part of the rejected char is removed from the bottom of the gasifier, but most of it (ca. 70%) is recovered by a cyclone separator from the exit gases.

Steam fed to the gasifier amounts to about 0.5 pound per pound of coal feed, while steam conversion including moisture in the coal feed is 27%. Oxygen consumed is 0.57 pounds per pound of coal feed.

A.8.2.3 Gas Cooling and Dust Removal

Hot raw gas leaving the reactor at about 1300°F passes through an exchanger to superheat steam, followed by a waste heat boiler and a cyclone to remove entrained char. The gas then goes to a scrubbing tower where it is cooled by direct contact with recirculated water.

Most of the particulates are removed by scrubbing and are separated from the water in a settler. They are included with the char for disposal. Clarified water is cooled by indirect exchange with cooling water before it is recirculated to the scrubber. Net production of this water or gas liquor constitutes sour water containing H_2S, ammonia, cyanides, etc., present in the raw gas. The sour water is processed in waste water treating so that it can be reused.

Since the scrubbed gas will still contain a small amount of dust, it is passed through an electrostatic precipitator for final cleanup. It can then be compressed, further processed, or used as desired. Traces of contaminants may remain in the gas after scrubbing, such as ammonia, sulfur, oil, etc., especially during upsets or start up. Depending on the intended use, further cleanup may be necessary.

A.8.2.4 Sulfur Removal

The next processing step on the gas is sulfur removal by scrubbing with a suitable solution such as amine, hot carbonate, or a glycol type solvent. These can be regenerated by stripping to give a concentrated H_2S stream that is sent to sulfur recovery. For this study scrubbing with hot carbonate is assumed, since it will remove perhaps half of the carbonyl sulfide present in the gas, and some 10% of the total sulfur will be in this form which is not removed by amines.

A.8.3 Auxiliary Facilities

In order to make a realistic and thorough evaluation of environmental impacts, a complete and self-sufficient plant must be considered, including items such as oxygen plant, sulfur recovery, water treating, and utilities generation. Oxygen is supplied from a conventional air liquefaction plant. The amount is large, equal to 11,536 tons/day. For sulfur recovery, a Claus plant is included with tail gas cleanup using one of the many processes offered for this service. Gas sent to the Claus plant from acid gas treatment contains about 15 vol. % sulfur compounds (mainly H_2S) and 85 vol.% CO_2 on a dry basis. A small amount of clean product gas is used as fuel to incinerate tail gas on the sulfur plant.

A major item is waste water treating on the gas liquor condensed in the scrubber. Flow rate is 11,140 tons/day, and cleanup is required to remove particulates, contaminants such as compounds containing sulfur, nitrogen, or oxygen, as well as arsenic, cadmium, lead, chlorine, fluorine, and other trace elements that are known to be volatile at conditions in the gasifier. This water stream must be thoroughly cleaned up in any case, and then represents a very desirable makeup water for the plant. Facilities include sour water stripping, biological oxidation (biox), and sand filtration prior to using it as cooling tower makeup. Production of phenols is expected to be relatively low at the conditions used in the gasifier (1700°F) so that solvent extraction to remove large amounts of phenols is not included at this time.

Other auxiliary facilities include treatment of makeup water for the cooling water system and for boiler feed water, plus plant utilities such as steam and electric power. It appears from the balances that the plant should be self-sufficient in steam and power during normal operation, although provision must also be made for startup. As far as energy balances and thermal efficiency are concerned, no coal or clean product gas need be consumed to generate plant utilities.

APPENDIX B

Process Descriptions - Liquefaction

APPENDIX B

PROCESS DESCRIPTIONS - LIQUEFACTION

In this appendix, a general description is presented of the liquefaction processes studied. The reader is referred to the individual process reports for details.

B.1 COED Process

B.1.1 General

The COED process being developed by the FMC Corporation is a continuous, staged fluidized-bed coal pyrolysis operating at low pressure, and is designed to recover liquid, gaseous, and solid fuel components from the pyrolysis train. Heat for the pyrolysis is generated by the reaction of oxygen with a portion of the char in the last pyrolysis stage, and is carried counter-currently through the train by the circulation of hot gases and char. Heat is also introduced by the air combustion of the gas used to dry feed coal and to heat fluidizing gas for the first stage. The number of stages in the pyrolysis and the operating temperatures in each may be varied to accommodate feed coals with widely ranging caking or agglomerating tendencies.

Oil that is condensed from the released volatiles is filtered on a rotary precoat pressure filter and catalytically hydrotreated at high pressure to produce a synthetic crude oil. Medium-Btu gas produced after the removal of acid gases is suitable as clean fuel, or may be converted to hydrogen or to high-Btu gas in auxiliary facilities. Residual char (50-60% of feed coal) that is produced has heating value and sulfur content about the same as feed coal, so that its ultimate utilization may largely determine process viability.

Fibure B.1.1 shows a condensation of the main process train and Figure B.1.2 shows each unit in the complex.

B.1.2 Main Gasification Stream

B.1.2.1 Coal Storage and Preparation

B.1.2.1.1 Coal Storage

On-site coal storage will be required to provide back-up for continuous conversion operations. For thirty days storage, there might be eight piles, each about 200 feet wide, 20 feet high, and 1000 feet long. Containment of air-borne dusts is generally the only air pollution control required for transport and storage operations, although odor may be a problem in some instances. Covered or enclosed conveyances with dust removal equipment may be necessary, but precautions must be taken against fire or explosion. Circulating gas streams which may be used to inert or blanket a particular operation or which may issue from drying operations will generally require treatment to limit particulate content before

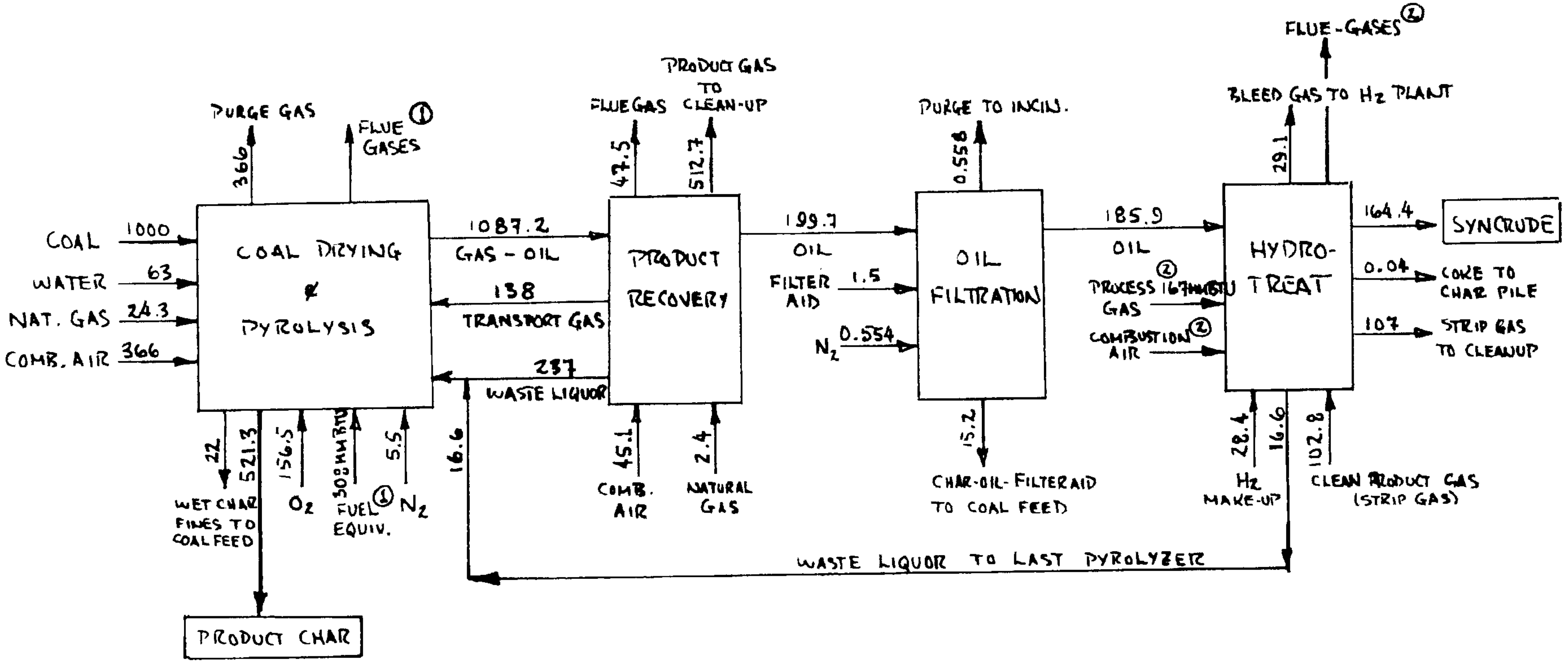

Figure B.1.1

COED Coal Conversion

(All rates in tph)

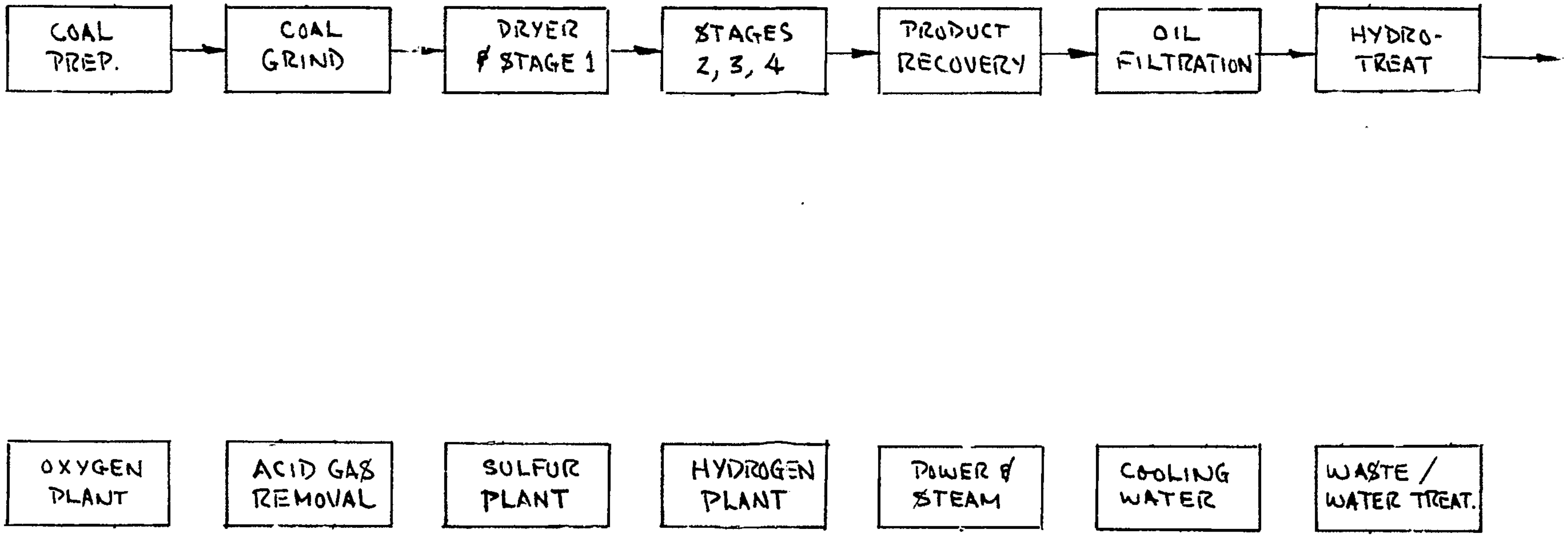

Figure B.1.2

COED Design Revised to Incorporate Environmental Controls and To Include Auxiliary Facilities discharge to the atmosphere. Careful management and planning will minimize dusting and wind loss and the hazard of combustion in storage facilities.

The as-received feed coal employed in this design is indicated to have 10-14 weight percent moisture content. The FMC process basis feeds coal of about 5.9 weight percent moisture to the coal dryer ahead of the first pyrolyzer. Hence the free or surface moisture is assumed to be removed in the upstream coal preparation plant, although, obviously, the coal dryer proper may be arranged to remove a larger fraction of the original moisture.

Illinois No. 6 coal is currently being supplied with about 17 percent moisture, but this moisture content is a function of the operation of laundering equipment. In a commercial conversion plant situated at the mine, closer control of the delivered moisture would be possible, but with corresponding increase in energy consumption.

The reactivity of coals may be markedly affected by exposure to air, and water serves to seal available pore volume, retarding oxidation. Hence the desired moisture content may be related to the average time-in-storage in a particular facility.

B.1.2.1.2 Coal Grinding

Free moisture will be removed from feed coal by milling in a stream of hot combustion gases, as is practiced in the FMC pilot plant. Coal sized 16 Tyler mesh or smaller, but with minimum fines, is required for the pilot plant, although other studies have indicated that particles up to 1/8 inch or 6-mesh may be suitable. In either case, the mechanical size reduction of an Illinois coal is expected to generate a considerable quantity of -200 mesh fines, especially if appreciable drying accompanies the milling operation. The quantity of such fines has been estimated to be 5 to 8 percent of the feed, depending on the type of equipment that may be used and on the acceptable size range, screening or separation efficiencies, and the recycle rates employed around the mill. Some small fraction of these fines will pass through the system with the sized coal. Additional fines will be produced in the coal dryer proper, and the ultimate consideration is that the total fines fed to the dryer or to the first pyrolyzer shall not overload the cyclone systems provided to effect their separation from the respective effluent streams. There may also be a relationship between the coal size fed to the system and the observable filter rates on raw pyrolysis oil. Fines generated in coal preparation, amounting to 5 percent of feed coal, will not be charged to pyrolysis, but will issue as a fuel product. Coal fines would probably be charged to the char gasification system, if this facility is included.

Clean product gas is fired in the mill heater (the basis indicates that natural gas is used). About 110 tph of water must be removed if coal is received with 14 percent moisture. This may require the firing of 15-20 tph of product gas with 180-200 tph of combustion air in the milling circuit. Assuming a dry particulate separation system is adequate, bag filters might be used to recover fines from the vented gas following primary classification in cyclones.

Depending on water-use constraints, it may be desirable to condense water from the vent gas for reuse. This stream could be combined with, or treated similarly to, gas issuing from the coal drying and first-stage pyrolysis section, wherein the gas is scrubbed in venturi scrubber-coolers. The additional cooling requirement would be about equal to that provided in the design basis for treating vent gas from that section. It is presumed, however, that the additional coal fines separated from scrubber effluent by filtration in this way could not be recycled to the pyrolyzer, and would issue from the system as sludge. This sludge, containing 50 percent water, would preferentially be charged along with char to gasification, if char gasification is included, or might be combusted with char in a char boiler. However, the dry separation system employing bag filters would be preferred in the latter case.

Vent gas which issues from the bag filters from the milling circuit may contain a significant carbon monoxide concentration, depending on the combustion parameters employed in the mill. It may be necessary to direct the stream to a boiler stack or incinerator to complete the combustion. Another possibility is to employ a noble-metal catalytic afterburner, which would minimize the additional fuel requirement, to neutralize the stream.

B.1.2.2 Coal Drying and First Stage Pyrolysis

Clean natural gas is burned sub-stoichiometrically 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 amount to about one percent of the coal feed, and the wet filter cake is 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 represents a loss of combustible equivalent to about 230 MM Btu/hr. It is indicated to be sulfur-free.

B.1.2.3 Stages 2, 3, 4 Pyrolysis

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 (~1550°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 counter-currently 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.

Char will be further cooled by cold-water exchange. In the pilot plant, a two-pass screw conveyor, in which cooling water is supplied to a hollow screw, as well as to the jackets of both flights, is used to cool char to about 100°F. About 180,000 lb/hr of 150 psia steam may be generated in the commercial operation if suitable equipment can be designed.

It has been assumed that clean product gas will be used to superheat the steam and oxygen feeds to the last pyrolysis stage. About 10.5 tons of gas is required, along with about 105 tons of air per hour. The combustion products should be dischargeable without further treatment.

B.1.2.4 Product Recovery System

Gas from the pyrolysis section is cooled and washed in two cascade 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 are dischargeable directly.

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

B.1.2.5 COED Oil Filtration

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 $ft.^2$-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 make-up, is directed to an incinerator. 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 added to the plant's char output in the process basis. FMC has recently suggested that filter cake will instead be recycled to coal feed. Filtered oil is directed to the hydrotreating facility.

B.1.2.6 Hydrotreating

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. In the FMC base design, hydrotreating is performed 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 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 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 H_2S from the water which separates from hydrotreater effluent. Stripped water is recycled to the last pyrolysis stage. The gas effluents from the stripper are 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 basis includes a large cooling requirement for hydrotreating effluent, even though preheating is supplied to hydrotreating feed. The developers have indicated that heat integration should be possible in a commercial installation to some degree. The concern involves possible degradation of raw oil feed in a heating system which is not precisely controlled. It has been assumed that 380,000 lb/hr of 600 psia steam will be generated in this cooler.

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. A major unresolved process question relates to the catalyst life that may be expected in commercial operation. Pilot plant results show that activity drops after 300-500 lb oil/lb catalyst, but pilot-plant conditions are considered more rigorous than should be the steady-state condition of the commercial unit.

Since high-temperatures are required generally for the regeneration of the cobalt molybdenum or nickel/tungsten sulfide catalysts used; regeneration, if it is practiced, will occur off-site. Moreover, it is assumed that the hydrotreaters will be designed to run continuously between maintenance shut-downs. It is not clear, however, whether two vessels provided are required to treat the total stream, or whether one represents stand-by capacity. Presumably some standby capacity will be required to permit catalyst changeout in the event of sudden activity loss or development of high pressure drop.

B.1.3 Hydrogen Plant

The COED process gas product is indicated to be the source of hydrogen for the hydrotreating of raw COED oil. Steam reforming, cryogenic separation, and partial oxidation have been investigated as means for recovering the required hydrogen from process gas, but the type of hydrogen plant that may ultimately be used will be a function of the location of the plant (or of the coal type being processed) and of the product sales slate, as well as of the size of the installation. For the present design, it has been assumed that the steam reforming case, as outlined by FMC, will be used.

COED process gas at 15 psia is compressed to 410 psia and passed through a Sulfinol system to remove CO_2 and H_2S. Regenerated acid gases are directed to the sulfur recovery plant. The cleaned process gas containing about 1 ppm H_2S 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:

$$CH_4 + H_2O \longrightarrow CO + 2H_2 \quad \text{(reforming)}$$
$$CO + H_2O \longrightarrow CO_2 + H_2 \quad \text{(CO shift)}$$

CO_2 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 $3H_2 + CO \longrightarrow CH_4 + H_2O$. Resulting product gas is available at 200 psig.

The bleed gas from the hydrotreating plant, containing about 2 percent H_2S and about 0.1 percent ammonia, is 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 H_2S must also be removed from this stream, and the H_2S residual, after water scrubbing, would be removed in an acid gas scrubber and directed to the sulfur recovery plant.

About 9.4 tph of hydrogen is consumed in hydrotreating 185 tph of raw oil (about 3000 ft^3/bbl). It is of course not required that initial acid gas removal be included in the hydrogen plant if acid gas removal is otherwise provided for the total product gas stream. Moreover, gas from the cleaning operation would be available at pressure so that compression is required only from that pressure level. About a third of the hydrogen requirement can be generated from excess CO and hydrocarbons present in the hydrotreating bleed stream. About 25 tph of clean product gas would be required additionally to be fed to the unit, and about 43 tph of water would be consumed in the reformer.

If a hydrogen plant design as described is employed, it should be possible to recover energy from the expansion of the hydrotreating bleed gas through use of turboexpanders or equivalent facilities to offset the energy required for recompression to the level required in the hydrogen plant.

The major gaseous effluents from the hydrogen plant will be the products of combustion from the fired heaters and the CO_2 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 CO_2 will be removed from the process gas, and this too may be discharged.

B.1.4 Auxiliary Facilities

B.1.4.1 Oxygen Plant

The oxygen plant provides a total of 3760 tons per day of oxygen from 440 MM scfd of air to the last pyrolysis stage. 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, as an inert stripping agent in regeneration or distillation, or to dilute other effluent gas streams. Nitrogen is also used to pressurize the rotary pressure raw-oil filters.

B.1.4.2 Acid Gas Removal

The "Benfield" hot potassium carbonate system is assumed in the present study. 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. The actual pressure level that will be employed will be a trade-off between compression costs and the utilities consumptions required otherwise. Based on the concentration of acid gases present in raw gas, a total scrubbing pressure between 100 and 200 psia is indicated, whether an amine or hot carbonate system is employed. It is 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 and as cooling water will be required to treat the stripping gas stream.

Clean gas may be directed to the various fired heaters throughout the plant, and to the utility boiler (see below). Product gas loss into the regenerator off-gas stream can be held to less than 0.1 percent in proprietary configurations of the process. Moreover, it is possible to selectively remove H_2S, if this is required to produce a suitable feed for a Claus sulfur plant.

B.1.4.3 Sulfur Plant

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.

For this study, it has been assumed that acid gas will be sufficiently high in H_2S content to permit use of a Claus recovery system. Depending on the acid gas removal process employed, H_2S may be preferentially absorbed to increase its concentration in off-gas fed to the sulfur plant. Claus units are operated commercially with entering H_2S concentrations as low as 6 percent. But these systems generally employ oxygen, so that some of the cost advantage relative to a process like Stretford, which does effectively treat low concentrations, may dissipate.

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. It may also be feasible to employ one of the flue-gas desulfurization variants using limestone to scrub tail gas, or processes such as the Wellman-Lord SO_2 Recovery Process or the IFP Secondary Recovery Process may be applied.

Most proprietary tail-gas treatment processes operate to convert SO_2 to H_2S, which may then be selectively removed. 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.

B.1.4.4 Utilities

B.1.4.4.1 Power and Steam Generation

The choice of fuel for the generation of the auxiliary electric power and steam required by coal gasification plants markedly affects the overall process thermal efficiency. It is generally least efficient to burn the clean product gas for this purpose. On the other hand, investment in power-plant facilities, including those required to handle the fuel and to treat the flue gas, is generally least when product gas is so used.

COED conversion generates a carbon-containing char equivalent to some 50-60 weight percent of the coal fed to pyrolysis. Since this is considered a fuel product, it would appear that it should be so used in the plant proper. However, it suffers as an acceptable fuel in this case to about the same extent as does the feed coal, in that its sulfur content is observed to be about the same as that of feed coal.

It has been assumed in this study that dirty fuels would not be combusted in the plant, so that clean product gas would be used also 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, so that the net available gas for fuel is 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, 4874 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 still be required. About 2.1 tph of SO_2 would be emitted, equivalent to about 2.0 lb/MM Btu, or above the level permitted by current standards for solid fuels.

Flue-gas treatment might be avoided if char were combusted with product gas throughout the plant. This would require additional investment in char handling and grinding equipment, as well as particulate control on all fired heaters and ash handling and disposal facilities, and may be less attractive than installation of flue-gas treating facilities on the main boiler. A variety of flue gas treatment processes for particulate and SO_x control are under development, and significant progress in this area may be expected by the time a commercial plant is constructed.

The coal fines estimated to be produced in the coal grinding operation could supply the fuel shortfall. This alternative may be attractive in a commercial facility because there would be no additional grinding debit and because the fines production might be entirely consumed. However, such coal fines may command a higher premium as a salable fuel than char, and it may be preferred to charge the coal fines to char gasification, depending on the system used for that purpose.

It has been assumed for the purpose of thermal efficiency calculations that char will be combusted in the plant to make-up the fuel shortfall, and the process for flue-gas treatment has not been debited. It is recognized that char treatment (gasification) is practically required in a commercial design.

B.1.4.4.2 Cooling Water

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. The cooling requirement to condense water from the coal grinding effluent gas stream has not been included. If water availability is constrained, this may be attractive.

It is probable that environmental considerations and the costs of water reclamation will operate to restrict industrial water consumption in most domestic locations. Hence a commercial design might maximize use of air-cooled heat exchangers, reserving the use of cold water only for "trim-cooling" or low-level heat transfer applications. The overall economic balance will consider added investments in heat-exchange and electrical hardware associated with air-fin usage, as well as investment in incremental electrical generation capacity. Running costs for the generation of power and for equipment operation would be balanced against the net reduction in water treatment and pumping costs, as well as the net reduction in water loss.

On the basis that half of the requirement may be displaced with forced draft air-cooled heat exchangers, the incremental electrical power requirement is estimated to amount to 26,000 KW. Added cooling water requirement associated with the incremental power generation would bring the net total cooling water requirement to an estimated 100,000 gpm, so that water loss by evaporation might be reduced to about 3025 gpm at the cooling towers. Drift loss would amount to 300 gpm on this basis. Blowdown, or draw-off from the system, might be held to 1200 gpm. There would be a reduction in the power requirement for pumping cooling water. On the other hand, direct discharge of heat to the air environment in certain locations may be less desirable than the humidification associated with cooling towers.

The physical environmental situation at a particular site, including water availability, climatic conditions, and available area, will set limits on the designer's options for heat rejection. Other means, such as cooling ponds, may be practicable. In very special situations, it may prove economic to recover some of the low-level heat, as by circulation in central heating systems to nearby communities or in trade-off situations with irrigation water supplies, where hot water may be used to extend growing seasons. In all situations, the sociological impact of the use of the environment will be an over-riding factor.

B.1.4.4.3 Water Treatment

Analyses of the aqueous condensates produced in the pyrolysis and hydrotreating plants have not been specified. 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 "by-pass" through the fluidized bed system. Demonstration of such long-term recycle, however, would considerably reduce investment in treatment facilities. The question may be largely academic, however, because it would appear that a large-scale installation, unless it were arranged to combust char onsite or in an adjacent facility, would include some form of high-temperature char gasification. We have assumed that pyrolysis liquor may be recycled in the present design.

Facilities required to treat water, including raw water, boiler feed water, and aqueous effluents, will include 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 run-offs and for flow equalization within the system will be required. Run-off from the paved process area could easily exceed 15,000 gpm during rainstorms. Run-off from the unpaved process and storage areas could exceed 80,000 gpm in a maximum one-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.

The COED plant may be able to take advantage of the properties of char and of attractive incremental costs for oxygen to assist its waste water treatment. Hence, the char produced by the process may have some of the attributes of activated carbon, which has been shown to be effective in the removal of a wide variety of the water contaminants expected.

Similarly, oxidation of contaminants in water using oxygen, and especially ozone, is normally reserved for polishing drinking water supplies because of high costs. Direct oxidation, however, is very effective in reducing phenol, cyanide and thiocyanate levels in waste water, and has particular advantage in that solids concentrations are not thereby increased.

B.2 SRC Process

B.2.1 General

The SRC design is based on converting 10,000 tons/day of Illinois type bituminous coal to net liquid products amounting to 25,000 barrels/day of heavy clean liquid fuel, of which 2/3 has a sulfur content of 0.5% while the remaining 1/3 contains about 0.2% sulfur. The plant facilities can be conveniently grouped into several areas including coal preparation and handling, coal liquefaction and filtration, gas cleaning and acid gas removal, product handling and treating, char gasification, hydrogen production, and finally auxiliary facilities such as utilities, oxygen manufacture, water treating, and a sulfur plant. A black flow diagram of the process is shown in Figure B.2.1.

B.2.2 Main Liquefaction Stream

B.2.2.1 Coal Storage and Preparation

Run of mine coal is delivered in rail cars, unloaded, and mechanically stacked in a storage pile with 3 days capacity. Coal containing moisture is reclaimed from storage and conveyed to a breaker. Refuse larger than 3 inches in size from the breaker is returned to the mine for disposal. Coal smaller than 3 inches goes to a second storage pile with 8000 tons capacity, which feeds the washing and cleaning operation. Here it is processed through a series of jigs, screens, centrifuges and cyclones, followed by a roll crusher to reduce it in size to 1-1/4 inch or smaller. Refuse from this cleaning operation goes to a settling pond to clean-up the water for reuse.

The next process step is to dry the washed coal, using a flow dryer to reduce the moisture content to 2.7%. Part of the dried coal supplies the fuel required for drying. However, the sulfur content of this coal is very high and flue gas clean-up would be required to remove sulfur as well as particulates. An alternative is to burn part of the product gas as fuel in the dryer and use bag filters or a water scrubber to control particulates. Fuel consumption can be reduced by using a

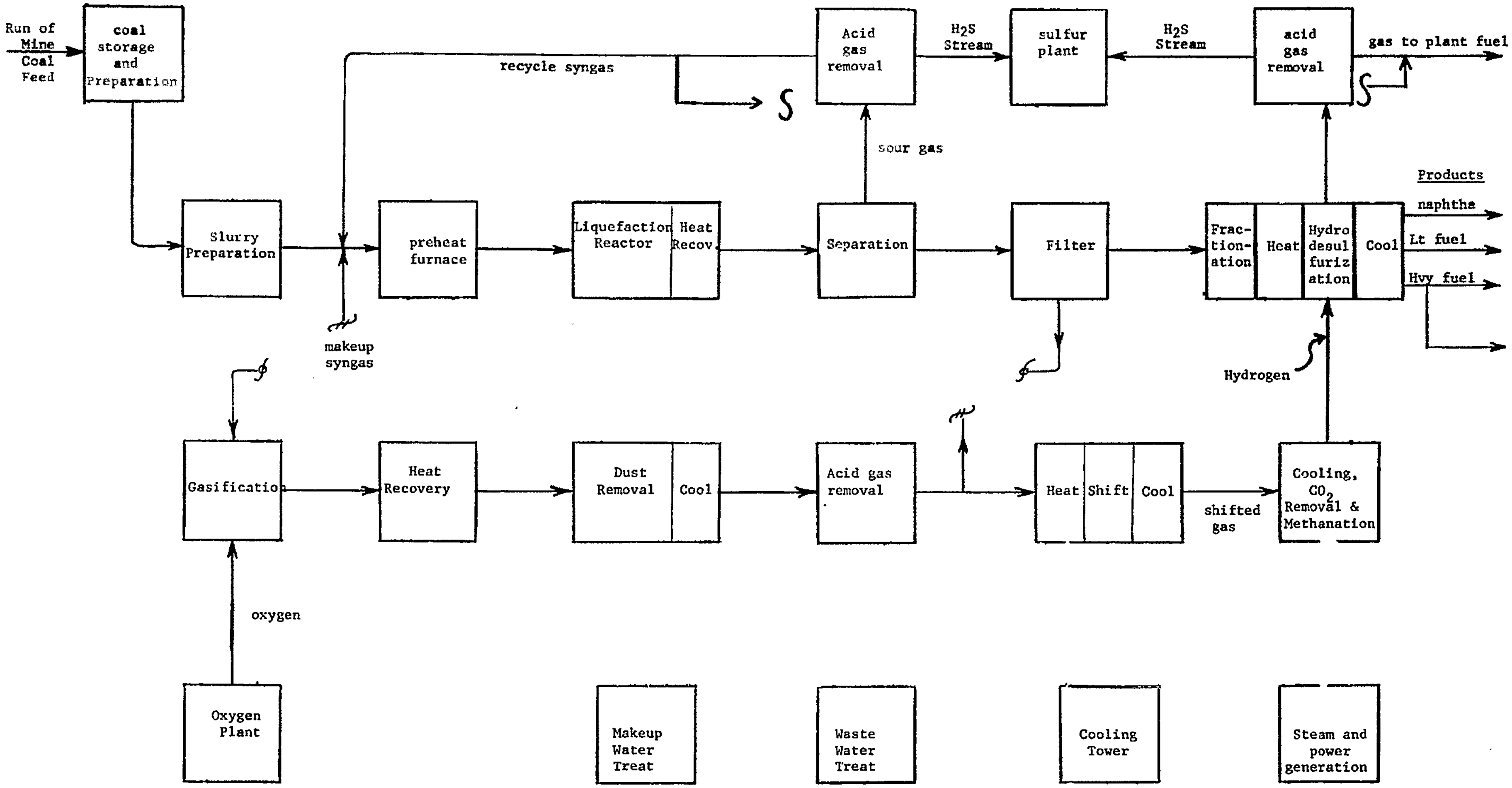

Figure B.2.1

SRC Coal Liquefaction Process

minimum amount of excess air and allowing a higher moisture content in the flue gas. At the same time, the volume of vent gas to clean-up is similarly reduced. The dried coal is then pulverized to 1/8" and smaller and fed to the liquefaction section at a rate of 416 tph.

B.2.2.2 Slurry Formation and Liquefaction

The coal is mixed with 20,000 tpd of recycle oil at 550°F, to form a slurry at 368°F. Upon mixing, moisture in the coal evaporates, is recovered in a condenser, and is returned to the slurry, so that this water does not become an effluent from the plant. The resulting slurry is recycled through a system supplying the high pressure feed pumps which deliver slurry to the reactor section at 1,000 psig pressure. The slurry of coal and recycled oil is mixed with makeup synthesis gas and recycle gas containing steam formed by injecting and vaporizing sour water recovered from the products leaving the reactor. This mixture of gas and slurry goes through a pre-heat furnace, where it is heated to 900°F, and then to a reactor which operates at about 840°F and 1,000 psig, with about one hour holding time. Total gas flow to the reactor corresponds to about 45,000 cu. ft. per ton of coal processed. In this particular design, synthesis-gas is used in the reactor rather than pure hydrogen. Carbon monoxide in this gas is shifted to hydrogen in the reactor and, the water needed for this is added in the feed. Conversion of coal is about 91% on a moisture and ash-free basis.

The stream leaving the liquefaction reactor passes to a separator at 840°F from which gas is removed overhead and recycled to the reactor after passing through acid gas removal. Liquid from the bottom of the separator is cooled and recycled in part to the slurry mixing tank where it is used to suspend the coal feed so that it can be pumped to high pressure. This recycle portion does not have to be filtered. The remaining liquid from the separator after the reactor goes to a rotary pre-coat filter where ash and solid particles are removed. Liquid product from the filter contains about 0.5% sulfur and constitutes the main clean liquid product from the process. About one third of it is further processed by catalytic hydrotreating with pure hydrogen to reduce its sulfur content to 0.2%.

B.2.2.3 Hydrotreating

The primary product stream of filtered reactor liquid is fractionated to give naphtha and a light distillate, both of which are further hydrotreated. Heat for distillation is provided by a furnace which generates a significant amount of flue gas. Since product gas is used as fuel, it should be practical to meet the emissions requirement for large stationary boilers with regard to sulfur, particulates, NO_x, and CO.

The product hydrotreating section also uses furnaces for preheating before the reactor and on stripping the product. The comment made on the distillation furnace applies here also. Hydrogen compression is included in this section, and since it involves high pressure, the possibility of leaks requires special consideration as discussed previously.

When the high pressure liquid products are depressured, a considerable amount of dissolved gas is released, which should be recovered or used for fuel. Similarly, when the sour water is depressured, gas will be released which would cause a serious odor problem if vented to the air. Facilities are, therefore, needed to recover this gas and send it to the sulfur plant.

B.2.3 Acid Gas Removal

Separate acid gas removal units are provided on: the gas recycled to the reactor, product fuel gas, after the gasifier, and in hydrogen manufacture. Amine scrubbing is used to remove sulfur from the recycle gas to aid desulfurization, and on the product gas so as to provide clean fuel for use in the plant. Scrubbing removes H_2S which goes to a sulfur plant. It is expected that there will be other forms of sulfur present such as carbonyl sulfide which will not be removed effectively by amine scrubbing. This is particularly true for the gasification system supplying raw gas for hydrogen manufacture since the high CO content of the gas results in a high formation of COS, as much as 10% of the total sulfur content in some similar systems. This will be removed by caustic scrubbing but creates a very large amount of spent caustic that needs disposal. Some work has been reported on hydrolyzing COS etc. to H_2S over catalyst, prior to amine scrubbing, which would improve the situation. Scrubbing the raw gas with hot carbonate may be preferrable, as it should remove COS without consuming caustic. Perhaps a better alternative is to use the low Btu gas from gasification as plant fuel where the clean-up requirements are less stringent, and then make hydrogen from product gas using well demonstrated technology.

B.2.4 Hydrogen Manufacture

In the section making pure hydrogen for hydrotreating, all CO in the feed gas is shifted with steam and the CO_2 scrubbed out using the proprietary Benfield hot carbonate process. This makes a concentrated CO_2 stream which is vented to the atmosphere (809 tpd CO_2), and assurance is needed that it is low enough in sulfur, mist, and chemicals, etc., to be acceptable, and that it is vented in a way to avoid hazards. One concern is that various sulfur and other compounds from gasification may be removed along with CO_2 and contaminate the CO_2 vent stream. Additional facilities may be required to clean up this stream, and we have added a scrubbing system for this purpose to recover sulfur compounds. These compounds are then combined with the feed to the Claus plant for processing.

B.2.5 Gasification and Slag Disposal

In this section, synthesis gas is made by reacting a slurry of the filter cake with steam and oxygen in a slagging gasifier. The filter cake contains residual ash from the coal amounting to 713 tons per day, together with 818 tpd of unreacted char, and is mixed with 1530 tpd of oil to form a pumpable slurry. Oxygen consumption is 1964 tpd while the total steam rate to gasification is 1837 tpd and the steam conversion

65%. The gasifier operates at 1700°F in the top zone, 3000°F in the bottom zone, and 200 psig. It is a modification of a system under development known as BI-GAS. Molten slag is removed at the bottom and quenched to form steam which is returned to the gasifier, while excess water forms a slurry with the fragmented slag so that it can be withdrawn.

Of the oil-filter cake slurry charged to gasification, 30% of it goes to a top zone where the temperature is 1700°F. Consequently, small amounts of tar or oil and soot may be present, in which case additional recovery facilities may be required due to problems with exchanger fouling, emulsion, etc. The design does provide a cyclone to recover dry char from the raw gas and recycle it to the 3000°F zone, since the cake is not completely gasified in one pass. A venturi scrubber is included for final dust removal.

The main effluents to the air from this section are from two furnaces preheating the feed streams to gasification. These furnaces fire clean gas so that there should be no problem in meeting target emissions, as discussed in the section on Product Handling and Hydrotreating. One furnace preheats clean steam to 1050°F for feeding to the top of the gasifier along with 30% of the slurry feed. The other furnace heats recycle char suspended in gas and steam, for feeding to the 2000°F zone along with the other 70% of the slurry feed.

Sour water from scrubbing the raw gas contains sulfur compounds, ammonia, phenols, etc. This stream is treated before discharge to extract phenols, and goes to a sour water stripper which removes light gases that are sent to the sulfur plant. It then flows through oil separators and to a biox pond.

The slag quenching operation is described in general terms, and the 3000°F gasifier zone is segregated from the water slurry, quenching zone. No specific facilities are shown for particle size control, such as grinding, and the system depends on the shattering effect of quenching to form a pumpable slurry.

The design provides a slag storage pile in the coal storage area, prior to back-hauling it to the mine. Since the slag is removed as a slurry, it will have to be drained and stacked. Some of the slag may be very fine, consequently there could be dust problems when it dries out. The extent of odors and sulfur emissions in this operation needs to be determined. Also, water from draining must be recovered and reused, since it will contain considerable suspended solids. It can be recirculated through the storm pond, provided this does not cause secondary pollution problems due to odors or leachable materials.

B.2.6 Auxiliary Facilities

In addition to the main process, various auxiliary facilities are needed, such as the oxygen plant, sulfur plant, utilities, water treating, and product storage, which must be considered from the standpoint of effluents to the air. The oxygen plant is a large consumer of power and therefore has an important effect on thermal efficiency and energy consumption. One approach uses electric drives on the main air compressor, but where clean fuel is available a flue gas turbine may be more attractive. Or a high pressure bleeder steam turbine can be used, for example generating steam at 600 psig or higher and depressuring it through the turbine to say 125 psig to supply steam for reboilers on acid gas removal, preheating, etc. When a specific plant design is made, it will be important to optimize the utilities system.

The sulfur plant uses a Claus unit, with tail gas clean-up. Concentration of H_2S in the feed is only 7.7 mole percent, resulting in a low sulfur recovery on the Claus unit. Therefore an efficient tail gas clean-up system is needed and there are a number of available processes to choose from. The design is based on using the proprietary Beavon process to reduce residual sulfur compounds to H_2S, which is then removed in a Stretford type scrubbing operation. Other systems could be used for tail gas clean-up such as the IFP, Takahax, Wellman-Lord or Scot processes. Vent gas from the tail gas clean-up operation can be vented to the atmosphere without incineration in some cases.

The Stretford type process uses a scrubbing liquid containing catalyst to oxidize H_2S to free sulfur. The scrubbing liquid is then reoxidized by blowing with air, and precautions must be taken to avoid release of odors or entrained liquid etc. to the atmosphere. This air effluent should pass through an incinerator or furnace unless it is clear that H_2S and other emissions will be acceptable.

Product sulfur may be handled and stored as a liquid in completely enclosed equipment to avoid emissions. If it is handled and stored as a solid, control of dusting will be required.

The largest volume of discharge to the atmosphere from the utility area is on the cooling tower. Air flow through it is about 31,000 MM cfd, and it is therefore critical from the standpoint of pollutants. It might be expected that the recirculated cooling water would be perfectly clean and free of contaminants, however, experience shows that there will be appreciable leakage in exchangers and occasionally tube failures, especially with high pressure operations. In the present design cooling water is exchanged with oil, sour water, raw gas, amines, etc.; therefore, contaminants may get into the circulating cooling water and then be transferred to the air in the cooling tower, which necessarily provides effective contacting and stripping.

Cooling towers also have a potential problem due to drift loss, that is mist or spray which is carried out with the effluent air. Since this contains dissolved solids it can result in deposits when the mist settles and evaporates. In addition there is a potential plume or fog problem, if the atmospheric conditions are such that moisture in the air leaving the cooling tower condenses upon mixing with cooler ambient air. This occurs whenever the mix temperature is below that corresponding to saturation. Although reheating the effluent air will prevent the plume, it is not normally warranted and consumes energy unless it can be accomplished using waste heat.

The utilities section includes a boiler to provide steam and electric power. It has a large gas effluent, so that emissions of dust, sulfur, NO_x and CO must be controlled. The large fuel consumption of the boiler has a correspondingly large effect on thermal efficiency of the overall plant.

Thermal efficiency of any coal conversion process must take into account the fuel consumed in utilities generation, since this can amount to 15-25% of the main process. In general it is desirable to burn low grade fuel such as char or coal rather than high value product gas or liquid. In the case of the SRC process its purpose is to produce clean boiler fuel so that it is reasonable to use this product to supply utilities fuel, as required. It is important to achieve high efficiency in generating utilities and the combined cycle is, therefore, receiving a lot of attention. In the combined cycle, a gas or liquid fuel is burned at perhaps 10 atmospheres pressure, giving hot gases which are passed through a turbine to generate electric power and then to a boiler generating high pressure steam. Solid fuel, such as coal, can also be used by gasifying the coal and cleaning up the raw gas to provide low Btu gas fuel for the turbine. Such alternatives need to be evaluated carefully in each specific application in order to define the best combination.

Sour water from liquefaction contains compounds with strong odors, such as phenols, H_2S, and ammonia. In the waste water treating section, phenols, etc. are extracted from the sour water by contacting it with a light oil, which is then recycled through catalytic hydrogenation to destroy compounds containing oxygen or nitrogen. The raffinate is then stripped to remove H_2S, ammonia, and traces of oil and solvent which are disposed of to the sulfur plant. Ammonia might be recovered as a by-product. However, most of the nitrogen in the coal remains in the oil product and, therefore, the production of ammonia is small.

Depending upon the efficiency of the extraction and stripping operations, the level of contaminants in the waste water may be reduced to a level low enough to be acceptable without over-loading the biox unit. An oil separator is provided ahead of the biox. Except for this and the biox unit, these facilities are all enclosed in order to avoid any direct effluents to the atmosphere. Sour water from the gasification and product hydrotreating areas is also stripped to remove H_2S and ammonia prior to discharging to the biox unit.

In view of the very strong odor created by phenols and by components in the sour water, careful consideration should be given to this in planning and designing all plant facilities. All oil-water separators should be covered to contain odors, and it is possible that the biox unit will also need to be covered. Further experimental data should be obtained to define the requirements for this. The SRC oil product contains various oxygenated compounds, including phenols and cresols, as well as relatively large amounts of nitrogen compounds such as pyridine types. These have very strong odors and can create problems in handling and storage.

If the product is solidified by cooling in a prilling tower with direct contact with air, obnoxious fumes can be formed (similar to those generated in asphalt oxidation). These cannot be discharged to the atmosphere and might be incinerated, or gas recirculation could be used with indirect cooling. An alternative is to solidify the product on a metal belt which is cooled by exchange with water. Instead of making a solid product, it could be kept hot above the melting point and handled as a liquid, in which case it will be important to exclude air from the storage and handling facilities. Tests on similar type materials have shown that oxidation reactions induce polymerization, resulting in a large increase in viscosity, and potential gum and asphaltic deposits. Storage tanks are needed with inert gas purge which is vented to the incinerator to control emissions and odors.

This design has a rather large waste water discharge amounting to 30% of the make-up. This includes boiler feed-water blow down, cooling tower blow down, sour water to biox, and the water from sanitary sewers. The total waste water discharge is 1,064 gpm compared to the make-up of 3,626 gpm. It appears that much of the water blow down could be treated and reused without reaching excessive levels of dissolved solids in the cooling tower circuit. Thus, the boiler blow down of 120 gpm can be used as make up to the cooling tower. Evaporation from the cooling tower is about 1800 gpm and it would be expected that the water blow down rate could be appreciably less than the 600 gpm provided, without having too much build-up in dissolved solids. The best disposition of the water effluent from the plant will depend upon its location and the specific situation. It might be used to slurry the ash and solid refuse from coal cleaning for return to the mine, or it may be acceptable to discharge it to a river. Composition of the major components in this discharge water are needed in a specific case in order to determine whether the method of disposal will be satisfactory.

B.3 H-Coal Process

B.3.1 General

In the H-Coal process, coal is reacted catalytically with hydrogen in a slurry system to make synthetic crude. The process can also be used to make low sulfur fuel oil by operating at lower severity. For syncrude operation, reaction conditions are about 850°F and high pressure, such as 2000 psig. Syncrude production is 91,240 barrells/day for the plant feeding 25,000 tons/day of dry coal to the H-Coal reactor. An overall flowplan for the process is shown in Figure B.3.1.

An ebullating bed reactor is used wherein the slurry of coal and catalyst in oil is agitated by bubbling hydrogen gas through it. Size of the catalyst is large relative to the coal, so that, although the catalyst

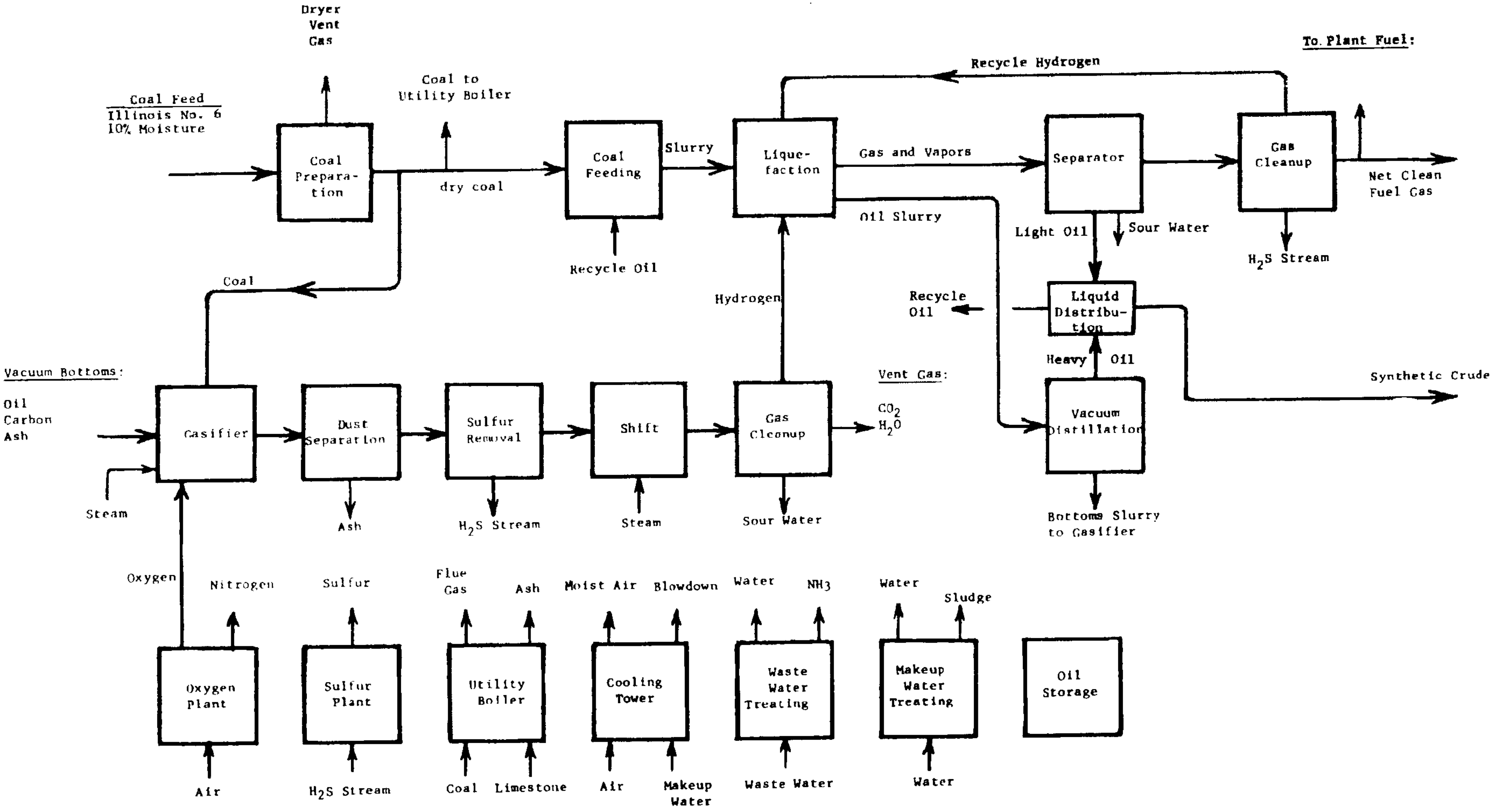

Figure B.3.1

Block Flow Plan of H-Coal Plant for Coal Liquefaction is fluidized, it is retained in the reactor and is not carried out with the liquid oil sidestream leaving the reactor. In addition, a gas stream is withdrawn separately from the reactor top.

The following subsections describe the various operations in the overall plant. These can be conviently grouped into several areas covering coal preparation and handling, coal liquefaction, gas separation and cleanup, liquid product recovery, hydrogen manufacture, and auxiliary facilities such as utilities, water treating, oxygen plant, and sulfur plant. This grouping will be followed through the report.

B.3.2 Main Liquefaction Stream

B.3.2.1 Coal Preparation and Feeding

This study assumes that cleaned coal is delivered to the plant, consequently the facilities and environmental concerns associated with coal cleaning will be at a different location, and therefore are not covered. Coal cleaning generates considerable amounts of solid refuse to dispose of and wash water to be cleaned up for reuse. A very large coal storage pile is included, having 30 days supply for example.

Coal feed having a nominal 10% moisture is sent first to a dryer where essentially all moisture is removed, and the coal is then crushed through 40 mesh. Crushed coal is mixed with recycle oil to form a slurry that can be pumped into the high pressure hydrogenation system. In addition, part of the dried coal goes to the gasifier so that hydrogen production can be increased to balance consumption, and dried coal also supplies the fuel used on the utility boiler.

B.3.2.2 Liquefaction Section

The coal slurry, together with makeup and recycle hydrogen, goes to a preheat furnace and then to the H-Coal reactor where hydrogenation takes place in the presence of an ebullating bed of coarse catalyst particles. About 96% of the carbon in the coal is converted to liquid or gas products, while the remaining carbon is retained in the ash which is withdrawm as a sidestream from the reactor in the form of a slurry with product oil. Part of this slurry is recirculated to the bottom of the reactor to maintain desired flow conditions.

Gases are withdrawn as a separate stream from the top of the reactor - part of the gas being recycled to the reactor inlet after cleanup to remove sulfur compounds. The remaining gas is withdrawn as a product from the process, and part of it is used to supply clean fuel to the coal dryer, reactor preheat furnace, and tail gas incinerator on the Claus plant. In the gas cleanup operation, water and oil are condensed from the gases leaving the reactor. The resulting sour water is sent to waste water treating while the oil is combined with the main liquid product.

The main oil product is withdrawn from the reactor via a liquid phase settling zone within the reactor so that the large catalyst particles are separated from the oil product and retained in the reactor. The withdrawn liquid contains ash and unreacted coal particles which are segregated by vacuum distillation into the heaviest bottom fraction of the oil. This vacuum bottoms is used to make hydrogen for the process by gasification with oxygen and steam.

Heat is recovered from the hot effluents leaving the reactor, and used to preheat feed streams or to make steam. Hydrogenation is an exothermic reaction, giving an estimated heat release for this study case of 700 MM Btu/hr, corresponding to 7700 Btu/lb hydrogen consumed, which heat is also recovered and used.

B.3.2.3 Gas Separation and Cleanup

A gas and vapor stream is withdrawn from the top of the liquefaction reactor, above the liquid level. It is substantially free of entrained liquid, and therefore contains little or no solids. Upon cooling, oil and water condense out and are separated. The sour water is sent to waste water treating, while part of the oil is recycled to form a slurry with the coal feed and the remainder of the oil is included in the final syncrude product.

The gas after condensation is cleaned up to remove sulfur compounds which are sent to sulfur recovery. Part of the clean gas is recycled to the H-Oil unit to supply hydrogen, and the rest is available as byproduct fuel gas or for plant fuel. The process used for removing sulfur from the gas is assumed to be scrubbing with an aqueous solution of amine, although hot carbonate could be used instead.

B.3.2.4 Liquid Product Recovery

A liquid stream is drawn off separately from the reactor, consisting of a slurry of ash and unreacted coal in heavy oil. This slurry is distilled under vacuum to produce a clean light distillate oil, part of which is recycled for slurrying the coal feed while the remainder is withdrawn as syncrude product along with some of the light oil condensed from the gases leaving the reactor.

Heavy bottoms from the vacuum tower, containing ash and unreacted coal, is used to make hydrogen in a partial oxidation gasifier.

B.3.3 Hydrogen Manufacture

A partial oxidation system is used for manufacturing hydrogen, consuming as raw material the slurry of vacuum bottoms which may otherwise present a disposal problem. The developer has indicated that a Texaco type partial oxidation process is used, since this type of gasifier is expected to be able to handle such a feedstock whereas some alternative processes may not be able to.

The amount of vacuum bottoms is not sufficient to make all of the hydrogen needed, so some coal feed is also sent to the gasifier, adding to the coal consumption for the plant. Oxygen for gasification is supplied by an onsite oxygen plant, while the required steam is provided from waste heat boilers. The gasification reactor operates at slagging conditions, over 2000°F, and 500 psig pressure.

Raw gas is quenched and then scrubbed with water to remove particulates including ash and soot. Water condensed at this point contains a wide spectrum of contaminants including ammonia, HCN and other nitrogen compounds, various sulfur compounds, phenols, etc., this sour water is sent to waste water cleanup.

Sulfur compounds are removed from the gas in the next processing step by scrubbing with amine. Some CO_2 is also removed but this is incidental. Amine solution from the absorber is regenerated in a stripping tower with reboiler. The sulfur containing gas stream from amine regeneration is sent to a Claus plant for sulfur recovery. Tail gas cleanup is included, as is common practice, so that the sulfur plant will meet emission requirements.

The clean desulfurized gas is reheated and mixed with supplemental steam for processing in the shift conversion reactor. After shifting, the gas is cooled, and scrubbed to remove CO_2 using one of the available conventional systems such as hot carbonate. The CO_2 stream is vented to the atmosphere as a waste product.

Finally, the product hydrogen is compressed and fed to the hydroliquefaction reactor which operates at about 2000 psig.

B.3.4 Auxiliary Facilities

The discussion so far has described the basic processing units used in a plant for hydroliquefaction of coal. In addition, auxiliary facilities are needed such as an oxygen plant, sulfur plant, and utilities systems to supply steam, electric power, and water. Waste water treating is also required. In addition to contributing effluents and emissions, these auxiliary facilities may also consume additional fuel in the form of coal or clean products from the process.

Oxygen is made by liquefaction of air, giving a waste stream of nitrogen that is clean and can be vented directly to the atmosphere. A sulfur plant is needed to recover by-product sulfur from the various sulfur compounds removed in the gas cleanup operations on the H-Oil unit and in hydrogen manufacture. A Claus type sulfur plant is used, with tail gas cleanup in order to meet environmental requirements. Total sulfur production amounts to 1295 tons/day.

In order to make the plant self-sufficient, utility steam and electric power are generated for use in the process so that purchase of utilities is avoided.

Utility steam is generated at 1000 psig pressure and used to drive the turbogenerator and compressors. In some cases, bleeder turbines are used in order to balance out the generation and consumption of steam at

600 psig and 70 psig. Coal is used as fuel in the utility boiler, on the basis that stack gas cleanup will be provided to control emissions of sulfur and particulates. The amount of coal used in the boiler is 3020 tons/day on a dry basis, giving 299 tons of ash to dispose of.

Water is used for cooling, primarily to condense steam from turbines or on overhead condensers. Cooling water is recirculated at 200,000 gpm through a cooling tower where about three-quarters of the heat is dissipated by evaporation, and the remainder is taken up as sensible heat of the air passing through.

Waste water from the hydroliquefaction section contains a wide range of pollutants including H_2S and other sulfur compounds, nitrogen compounds such as ammonia, HCN, pyridines, etc., phenols and other oxygenated compounds, plus suspended solids, oil, and tar. It would not be acceptable to discharge such water directly from the plant; therefore it is cleaned up and reused. Cleanup of waste water involves the following operations:

- **Settling and filtration to remove solids.**
- **Extraction of phenols using a suitable solvent.**
- **Sour water stripping to remove H_2S, NH_3, and other low boiling materials.**
- **Biological oxidation (biox) to consume residual small amounts of various contaminants, which are converted to cellular sludge.**
- **Activated carbon adsorption, if needed, for final polishing.**
- **Possibly special treatment for trace elements.**

Ammonia will be recovered as a by-product, amounting to 205 tons/day while other contaminants removed from the waste water, such as H_2S and phenols can be sent to the sulfur plant for incineration, or returned to the process where they can be converted and destroyed.

Treated waste water is used as cooling tower makeup, supplemented by boiler blowdown and fresh water. Blowdown from the cooling tower constitutes the net water discharge from the plant amounting to 5100 tons/day (850 gpm). This blowdown, together with drift loss from the cooling tower, serves to purge dissolved solids from the system so as to prevent excessive buildup in the cooling water circuit.

Fresh water makeup is supplied to the cooling tower, as well as to boiler feed water preparation. Combined, these amount to 37,680 tons/day or 6300 gpm, which is the overall water consumption of the plant. Treating of makeup water includes lime softening and clarification, plus demineralization on the portion going to boiler feed water.

APPENDIX C

Process Descriptions - Coal Treating

APPENDIX C

PROCESS DESCRIPTIONS - COAL TREATING

In this appendix on Coal Treating, only the Meyers Process has been investigated in depth. A summary description is included here. For a more detailed description, see the process report.

C.1 Meyers Process

C.1.1 General

In the Meyers process, the pyrites in the coal are removed by reaction with ferric sulfate in a solution containing ferric and ferrous sulfates and sulfuric acid. The ferric ion is continuously regenerated by reaction of oxygen and ferrous ion. The elemental sulfur product is extracted with an organic solvent. The iron product from the pyrites is removed as solid ferric and ferrous sulfates.

A block flow diagram of the basic Meyers process is shown in Figure C.1.

C.1.2 Main Process Streams

C.1.2.1 Coal Storage and Preparation

ROM coal, 8 in. X 0, is received at the plant and stored. Three days storage (7920 tons, wet) has been suggested. This quantity of coal would probably be stored in silos with nitrogen blanketing. It would probably be advisable to store more coal (e.g., 30 days supply) in a "permanent" pile for emergency use. This pile could be covered with asphalt and used only in case of mine outage.

The ROM coal is conveyed to pulverizers where the coal is reduced to 80% less than 200 mesh. The coal from the pulverizers is then fed to the Reaction Section.

It is not necessary to dry the coal as it is subsequently slurried in a water solution. It is assumed that covered conveyers will be used throughout to minimize dust problems. The coal dimunition equipment can be enclosed, with air vented to bag filters. This will reduce outside noise as well as provide for dust containment.

C.1.2.2 Reactor Section

Pulverized coal is mixed with recycled leach solution in a flow through mixing tank. The mixing vessel is maintained at about 210°F. The slurry is continually pumped from the mixing vessel to one of 10 reactor vessels.

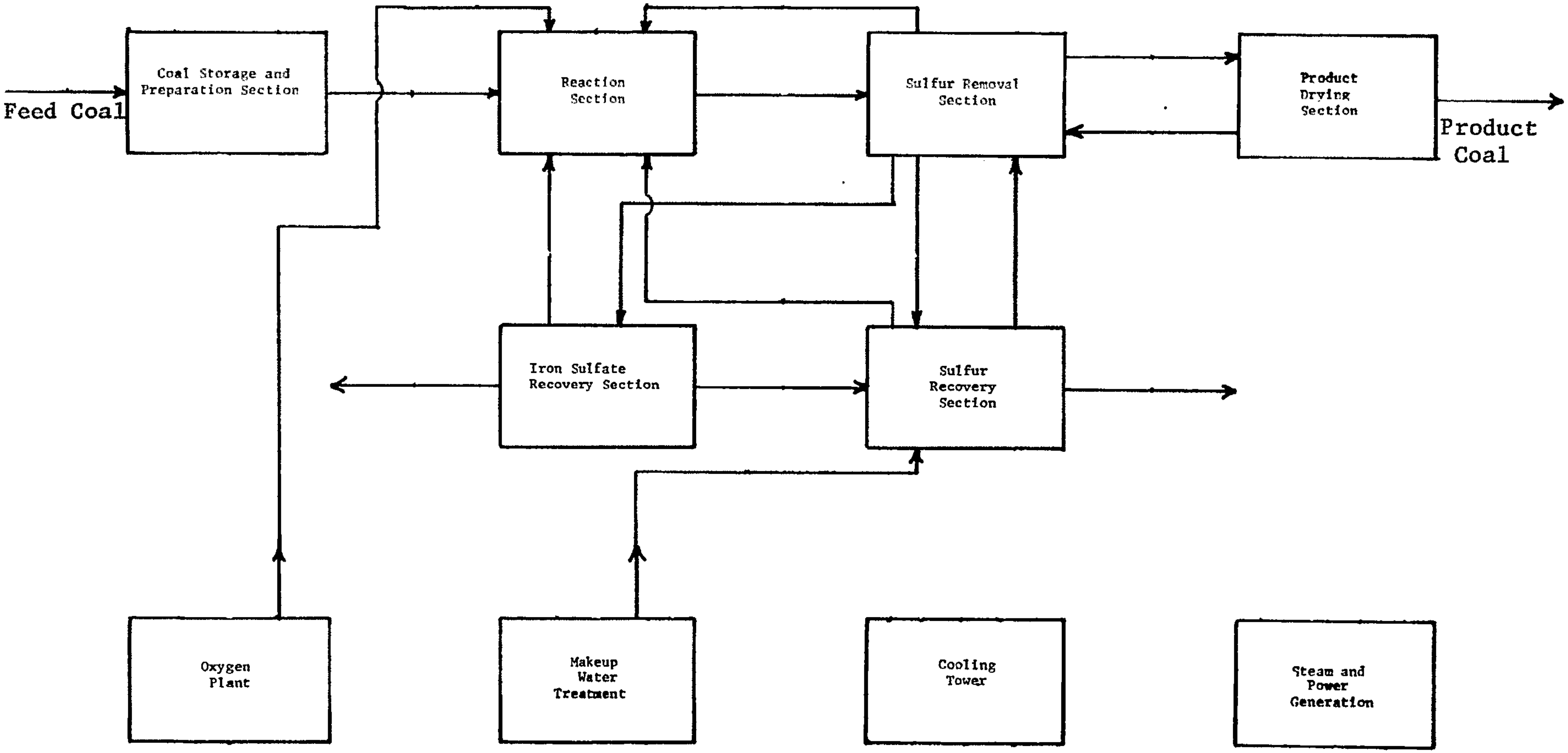

Figure C.1

Flow Diagram of Meyers Process

In the reactor vessels, the slurry is contacted with oxygen at about 300°F. The pyritic sulfur is 95% converted to elemental sulfur and sulfate in the reactor vessels. The reactions taking place in the reactors are shown below:

Leaching Reactions

(1) $FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S$

(2) $FeS_2 + 7Fe_2(SO_4)_3 + 8H_2O \rightarrow 15FeSO_4 + 8H_2SO_4$

Since ι ɜt SO_4:S production from FeS_2 is approximately 1.5:1, the overall lea reaction is:

$$FeS_2 + 4.6Fe_2(SO_4)_3 + 4.8H_2O \rightarrow 10.2FeSO_4 + 4.8H_2SO_4 + 0.8S$$

'eration Reaction

($.6FeSO_4 + 4.8H_2SO_4 + 2.4O_2 \rightarrow 4.8Fe_2(SO_4)_3 + 4.8H_2O$

Net :all Reaction

(5) $FeS_2 + 2.4O_2 \quad 0.2Fe_2(SO_4)_3 + 0.6FeSO_4 + 0.8S$

The excess ferric and ferrous sulfates must be removed from the system. The slurry is cooled by heat exchange with fresh feed and then by cooling water and is pumped to the Sulfur Removal Section.

C.1.2.3 Sulfur Removal Section

In the Sulfur Removal Section, approximately 60% of the leach solution is removed in hydroclones and recycled to the Reaction Section. The remaining leach solution is removed by filtration and is passed to the Iron Sulfate Recovery Section.

The wet filter cake is washed with water and then mixed with recycle solvent (e.g., light naphtha) at 160°F and most of the elemental sulfur is dissolved. The resulting slurry is filtered to remove the 'hich passes to the Product Drying Section. The sulfur-rich arated from water by decantation and passes to the Sulfur Recovery Section.

C.1.2.4 Product Drying Section

The treated coal, containing about 25% moisture and 5% solvent (dry b .s conducted to the drying section. The coal is partially dried ıcuum; the sensible heat of the coal is sufficient to remove all the nt and about 20% of the water. The vapors are returned to the Sulfur moval Section where they are condensed in a water cooled vessel. The water and solvent are separated by decantation and reused in the process. The coal product, containing 20% moisture (dry basis) then leave cess.

C.1.2.5 Sulfur Recovery Section

The sulfur-laden solvent and miscellaneous solvent and water streams are passed to the Sulfur Recovery Section. The solvent is removed from the sulfur by distillation and the sulfur leaves the process. Water and rich solvent are separated by decantation. The water is recycled to the Reaction Section and the solvent is returned to the Sulfur Removal Section. Makeup water and solvent are added to the system through the Sulfur Recovery Section.

C.1.2.6 Iron Sulfate Recovery Section

The water filtrate from filtration in the Sulfur Removal Section passes to the Iron Sulfate Recovery Section. Since the process produces iron from the pyrites, it is necessary to remove iron from the system. The filtrate is heated to about 265°F, and some of the water is flashed overhead. Part of the steam thus formed is returned to the Reaction Section and part passes to the Sulfur Recovery Section. The remaining slurry of iron sulfates is filtered at 215°F to produce an iron sulfate filter cake for disposal. The filtrate is returned to the Reaction Section.

C.1.3 Auxiliary Facilities

The auxiliary facilities in the complex include an oxygen plant, raw water treatment, cooling towers and steam and power generating facilities. These auxiliary units must be considered to evaluate effluent problems and overall thermal efficiency.

The oxygen plant is a major consumer of power and there is a large gaseous effluent. It has been assumed in the present design that an extraction turbine, using 600 psig steam, is used to drive the air compressor in the oxygen plant. The extraction steam, at 115 psig, is utilized in the rest of the plant.

A raw water treatment system is provided to furnish makeup water to the steam boiler and cooling tower. Cooling tower blowdown is sent to an evaporation pond. Product coal is burned in the steam plant. The use of product in the boiler furnace affects the thermal efficiency of the overall plant. Control of particulate matter can be effected by the use of commercial electrostatic precipitators, cyclones and/or scrubbers.

APPENDIX D

Trace Elements in Petroleum and Shale

APPENDIX D

TRACE ELEMENTS IN PETROLEUM AND SHALE

D.1 Domestic Crude Oils

Approximately two-thirds of domestic crude oil production is obtained from a relatively small number of large oil fields, sometimes termed "giant" fields.* Generally, U.S. giant fields are defined as those possessing reserves in excess of 100,000,000 bbl. (Some of the older fields which have been in continual production may now possess reserves less than this level. Additionally, certain large new fields may presently be shut in or in a state of development thereby accounting for their relatively low production.) These large oil fields are responsible for a majority of U.S. oil production and they are also representative of the nation's total oil production. This occurs because many smaller oil fields in close proximity to the giant fields possess very similar characteristics including similar trace element concentrations. In practice, the production of these smaller fields is generally combined with that from the large fields in the pipe line networks that grid oil producing regions. Thus, the oil arriving at refineries is a mixture, dominated by production of the giant fields. Consequently, for practical purposes, the characteristics of the larger fields characterize the great bulk of all domestic petroleum production.

D.1.1 Sulfur and Nitrogen Data

Because of the prominence of the giant fields, their crudes have been subject to much of the trace element data that are available. Sulfur and nitrogen data for crude oils from these fields are the most complete and consequently will be considered separately. Of a total of 259 giant U.S. oil fields, sulfur data were obtained for 251 fields (96.9%) and nitrogen data were acquired for 229 fields (88.4%). On a production basis, sulfur data covered 94.6% of giant field's production, and the nitrogen data 88.5%. Most of the sulfur and nitrogen data were obtained from Bureau of Mines sources through either publications or open files of crude oil analyses.

In assembling this compilation, data from published, widely available sources were utilized in preference to data from less available sources. Consequently, published Bureau of Mines data took precedence over Bureau of Mines open file analysis data. An average was obtained when duplicate BuMines data were available for a given field. Data officially published by the Bureau were used in preference to those appearing elseswhere, even if the authors of these other works were Bureau personnel. The giant field sulfur and nitrogen data follow in Table D.1.

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* "Giant field" is a relative term. Of the current producers, the two largest are the Wilmington (California) and East Texas fields. Each produces approximately 70-75 thousands barrels per day. This may be contrasted with the Ghawar field in Saudi Arabia, the world's largest, which has a production level more than ten fold greater than Wilmington. Reserves of the Ghawar field are estimated to approach 70 billion barrels.

The data presented in Table D.1 were evaluated on both a production and a geometric average basis. These evaluations are discussed below by element.

Sulfur - The sulfur data were plotted as a histogram. The resulting frequency distribution is shown as Figure D.1. In this figure, each sulfur percentage increment covers a range centering on the value shown. For example, the sulfur value of 0.3 covers a range of 0.25 to 0.3499% sulfur. The sulfur data are log normally distributed about the 0.2% level, although the distribution possesses a long tail. A distribution of this type is the classic one found for the distribution of many trace elements in the earth's crust.

The geometric mean of the sulfur data as calculated from Table D.1 was 0.42%. A production average calculated from this same data was 0.77% S, indicating that certain large production fields possessed a greater than average sulfur content. Crudes possessing a sulfur level of <0.1 were treated as if this level were 0.1 for calculation purposes.

The sulfur data ranged from less than 0.1% for a number of fields in southern Texas near the Gulf Coast (Texas Railroad Commission Corpus Christi District 4) to 5.07% and 4.99% for the Cat Canyon West and Santa Maria Valley fields of the coastal area of California.

Nitrogen - A histogram of the nitrogen data is shown in Figure D.2. As with the sulfur graph, each nitrogen percentage increment is centered on the value shown so that the value of 0.25 covers a range of 0.24 to 0.2599% N. Once again the data appear to be log normally distributed with a long tail. The modal value occurs at 0.03% N.

The geometric mean of the nitrogen data of Table D.1 was 0.028%. This is in contrast to a production average of 0.159%. As with sulfur content, substantial production from high nitrogen content fields has made the production average greater than the geometric mean.

The lowest nitrogen level, 0.002%, was observed for crude from the recently discovered Jay field in Florida. The highest, 0.913%, was found for crude from the San Ardo field in the coastal region of California. It is well known that many California crudes possess very high nitrogen as well as sulfur levels. Consequently, it was not unexpected that all crudes possessing nitrogen levels above 0.5% were from California.

D.1.2 Other Trace Element Data

With the exception of sulfur and nitrogen, the Bureau of Mines has not performed trace element analysis as part of their routine analyses of crude oils. This factor, coupled with the lack of widespread published data in this area from other sources, means that a large gap exists in reliable information on trace elements. Consequently, no complete trace element distribution is possible even for the giant fields.

Table D.1

Sulfur and Nitrogen Content of The Giant U.S. Oil Fields

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
ALABAMA			
Citronelle	0.38	0.02	6,390
ALASKA			
Granite Point	0.02	0.039	5,552
McArthur River	0.16	0.160	40,683
Middle Ground Shoal	0.05	0.119	11,277
Prudhoe Bay (North Slope)	1.07	0.23	1,076
Swanson River	0.16	0.203	11,709
APPALACHIAN			
Allegany	0.12	0.028	388
Bradford	0.11	0.010	2,470
ARKANSAS			
Magnolia	0.90	0.02	850
Schuler and East	1.55	0.112	800
Smackover	2.10	0.08	2,800
CALIFORNIA			
SAN JOAQUIN VALLEY			
Belridge South	0.23	0.773	9,211
Buena Vista	0.59	--	5,429
Coalinga	0.43	0.303	7,866
Coalinga Nose	0.25	0.194	4,752
Coles Levee North	0.39	0.309	1,006
Cuyama South	0.42	0.337	2,034
Cymric	1.16	0.63	3,345
Edison	0.20	0.446	1,417
Elk Hills	0.68	0.472	951
Fruitvale	0.93	0.527	1,109
Greeley	0.31	0.266	761
Kern Front	0.85	0.676	3,440
Kern River	1.19	0.604	25,542
Kettleman North Dome	0.40	0.212	840
Lost Hills	0.33	0.094	2,328
McKittrick - Main Area	0.96	0.67	5,348
Midway Sunset	0.94	0.42	33,583
Mount Poso	0.68	0.475	1,378
Rio Bravo	0.35	0.158	425
COASTAL AREA			
Carpenteria Offshore	--	--	5,295
Cat Canyon West	5.07	0.54	2,705
Dos Cuadras	--	--	27,739
Elwood	--	--	108

* Oil and Gas Journal, January 31, 1972 pp. 95-100.

Table D.1 (Cont'd)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
Orcutt	2.48	0.525	2,173
Rincon	0.40	0.48	4,580
San Ardo	2.25	0.913	9,939
Santa Ynez***	--	--	--
Santa Maria Valley	4.99	0.56	1,966
South Mountain	2.79	--	1,962
Ventura	0.94	0.413	10,188
LOS ANGELES BASIN			
Beverly Hills	2.45	0.612	8,400
Brea Olinda	0.75	0.525	4,228
Coyote East	0.95	0.336	864
Coyote West	0.82	0.347	2,436
Dominguez	0.40	0.360	1,717
Huntington Beach	1.57	0.648	16,249
Inglewood	2.50	0.640	3,992
Long Beach	1.29	0.55	3,183
Montebello	0.68	0.316	740
Richfield	1.86	0.575	1,910
Santa Fe Springs	0.33	0.271	953
Seal Beach	0.55	0.394	1,468
Torrance	1.84	0.555	1,338
Wilmington	1.44	0.65	72,859
COLORADO			
Rangely	0.56	0.073	10,040
FLORIDA			
Jay	0.32	0.002	370
ILLINOIS			
Clay City	0.19	0.082	4,650
Dale	0.15	0.080	690
Loudon	0.27	0.097	4,420
New Harmony	0.23	0.158	2,740
Salem	0.17	0.102	3,360
KANSAS			
Bemis-Shutts	0.57	0.162	2,590
Chase-Silica	0.44	0.13	1,600
Eldorado	0.18	0.085	1,500
Hall-Gurney	0.34	0.108	2,480
Kraft-Prusa	0.27	0.171	3,200
Trapp	0.41	0.076	1,930
LOUISIANA			
NORTH			
Black Lake	--	--	--
Caddo-Pine Island	0.37	0.026	3,500
Delhi	0.82	0.053	5,870
Haynesville (Ark.-La.)	0.66	0.022	2,730
Homer	0.83	0.081	330
Lake St. John	0.17	--	1,170
Rodessa (La.-Tex.)	0.46	0.032	900

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* Oil and Gas Journal, January 31, 1972, pp. 95-100.

*** Undeveloped field, Santa Barbara Channel. Uncorroborated estimate of reserves of 1 to 3 billion bbl.

Table D.1 (Cont'd)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
OFFSHORE			
Bay Marchand Block 2 (Incl. onshore)	0.46	0.11	30,806
Eugene Island Block 126	0.15	0.030	5,621
Grand Isle Block 16	0.18	0.04	21,681
Grand Isle Block 43	--	--	22,776
Grand Isle Block 47	0.23	0.04	4,271
Main Pass Block 35	0.19	0.071	3,504
Main Pass Block 41	0.16	0.025	18,469
Main Pass Block 69	0.25	0.098	12,775
Ship Shoal Block 208	0.38	0.02	10,038
South Pass Block 24 (Incl. onshore)	0.26	0.068	20,330
South Pass Block 27	0.18	0.049	21,425
Timbalier S. Block 135	0.66	0.088	13,578
Timbalier Bay	--	--	
(Incl. onshore)	0.33	0.081	30,988
West Delta Block 30	0.33	0.09	26,390
West Delta Block 73	--	--	15,987
SOUTH, ONSHORE			
Avery Island	0.12	--	3,400
Bay De Chene	0.27	0.060	6,643
Bay St. Elaine	0.39	0.04	7,775
Bayou Sale	0.16	--	5,293
Black Bay West	0.19	0.04	9,892
Caillou Island (Incl. offshore)	0.23	0.04	31,828
Cote Blanche Bay West	0.16	0.033	15,658
Cote Blanche Island	0.10	0.01	8,797
Delta Farms	0.26	0.055	1,278
Garden Island Bay	0.22	0.06	16,096
Golden Meadow	0.18	--	2,738
Grand Bay	0.31	--	6,680
Hackberry East	0.30	0.054	2,226
Hackberry West	0.29	--	3,760
Iowa	0.20	0.039	876
Jennings	0.26	--	292
Lafitte	0.30	--	10,877
Lake Barre	0.14	0.02	7,592
Lake Pelto	0.21	0.035	4,891
Lake Salvador	0.14	0.02	4,380
Lake Washington (Incl. offshore)	0.37	0.146	10,913
Leeville	0.20	0.019	4,343
Paradis	0.23	--	1,898
Quarantine Bay	0.27	0.061	7,117
Romere Pass	0.30	--	3,759
Venice	0.24	--	5,475
Vinton	0.34	0.044	2,299
Weeks Island	0.19	--	10,183
West Bay	0.27	0.071	9,563

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* Oil and Gas Journal, January 31, 1972, pp. 95-100.

Table D.1 (Cont'd)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Product (Thousands of Barrels)*
MISSISSIPPI			
Baxterville	2.71	0.111	9,300
Heidelberg	3.75	0.112	3,450
Tinsley	1.02	0.08	2,450
MONTANA			
Bell Creek	0.24	0.13	5,950
Cut Bank	0.80	0.055	5,180
NEW MEXICO			
Caprock and East	0.17	0.034	905
Denton	0.17	0.014	2,350
Empire Abo	0.27	0.014	9,520
Eunice	1.14	0.071	1,330
Hobbs	1.41	0.08	5,700
Maljamar	0.55	0.062	6,040
Monument	1.14	0.071	3,720
Vacuum	0.95	0.075	17,030
NORTH DAKOTA			
Beaver Lodge	0.24	0.019	3,140
Tioga	0.31	0.016	1,790
OKLAHOMA			
Allen	0.70	0.21	2,920
Avant	0.18	--	365
Bowlegs	0.24	0.140	2,260
Burbank	0.24	0.051	5,240
Cement	0.47	0.152	2,370
Cushing	0.22	0.08	4,300
Earlsboro	0.47	--	765
Edmond West	0.21	0.045	730
Eola-Robberson	0.35	0.115	4,850
Fitts	0.27	--	1,420
Glenn Pool	0.31	0.096	2,480
Golden Trend	0.15	0.15	12,330
Healdton	0.92	0.15	4,600
Hewitt	0.65	0.148	5,660
Little River	0.28	0.065	440
Oklahoma City	0.16	0.079	1,750
Seminole, Greater	0.30	0.016	1,640
Sho-Vel-Tum	1.18	0.27	36,500
Sooner Trend	--	--	15,240
St. Louis	0.11	0.04	1,350
Tonkawa	0.16	0.033	290

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* Oil and Gas Journal, January 31, 1972, pp. 95-100.

Table D.1 (Cont'd)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
TEXAS			
DISTRICT 1			
Big Wells	--	--	5,840
Darst Creek	0.78	0.075	1,971
Luling-Branyon	0.86	0.110	1,679
DISTRICT 2			
Greta	0.17	0.038	3,577
Refugio	0.11	0.027	657
Tom O'Connor	0.17	0.038	23,360
West Ranch	0.14	0.029	17,009
DISTRICT 3			
Anahuac	0.23	0.041	9,052
Barbers Hill	0.27	0.06	766
Conroe	0.15	0.022	12,994
Dickison-Gillock	0.82	0.014	2,920
Goose Creek and East	0.13	0.028	1,095
Hastings E&W	0.20	0.03	17,191
High Island	0.26	0.048	2,081
Hull-Merchant	0.35	0.081	1,643
Humble	0.46	0.097	1,241
Liberty South	0.14	0.044	949
Magnet Withers	0.19	0.033	3,869
Old Ocean	0.14	0.029	1,132
Raccoon Bend	0.19	0.048	2,409
Sour Lake	0.14	0.016	1,058
Spindletop	0.15	0.03	328
Thompson	0.25	0.029	12,885
Webster	0.21	0.046	16,206
West Columbia	0.21	0.055	1,351
DISTRICT 4			
Agua Duke-Stratton	<.1	0.015	2,518
Alazan North	0.04	0.014	3,723
Borregas	<.1	0.029	4,818
Government Wells N.	0.22	0.043	511
Kelsey	0.13	0.008	6,059
La Gloria and South	<.1	0.008	936
Plymouth	0.15	0.049	986
Seeligson	<.1	0.015	6,424
Tijerina-Canales-Blucher	<.1	0.010	5,986
White Point East	0.13	0.02	1,606
DISTRICT 5			
Mexia	0.20	0.048	109
Powell	0.31	0.054	109
Van and Van Shallow	0.8	0.039	12,337

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* Oil and Gas Journal, January 31, 1972, pp. 95-100.

Table D.1 (Cont'd)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
DISTRICT 6			
East Texas	0.32	0.066	71,139
Fairway	0.24	--	14,271
Hawkins	2.19	0.076	29,054
Neches	0.13	0.083	3,942
New Hope	0.46	0.007	292
Quitman	0.92	0.036	3,103
Talco	2.98	--	4,380
DISTRICT 7-C			
Big Lake	0.26	0.071	474
Jameson	<.1	0.034	1,387
McCamey	2.26	0.139	985
Pegasus	0.73	0.200	4,052
DISTRICT 8			
Andector	0.22	0.033	5,694
Block 31	0.11	0.032	6,242
Cowden North	1.89	0.095	9,782
Cowden South, Foster, Johnson	1.77	0.127	14,198
Dollarhide	0.39	0.074	7,592
Dora Roberts	<.1	0.023	3,066
Dune	3.11	0.111	11,425
Emma and Triple N	<.1	0.025	3,030
Fuhrman-Mascho	2.06	0.085	1,935
Fullerton	0.37	0.041	6,607
Goldsmith	1.12	0.079	20,951
Headlee and North	<.1	0.083	1,460
Hendrick	1.73	0.094	766
Howard Glasscock	1.92	0.096	6,606
Iatan East	1.47	0.120	3,687
Jordan	1.48	0.10	3,212
Kermit	0.94	0.092	2,007
Keystone	0.57	0.042	8,322
McElroy	2.37	0.080	9,015
Means	1.75	0.205	7,921
Midland Farms	0.13	0.030	6,059
Penwell	1.75	0.205	2,044
Sand Hills	2.06	0.085	6,606
Shafter Lake	0.25	0.041	2,956
TXL	0.36	0.067	4,854
Waddell	1.69	0.098	4,453
Ward South	1.12	0.08	803
Ward Estes North	1.17	0.107	10,184
Yates	1.54	0.150	13,359

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* Oil and Gas Journal, January 31, 1972, pp. 95-100.

Table D.1 (Cont'd)

State/Region and Field	Sulfur, Weight Percent	Nitrogen, Weight Percent	1971 Production (Thousands of Barrels)*
DISTRICT 8-A			
Cogdell Area	0.38	0.063	14,235
Diamond M	0.20	0.131	7,373
Kelly-Snyder	0.29	0.066	52,487
Levelland	2.12	0.136	9,746
Prentice	2.64	0.117	5,913
Robertson	1.37	0.100	2,774
Russell	0.77	0.078	4,234
Salt Creek	0.57	0.094	9,271
Seminole	1.98	0.106	9,125
Slaughter	2.09	--	35,515
Spraberry Trend	0.18	0.173	18,688
Wasson	1.14	0.065	51,210
DISTRICT 9			
KMA	0.31	0.068	2,920
Walnut Bend	0.17	0.05	3,942
DISTRICT 10			
Panhandle	0.55	0.067	14,235
UTAH			
Greater Aneth	0.20	0.059	7,660
Greater Redwash	0.11	0.255	5,800
WYOMING			
Elk Basin (Mont.-Wyo.)	1.78	0.185	14,380
Garland	2.99	0.290	3,500
Grass Creek	2.63	0.311	3,760
Hamilton Dome	3.04	0.343	4,500
Hilight	--	--	11,300
Lance Creek	0.10	0.055	325
Lost Soldier	1.21	0.076	4,820
Oregon Basin	3.44	0.356	12,260
Salt Creek	0.23	0.109	11,750

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* Oil and Gas Journal, January 31, 1972, pp. 95-100.

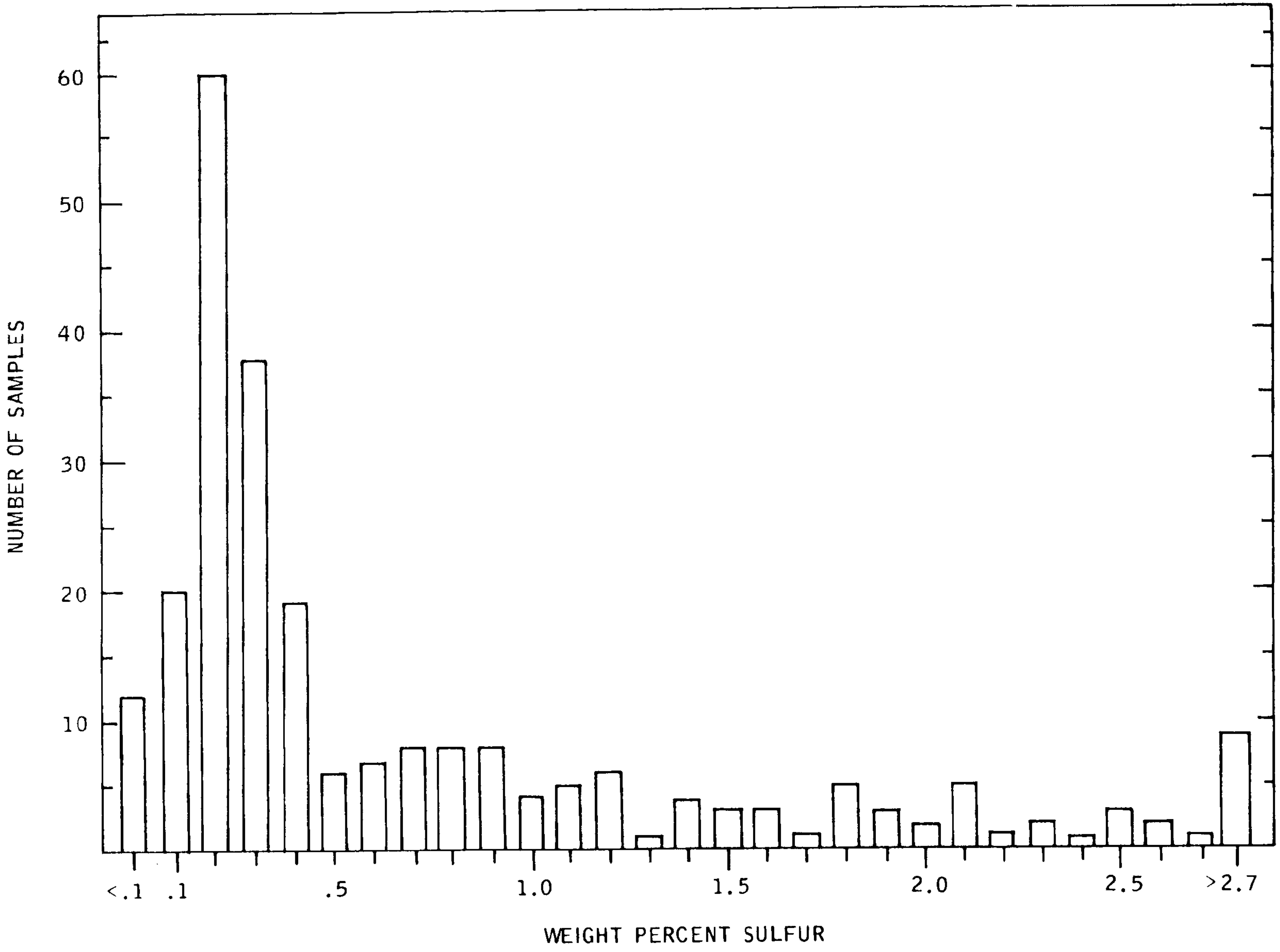

Figure D.1

Fequency Distribution of Sulfur Content in Crude Oils of U.S. Giant Oil Fields

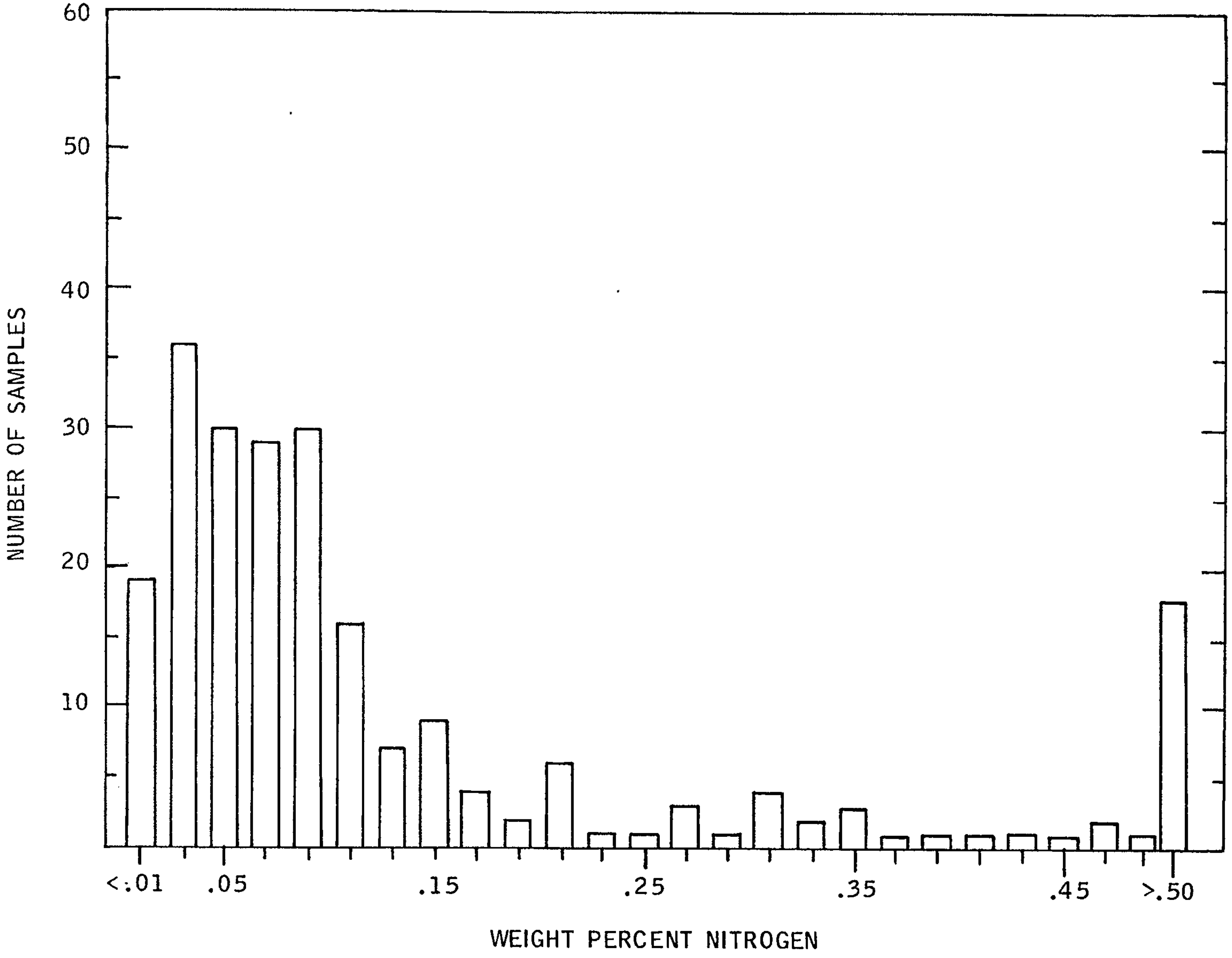

Figure D.2

Frequency Distribution of Nitrogen Content in Crude Oils of U.S. Giant Oil Fields

A number of more or less classical instrumental techniques has been used to obtain much of the trace element data that are available. These techniques include flame photometry, atomic absorption, emission spectroscopy, spectrochemical (colorimetric) analysis and x-ray fluorescence. Although most available trace element data especially on vanadium and nickel have been obtained using these techniques, considerable data are now being accumulated on many elements using activation analysis, a nuclear technique. As some of these data are at variance with those obtained using the more classical methods, activation analysis data are presented in a separate section.

Some trace element data on petroleum were published a number of years ago. It is possible that as a greater understanding of preparative and analytical techniques has developed, the ability to obtain reliable data has increased. It is likely, therefore, that the more recent data are more accurate although this is not necessairly so.

Virtually all of the available trace element data for U.S. oil fields were used to compile Table D.2. Included are the state, field, analytical method used if available, year of publication and the source of the data. Data are presented from all fields even those that are not significant producers. Conflicting data are also present for certain fields. Data from numerous published sources were utilized irrespective of analytical method or year of publication. No data were averaged. The search was limited to the following elements: V, Ni, Fe, As, Be, Cd, Hg, Se, Sb, Ba, Cr, Pb, Mn, Mo, Te, Sn. However, for the most part, data were found only for 10 of these elements. Data are presented in the order V, Ni, Fe, Ba, Cr, Mn, Mo, Sn plus the available data for other elements.

The trace element data presented in Table D.2 indicate that, in general, the lowest metal content domestic crudes are from the coastal and offshore fields of Louisiana and Texas. The highest metal content crudes are found in California. This parallels the observations made for sulfur and nitrogen. It is not surprising that the levels of nitrogen, vanadium and nickel should vary together because some nitrogen and some of these (and other) metals are frequently bound into a prophyrin ring. This type of chelate coordination complex is known for its high stability. All of the volatile metal compounds present in crude oil are metalloporphyrins. The nature of the nonvolatile metal compounds is not completely understood although they too may be complexes with more than one porphyrin ring or simple porphyrins with sizeable asphaltic side chains.

Data obtained from the Cymric field of California's San Joaquin Valley are worthy of comment. The high mercury levels reported for this field are in no way representative of domestic production in general or of California production in particular. Cymric's high mercury content can be attributed to its location on the southeast prolongation of the main mercury belt east of the San Andreas fault. It is, therefore, not surprising that the mercury ore cinnabar found in this region is saturated with hydrocarbons and that crude oil hydrocarbons appear to be saturated with mercury.

Table D.2

Trace Element Content of U.S. Crude Oils

State and Field	Trace Element, ppm									Analytical Method	Year
	V	Ni	Fe	Ba	Cr	Mn	Mo	Sn	Hg		
ALABAMA											
Toxey	9	14								Emission spectroscopy	1971
Toxey	10	16								Emission spectroscopy	1971
ALASKA											
Kuparuk, Prudhoe Bay	32	13								Emission spectroscopy	1971
Kuparuk, Prudhoe Bay	28	12								Emission spectroscopy	1971
McArthur River, Cook Inlet	nd	nd								Emission spectroscopy	1971
Prudhoe Bay	31	11								Emission spectroscopy	1971
Put River, Prudhoe Bay	16	6								Emission spectroscopy	1971
Redoubt Shoal, Cook Inlet	nd	4								Emission spectroscopy	1971
Trading Bay, Cook Inlet	nd	nd								Emission spectroscopy	1971
ARKANSAS											
Brister, Columbia	nd	nd								Emission spectroscopy	1971
El Dorado, East	12	11								Emission spectroscopy	1971
Schuler	15.2	10.3	1.2	<1	<1	<1	nd	nd		Emission spectroscopy	1961
Smackover	nd	4								Emission spectroscopy	1971
Stephens-Smart	18.5	22.7	6.3	<1	<1	<1	nd	<1		Emission spectroscopy	1961
Tubal, Union	nd	nd								Emission spectroscopy	1971
West Atlanta	<1	<1	<1	<1	<1	<1	nd	nd		Emission spectroscopy	1961
CALIFORNIA											
Ant Hill	14.3	66.5	28.5	<1	<1	nd	nd	nd		Emission spectroscopy	1961
Arwin	9.0	28.0								Emission spectroscopy	1956
Bradley Sands	134.5	--								(1)	1958
Cat Canyon	128	75								Emission spectroscopy	1971
Cat Canyon	209	102								Emission spectroscopy	1971
Coalinger	5.1	21.9	5.1	<1	<1	<1	<1	nd		Emission spectroscopy	1961
Coal Oil Canyon	6.0	20.0								Emission spectroscopy	1956
Coles Levee	11.0	31.0								Emission spectroscopy	1956
Coles Levee	2.2	21.6	2.2	<1	<1	nd	<1	nd		Emission spectroscopy	1961
Cuyama	10.0	32.0								Emission spectroscopy	1956
Cymric	30.0	43.0								Emission spectroscopy	1956
Cymric	0.8	2.3	2.0							Emission spectroscopy	1961
Cymric									2.6 2.4 1.9	Emission spectroscopy	1961
Cymric	0.6	1.1	2.0							Emission spectroscopy	1961
Cymric									21.0 14.0 2.9	Emission spectroscopy	1961
Cymric	1.0	2.0	2.0							Emission spectroscopy	1961
Edison	6.0	11.0								Emission spectroscopy	1956
Elk Hills	8.3	38.5	38.5	<1	<1	<1	<1	nd		Emission spectroscopy	1961
Elwood South	nd	11								Emission spectroscopy	1971
Gibson	37	125								X-ray fluorescence	1969
Gots Ridge	188	80								Emission spectroscopy	1971
Helm	14.0	27.0								Emission spectroscopy	1956
Helm	2.5	10.5	2.5	<1	<1	nd	nd	<1		Emission spectroscopy	1961
Huntington Beach	29	104								Emission spectroscopy	1971
Inglewood	125.7	125.7	125.7	<1	1.3	nd	<1	nd		Emission spectroscopy	1961
Kettleman	34.0	35.0	24.0							Colorimetric	1952
Kettleman Hills	11.0	24.0								(1)	1958
Las Flores	106.5	--								(1)	1958
Lompoc	37.6	--								(1)	1958
Lompoc	199	90								Emission spectroscopy	1971
Lost Hills	39.0	8.0								Emission spectroscopy	1956
Midway	82.6	82.6	82.6	1.8	1.8	<1	<1	nd		Emission spectroscopy	1961
Nicolai	246.5	--								(1)	1958
North Belridge	--	107								X-ray fluorescence (inter. std)	1959
North Belridge	--	80								Colorimetric	1959
North Belridge	--	83								Emission spectroscopy	1959
North Belridge	23	83								X-ray fluoresc. (ext. std.)	1960
Orcutt	162.5	--								(1)	1958
Oxnard	403.5	--								(1)	1958
Purisma	218.5	--								(1)	1958
Raisin City	8.0	21.0								Emission spectroscopy	1956

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(1) Not specified.

nd Sought but not detected.

Table D.2 (Cont'd)

	Trace Element, ppm										
State and Field	V	Ni	Fe	Ba	Cr	Mn	Mo	Sn	As	Analytical Method	Year
Rio Bravo	--	2.2								X-ray fluorescence (int. std.)	1962
Rio Bravo	--	--	2.6							X-ray fluorescence (int. std.)	1960
Rio Bravo	--	--	2.5							Emission spectroscopy	1960
Russell Ranch	12.0	26.0								Emission spectroscopy	1956
San Joaquin	44.8	--								(1)	1958
Santa Maria	223	97	17							Colorimetric	1952
Santa Maria	202	--								(1)	1958
Santa Maria	180	106								Emission spectroscopy	1956
Santa Maria	280	130								Emission spectroscopy	1960
Santa Maria Valley	207	97								Emission spectroscopy	1971
Santa Maria Valley	240	--								X-ray fluorescence (int. std.)	1960
Santa Maria Valley	280	--								X-ray fluorescence (int. std.)	1960
Santa Maria Valley	174	174	1.7	<1	1.7	<1	4.0	nd		Emission spectroscopy	1961
Signal Hill	28	--								(1)	1958
Signal Hill	25	57								Emission spectroscopy	1956
Tejon Hills	64	44								Emission spectroscopy	1956
Ventura	42	51								Emission spectroscopy	1956
Ventura	49	33	31							Colorimetric	1952
Ventura Avenue	25.2	--								(1)	1958
Wheeler Ridge	7	1.9								Emission spectroscopy	1956
Wilmington	43	61								Emission spectroscopy	1956
Wilmington	41	46	28							Colorimetric	1952
Wilmington	53	51								Emission spectroscopy	1971
Wilmington	--	53								X-ray fluorescence (int. std.)	1959
Wilmington	--	60								X-ray fluorescence (int. std.)	1959
Wilmington	46	60								Emission spectroscopy	1960
Wilmington	36.0	84	36	3.6	<1	nd	1	nd		Emission spectroscopy	1961
COLORADO											
Badger Creek	<1	<1	<1	<1	<1	<1	<1	<1		Emission spectroscopy	1961
Badger Creek	<1	<1	<1	<1	nd	<1	<1	<1		Emission spectroscopy	1961
Gramps	<1	<1	<1	<1	<1	<1	<1	<1		Emission spectroscopy	1961
Gramp	<1	<1	<1	<1	<1	<1	<1	<1		Emission spectroscopy	1961
Hiawatha	<1	<1	<1	<1	<1	<1	nd	<1		Emission spectroscopy	1961
Moffat Dome	<1	<1	<1	<1	<1	<1	<1	<1		Emission spectroscopy	1961
Rangely	2.7	<1	<1	<1	<1	<1	nd	<1		Emission spectroscopy	1961
Rangely	<1	<1	6.6	<1	<1	<1	<1	<1		Emission spectroscopy	1961
Rangely	<1	<1	2.7	<1	<1	<1	<1	<1		Emission spectroscopy	1961
Seep	0.24	4.70								Emission spectroscopy	1956
White River Area	<1	<1	96.0	<1	<1	2.2	nd	2.2		Emission spectroscopy	1961
FLORIDA											
Jay	nd	1								Emission spectroscopy	1971
ILLINOIS											
Loudon	1.22	0.62	0.57							Emission spectroscopy	1952
Loudon	0.56	--								(1)	1958
KANSAS											
Brewster	2.1	1.3	<1	<1	<1	nd	nd	nd		Emission spectroscopy	1961
Brewster	<1	3.9	<1	<1	<1	<1	nd	nd		Emission spectroscopy	1961
Brock	1	2.4	10.2	<1	<1	<1	<1	nd		Emission spectroscopy	1961
Coffeyville	3.8	1.2	7.2	<1	<1	<1	<1	<1		Emission spectroscopy	1961
Cunningham	44.2	9.9	<1	<1	<1	<1	nd	nd		Emission spectroscopy	1961
Cunningham	24.0	24.0	<1	<1	<1	<1	nd	nd		Emission spectroscopy	1961
Iola	15.6	9.0	3.9	2	<1	<1	nd	nd		Emission spectroscopy	1961
Iola	4.5	4.5	<1	<1	<1	<1	nd	nd		Emission spectroscopy	1961
"Kansas-1"	--	>5							< .021	Emission spectroscopy	1966
"Kansas-2"	--	>21							< .08	Emission spectroscopy	1966
McLouth	<1	6.3	<1	<1	<1	<1	<1	nd		Emission spectroscopy	1961
Otis Albert	21.3	6.0	<1	<1	<1	<1	<1	nd		Emission spectroscopy	1961
Otis Albert	39.0	9.1	9.1	<1	<1	<1	<1	<1		Emission spectroscopy	1961
Pawnee Rock	12.3	3.4	<1	<1	<1	<1	nd	nd		Emission spectroscopy	1961
Rhodes	145	--								X-ray fluorescence (int. std.)	1960
Rhodes	165	--								Emission spectroscopy	1960
Rhodes	133	--								X-ray fluorescence (int. std.)	1960
Rhodes	--	36								X-ray fluorescence (int. std.)	1960
Rhodes	--	38								Emission spectroscopy	1960
Rhodes	--	32								X-ray fluorescence (int. std.)	1959
Solomon	30	7	<1	<1	<1	<1	nd	nd		Emission spectroscopy	1961

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(1) Not specified

nd Sought but not detected

Table D.2 (Cont'd)

	Trace Elements, ppm										
State and Field	V	Ni	Fe	Ba	Cr	Mn	Mo	Sn	As	Analytical Method	Year
LOUISIANA											
Bay Marchard	nd	2								Emission spectroscopy	1971
Colquitt, Clairborne	nd	nd								Emission spectroscopy	1971
Colquitt, Clairborne	nd	nd								Emission spectroscopy	1971
Colquitt, Calirborne (Smackover B)	nd	nd								Emission spectroscopy	1971
Delta (West) Offshore, Block 117	nd	2								Emission spectroscopy	1971
Delta (West) Block 27	nd	2								Emission spectroscopy	1971
Delta (West) Block 41	nd	2								Emission spectroscopy	1971
Eugene Island, Offshore, Block 276	4	nd								Emission spectroscopy	1971
Eugene Island, Offshore, Block 238	nd	nd								Emission spectroscopy	1971
Lake Washington	nd	4								Emission spectroscopy	1971
Main Pass, Block 6	nd	3								Emission spectroscopy	1971
Main Pass, Block 41	nd	1								Emission spectroscopy	1971
Olla	<1	5.56	0.07							Emission spectroscopy	1952
Ship Shoal, Offshore, Block 176	nd	nd								Emission spectroscopy	1971
Ship Shoal, Offshore, Block 176	nd	nd								Emission spectroscopy	1971
Ship Shoal, Block 208	nd	2								Emission spectroscopy	1971
Shongaloo, N. Red Rock	nd	nd								Emission spectroscopy	1971
South Pass, Offshore, Block 62	nd	4								Emission spectroscopy	1971
Timbalier, S., Offshore, Block 54	nd	nd								Emission spectroscopy	1971
MICHIGAN											
Trent	—	0.23								Emission spectroscopy	1956
MISSISSIPPI											
Baxterville, Lamar and Marion	40	15								Emission spectroscopy	1971
Heidelberg	15.35	6.02	1.78							Emission spectroscopy	1952
Mississippi	—	.7							<.003	Emission spectroscopy	1966
Tallhalla Creek, Smith	nd	nd								Emission spectroscopy	1971
Tallhalla Creek, Smith	nd	nd								Emission spectroscopy	1971
Tallhalla Creek, Smith (Smackover)	nd	nd								Emission spectroscopy	1971
Tingley, Yazoo	7	5								Emission spectroscopy	1971
MONTANA											
Bell Creek	nd	2								Emission spectroscopy	1971
Big Wall	24	13.2		<1	<1	<1	<1	nd		Emission spectroscopy	1961
Soap Creek	132	13.2		<1	<1	<1	<1	nd		Emission spectroscopy	1961
NEW MEXICO											
Rattlesnake	<1	<1	<1	<1	<1	<1	<1	nd		Emission spectroscopy	1961
Rattlesnake	<1	<1	<1	<1	<1	<1	<1	nd		Emission spectroscopy	1961
Table Mesa	<1	<1	9.9	<1	<1	<1	<1	<1		Emission spectroscopy	1961
OKLAHOMA											
Allurve (Nowata)	<1	<1	1.4	6.0	<1	<1	<1	<1		Emission spectroscopy	1961
Allurve (Nowata)	1.1	1.2	51.0	11.9	<1	<1	nd	<1		Emission spectroscopy	1961
Allurve (Nowata)	<1	6.0	1.4	6.0	<1	<1	<1	<1		Emission spectroscopy	1961
Bechel	--	0.11								Emission spectroscopy	1956
Burbank	nd	nd								Emission spectroscopy	1971
Cary	0.15	0.65								Emission spectroscopy	1956
Chelsea (Nowata)	1.4	1.4	27.0	6.3	<1	<1	nd	nd		Emission Spectroscopy	1961
Chelsea (Nowata)	<1	<1	6.0	<1	<1	<1	<1	<1		Emission Spectroscopy	1961
Chelsea (Nowata)	<1	<1	<1	3.0	<1	<1	nd	<1		Emission Spectroscopy	1961
Cheyarha	0.32	0.70								Emission spectroscopy	1956
Cheyarha	0.34	0.95								Emission spectroscopy	1956
Cheyarha	0.21	0.36								Emission spectroscopy	1956
Cheyarha	0.36	4.10								Emission spectroscopy	1956
Cromwell	0.23	0.80								Emission spectroscopy	1956
Cromwell	0.11	0.23								Emission spectroscopy	1956
Cromwell	0.13	0.23								Emission spectroscopy	1956
Cromwell	--	0.27								Emission spectroscopy	1956
Cromwell	0.12	0.42								Emission spectroscopy	1956
Cromwell	--	0.23								Emission spectroscopy	1956
Dill	0.23	2.10								Emission spectroscopy	1956
Dover, Southeast	nd	nd								Emission spectroscopy	1971
Dustin	--	0.36								Emission spectroscopy	1956
E. Lindsay	--	0.10								Emission spectroscopy	1956
E. Seminole	0.23	0.46								Emission spectroscopy	1956
E. Yeager	--	0.12								Emission spectroscopy	1956
Fish	—	0.23								Emission spectroscopy	1956
Glen Pool	—	—	5.0							X-ray fluorescence (int. std.)	1960

(1) Not specified nd Sought but not detected

Table D.2 (Cont'd)

	Trace Element, ppm									
State and Field	V	Ni	Fe	Ba	Cr	Mn	Mo	Sn	Analytical Method	Year
Grief Creek	0.10	0.42							Emission spectroscopy	1956
Hawkins	2.10	8.50							Emission spectroscopy	1956
Hawkins	0.72	3.50							Emission spectroscopy	1956
Horns Corner	--	0.70							Emission spectroscopy	1956
Katie	0.17	0.52							Emission spectroscopy	1956
Katie	0.48	1.60							Emission spectroscopy	1956
Katie	0.29	1.00							Emission spectroscopy	1956
Katie	0.24	1.00							Emission spectroscopy	1956
Kendrick	<1	<1	<1	<1	<1	<1	nd	nd	Emission spectroscopy	1961
Konawa	0.10	0.65							Emission spectroscopy	1956
Laffoon	44.0	20.2	1.5	<1	<1	<1	nd	nd	Emission spectroscopy	1961
Little River	0.17	1.10							Emission spectroscopy	1956
Middle Gilliland	<1	<1	<1	<1	<1	<1	nd	nd	Emission spectroscopy	1961
Naval Reserve	<1	<1	<1	<1	<1	<1	nd	nd	Emission spectroscopy	1961
New England	<1	<1	<1	nd	<1	<1	nd	nd	Emission spectroscopy	1961
N. Dill	0.13	1.45							Emission spectroscopy	1956
N. E. Castle Ext.	0.29	1.50							Emission spectroscopy	1956
N. E. Elmore	0.15	0.60							Emission spectroscopy	1956
N. E. Elmore	0.17	0.70							Emission spectroscopy	1956
N. Okemah	0.11	0.70							Emission spectroscopy	1956
N. W. Horns Corner	--	0.10							Emission spectroscopy	1956
Olympia	0.88	2.40							Emission spectroscopy	1956
Osage City	2.9	1.6	6.9	nd	<1	<1	nd	nd	Emission spectroscopy	1961
S. W. Maysville	1.36	2.10							Emission spectroscopy	1956
S. W. Maysville	0.25	1.10							Emission spectroscopy	1956
Tatums	--	57							X-ray fluorescence	1959
Tatums	--	56							Emission spectroscopy	1959
Tatums	148	71							X-ray fluorescence (ext. std.)	1960
Weleetka	--	0.10							Emission spectroscopy	1956
W. Holdenville	0.13	0.46							Emission spectroscopy	1956
W. Wewoka	0.14	0.42							Emission spectroscopy	1956
Wewoka	--	0.15							Emission spectroscopy	1956
Wewoka Lake	0.33	0.95							Emission spectroscopy	1956
Wewoka Lake	0.15	0.30							Emission spectroscopy	1956
Wewoka Lake	0.18	0.27							Emission spectroscopy	1956
Wildhorse	2.6	1	<1	nd	nd	<1	nd	nd	Emission spectroscopy	1961
Wynona	<1	<1	1.8	<1	<1	<1	nd	<1	Emission spectroscopy	1961
Wynona	<1	<1	<1	<1	nd	<1	nd	<1	Emission spectroscopy	1961
TEXAS										
Anahuac	0.2	1.1	--						Emission spectroscopy	1958
Brantley-Jackson, Hopkins	nd	nd	--						Emission spectroscopy	1971
Brantley-Jackson, Smackover	nd	nd	--						Emission spectroscopy	1971
Conroe	0.008	<1	0.81						Chemical (V); emission (Ni)	1952
East Texas	4	3	--						Emission spectroscopy	1971
East Texas	1.2	0.88	0.51						Emission spectroscopy	1952
East Texas	1.05	1.69	--						Colorimetric	1952
East Texas	1.2	1.7	3.2						Colorimetric	1952
Edgewood, Van Zandt	nd	nd	--						Emission spectroscopy	1971
Finley	2.6	2	5.7	<1	<1	<1	<1	<1	Emission spectroscopy	1961
Jackson	0.9	1.8	4.4						Colorimetric	1952
Lake Irammel, Nolan			--						Emission spectroscopy	1971
Mirando	1.4	1.9	7.6						Colorimetric	1952
Panhandle, Carson	8	3	--						Emission spectroscopy	1971
Panhandle, Hutchinson	6	5	--						Emission spectroscopy	1971
Panhandle, West Texas	8.4	--	--						(1)	1952
Refugio	0.68	0.70	0.34						Chemical	1952
Refugio, Light	0.56	--	--						(1)	1958
Salt Flat	8.3	1.43	1.71						Chemical	1952
Scurry County	0.8	1.0	3.4						Colorimetric	1952
Sweden	0.8	0.6	--						Emission spectroscopy	1958
Talco	8.8	2.57	2.06						Chemical	1952
Talco	5.16	--	--						(1)	1958
Wasson	15	nd	--						Emission spectroscopy	1971
West Texas	23	9	--						X-ray fluoresc. spectro. (ext. std.) or emission spectroscopy	1960
West Texas	6.7	--	--						(1)	1952
West Texas	6.3	--	--						Emission spectroscopy	1956
West Texas	11.8,	3.8	--						Emission spectroscopy	1958
West Texas	8.5	4.2							Emission spectroscopy	1958
West Texas	8.96	--	--						(1)	1958
West Texas	7.9	4.8	5.1						Colorimetric	1952
West Texas (Imogene)	8.5	1.73	0.88						Chemical	1952
Yates-Pecos	7.8	2.6	0.11						Chemical	1952

---

(1) Not specified

nd Sought but not detected

Table D.2 (Cont'd)

State and Field	Trace Element, ppm								Analytical Method	Year
	V	Ni	Fe	Ba	Cr	Mn	Mo	Sn		
UTAH										
Duchesne	<1	<1	3.9	3.9	<1	<1	<1	<1	Emission spectroscopy	1961
Duchesne	<1	<1	1.4	<1	<1	<1	<1	<1	Emission spectroscopy	1961
Duchesne County	<1	12.3	12.3	2.9	<1	<1	nd	nd	Emission spectroscopy	1961
Red Wash	nd	nd	—						Emission spectroscopy	1971
Red Wash	nd	nd	—						Emission spectroscopy	1971
Roosevelt	<1	3.2	<1	<1	<1	<1	<1	<1	Emission spectroscopy	1961
Roosevelt	<1	5.4	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Virgin	14.4	14.4	3.4	<1	<1	<1	nd	<1	Emission spectroscopy	1961
Virgin	8.1	8.1	1.9	<1	<1	<1	nd	<1	Emission spectroscopy	1961
West Pleasant Valley	11.4	57	1140.0	26.6	1.1	11.4	2.7		Emission spectroscopy	1961
Wildcat	0.14	7.5							Emission spectroscopy	1956
WYOMING										
Beaver Creek	nd	nd							Emission spectroscopy	1971
Big Horn Mix	15.97	3.6	0.8						Emission spectroscopy	1952
Bison Basin	1.1	2.7	<1	<1	<1	<1	<1	<1	Emission spectroscopy	1961
Circle Ridge	48	11.2	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Corral Creek	59	11	—						Emission spectroscopy	1971
Crooks Gap	2.1	2.2	1.0	<1	<1	<1	<1	<1	Emission spectroscopy	1961
Dallas	66	15.4	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Dallas	66	66	1.5	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Derby	39	39	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Elk Basin	38	9.2	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Elk Basin	8.4	2	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Garland	36	24	3.6	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Grass Creek	106.4	28.9	1.1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Half Moon	98.6	27.8	1.7	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Half Moon	50.6	<1	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Hamilton Dome	106.4	26.6	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Hamilton Dome	55.2	8.6	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Hamilton Dome	106.4	24.3	2.7	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Little Mo	83	16	—						Emission spectroscopy	1971
Lost Soldier	<1	<1	<1	<1	<1	<1	<1	<1	Emission spectroscopy	1961
Lost Soldier	<1	<1	<1	<1	<1	<1	<1	<1	Emission spectroscopy	1961
Lost Soldier	<1	<1	<1	<1	<1	<1	<1	<1	Emission spectroscopy	1961
Mitchell Creek	72.0	72.0	7.2	<1	<1	<1	<1	nd	Emission spectroscopy	1961
North Oregon Basin	77.0	22.4	1.0	<1	<1	<1	<1	nd	Emission spectroscopy	1961
North Oregon Basin	72.0	14.8	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
North Oregon Basin	60.0	11.5	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Oil Mountain	144.0	33.6	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Pilot Butte	45.0	10.5	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Pilot Butte	24.0	5.6	<1	<1	<1	<1	nd	nd	Emission spectroscopy	1961
Pihe Ridge	nd	nd	—						Emission spectroscopy	1971
Prescott No. 3	21.0	7.1	—						(1)	1959
Recluse	nd	nd	—						Emission spectroscopy	1971
Roelis	88	15	—						Emission spectroscopy	1971
Salt Creek	84.0	8.4	<1	<1	<1	<1	nd	nd	Emission spectroscopy	1961
Salt Creek	1.4	1.4	<1	<1	<1	<1	nd	nd	Emission spectroscopy	1961
Salt Creek	<1	<1	23.4	<1	<1	<1	nd	nd	Emission spectroscopy	1961
Salt Creek	<1	3.9	3.9	<1	<1	<1	nd	nd	Emission spectroscopy	1961
Skull Creek	—	0.42							Emission spectroscopy	1956
South Casper Creek	12.9	3.0	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
South Fork	21.9	21.9	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
South Spring Creek	102.0	102.0	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
South Spring Creek	117.0	27.3	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Steamboat Butte	29.1	6.79	<1	<1	<1	<1	<1	nd	Emission spectroscopy	1961
Washakie	74.0	25.0	—						(1)	1934
Winkleman Dome	48.0	11.2	1	<1	<1	<1	<1	nd	Emission spectroscopy	1961

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(1) Not specified

nd Sought but not detected.

D.2 Shale Oil

The term oil shale covers a wide variety of fine-grained sedimentary rocks that contain organic material. Upon destructive distillation much of this organic material is released largely as an oil which is termed shale oil. The rock is only slightly soluble in organic solvents and frequently does not appear or feel oily. It is tough, elastic, resistant to fracture and has essentially no permeability or porosity.

The organic component of oil shale can be divided into two parts, a part that is soluble in organic solvents and a part that is not. It is the insoluble part, generally termed kerogen, which constitutes the bulk of the shale organic matter responsible for shale oil. The composition of kerogen varies considerably from shale deposit to deposit but it is thought to consist of largely cyclic polymeric material probably held together by cross linkages involving hetero atoms such as nitrogen, sulfur and oxygen.

There is no truly typical shale oil but shale oils have some properties in common. In general, most shale oils are black, waxy and possess high pour points. Relative to conventional crude oils, the nitrogen content of crude shale oil is high although the sulfur level is moderate.

Oil shales are widely distributed geographically. However, only certain deposits are considered to be sufficiently rich in kerogen to warrant commercial development. In the U.S. oil shale deposits are found in Tennessee and Nevada but the most important are in the Green River Formation of Colorado, Utah and Wyoming. The Green River formation has received attention as a possible source of fuels. Within this formation, shale deposits underlie an area of 17,000 square miles in four basins: the Piceance Creek basin of Colorado, the Unita basin of Utah and the Washakie and Green River basins of Wyoming.

The energy potential of the Green River formation has been estimated to be more than 1 trillion barrels of oil with 600 billion coming from easily accessible, richer deposits which contain more than 25 gallons of oil per ton of shale. Shale deposits vary in accessability from those at the surface to very deeply buried shales in the Unita basin. The outcrop called the Mahogany Ledge (because of its color) is the location of an experimental mine and consequently has been used to study mining and retorting methods. Most U.S. elemental shale oil analyses come from shale mined here. The oil shales of the Mahogany zone will probably be the first to be developed commercially.

Table D.3 presents sulfur and nitrogen data of crude shale oil obtained from shale deposits throughout the world. While many of the samples were retorted using different techniques, it has been found that generally the retorting method utilized has relatively little effect on the characteristics of the oil produced unless extreme

Table D.3

SULFUR AND NITROGEN CONTENT OF CRUDE SHALE OILS

Country	Formation/Location	Sulfur, weight per cent	Nitrogen, weight per cent
United States	Green River, Colorado	0.74	1.78
	Green River	0.69	2.13
	Green River	0.77	1.57
	Green River	0.51	2.10
	Green River	0.67	1.97
	Green River	0.72	1.73
	Green River	0.71	1.89
	Green River	0.64	1.95
	Green River*	1.10	1.73
	Green River	0.66	1.76
	Green River	0.59	1.96
	De Kalb County, Tenn.	3.38	0.88
Australia	Glen Davis, N.S.W.	0.56	0.52
Brazil	Paraiba Valley	0.41	0.98
China	Hwatien Mine, Manchuria	0.19	0.84
Estonia	Kukersite	1.10	0.10
France	Autun	0.51	0.90
	Severac	3.00	0.53
	Severac	3.40	0.65
	St. Hilaire	0.61	0.54
Israel	Um Barek	6.2	1.40
Lebanon	--	1.5	0.6
New Zealand	Orepuki	0.64	0.60
Scotland	--	0.35	0.77
South Africa	Boksburg, Transvaal	0.64	0.85
	Breyten, Transvaal	0.61	--
Spain	Puertollano	0.40	0.68
Sweden	Kvarntorp	1.65	0.68
Thailand	Maesod Area	0.41	1.10

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* Core drilling sample.

retorting conditions have been employed. Of the deposits listed, only the Green River can be considered to be a possible commercial source of fuels for consumption in the U.S. The others are included for the purposes of comparison.

Crude shale oil derived from the Green River formation possesses an unusually high nitrogen level. It has been found that generally the nitrogen content is higher and the sulfur level lower in the higher boiling shale oil fractions. As of this writing, no metal content data for shale oil appear to be available in the published literature. An unpublished analysis by the Bureau of Mines of shale oil obtained from Green River shale indicates that this oil is high in iron and low in vanadium and nickel. The results obtained were: vanadium, 0 ppm; nickel, 4 ppm; and iron 67 ppm. Most of the metals were associated with the asphaltene fraction.

The nitrogen compounds present in shale oil are particularly troublesome in processing and must be removed before shale can be converted into useful liquid or gaseous fuels. Nitrogen removal can be accomplished by severe hydrogen treatment which also reduces the sulfur content to a low level.

APPENDIX E

Table of Conversion Units

APPENDIX E

TABLE OF CONVERSION UNITS

To Convert From	To	Multiply By
Btu	Calories, kg	0.25198
Btu/pound	Calories, kg/kilogram	0.55552
Cubic feet/day	Cubic meters/day	0.028317
Feet	Meters	0.30480
Gallons/minute	Cubic meters/minute	0.0037854
Inches	Centimeters	2.5400
Pounds	Kilograms	0.45359
Pounds/Btu	Kilograms/calorie, kg	1.8001
Pounds/hour	Kilograms/hour	0.45359
Pounds/square inch	Kilograms/square centimeter	0.070307
Tons	Metric tons	0.90719
Tons/day	Metric tons/day	0.90719

In line with usage current when this work was begun, in this report M represents thousand and MM represents million.

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