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FUEL GAS ENVIRONMENTAL IMPACT

Industrial Environmental Research Laboratory
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FUEL GAS ENVIRONMENTAL IMPACT

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ABSTRACT

The program carried out under EPA Contract 68-02-1099 (from July 1, 1973, to November 1, 1974) evaluated the technical and economic feasibility of: (1) fixed-bed gasifiers (Bureau of Mines) and two-stage entrained-flow gasifiers (BCR) in combination with low- and high-temperature fuel gas cleanup systems, (2) advanced technology combined-cycle power systems, and (3) integrated gasification systems, cleanup processes and power systems. This follow-on extended the study to cover atmospheric pressure, oxygen-blown coal gasifiers (Koppers-Totzek) and pressurized, air-blown, partial-oxidation residual oil gasifiers (Shell/Texaco). Cleanup process modifications were made on paper to improve the efficiency of the integrated systems. Processes and systems considered were those using technology currently available for power station configurations which the Contractor judges could appear in commercial applications in the 1975-1978 time frame (first-generation systems) and those using technology potentially applicable in the 1980-decade time period (second-generation systems). The objective of this analysis of fuel gas environmental impact is the definition of combinations of: (1) fossil fuel gasification systems, (2) low- and high-temperature fuel gas cleanup processes, and (3) advanced-cycle power systems for central power stations that appear to result in the lowest practicable emissions of air, water, and solid pollutants consistent with the environmental constraints, while producing low-cost electrical power.

The method of analysis is based upon the systems approach in which the technical and economic characteristics of the overall integrated gasification, cleanup and power systems are evaluated as a whole. A Contractor-owned digital computer program was utilized to define the performance of the system from coal or residual oil into kilowatts out. The modular approach to analysis by this unique analytical tool permits wide flexibility in fuel process configurations and power cycle arrangement. However, lack of substantial data on gasifier operation limited the approach to design point calculations.

The analyses indicate that high-temperature cleanup systems have the potential of improving the efficiency and reducing the capital costs of integrated gasification systems. However, unacceptable emission levels for NO_x could result with some gasifier types due to the carryover of fuel-bound nitrogen compounds. No viable method of removing these compounds at high temperature was identified. Suitable process modifications of commercially available low-temperature cleanup systems resulted in increases in overall system efficiencies which approached those of the high-temperature systems; but at higher costs. These systems would still allow generation of electrical power at costs competitive with conventional steam stations with stack gas cleanup while having emissions which are far below current EPA regulations for solid fuels.

This report was submitted in partial fulfillment of Project No. 21ADD 27 104, Contract No. 68-02-1099, by the Research Center of the United Technologies Corporation, under the sponsorship of the Environmental Protection Agency. This report covers work performed between November 1, 1974 and November 1, 1975. A previous report, EPA-600/2-75-078, covers work performed between July 1973 and November 1974.

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LIST OF CONVERSION FACTORS

Btu x 0.252 = Kcal

ft x 0.3048 = m

in. x 25.4 = mm

F subtract 32 x 0.555 = C

lb x 0.453 = Kg

lb x 0.453 = Kg

scf (@ 60 F & 30 in. Hg) x 0.0284 = m^3 (@ 15.5 C & 762 mm Hg)

Btu/scf x 8.88 = Kcal/m^3 (@ 15.5 C & 762 mm Hg)

lb/10^6 Btu x 1.798 = Kg/10^6 Kcal

ton x 1.104 = metric ton

CONCLUSIONS

1. High-pressure gasification of high-sulfur coal and residual oil followed by either low-or high-temperature cleanup offers the potential for lower emission levels than conventional coal-fired systems with flue gas desulfurization as well as the ability to recover sulfur in elemental form.

2. The addition of gasification and cleanup equipment to a conventional steam system would increase the unit capital cost per kW by more than 50%.

3. Inefficiencies and utility requirements associated with coal gasification and cleanup processes can effectively reduce the efficiency of power conversion by as much as 15 to 25 percent over a comparable clean fuel fired steam power system.

4. Production of electrical power from coal using a combined-cycle generation system integrated with a low-Btu gasifier and fuel gas cleanup system can more than offset the inefficiencies attributed to gasification and cleanup processes. Overall efficiencies some 10 to 15 percent better than a conventional coal-fired steam plant with flue gas desulfurization appear realistic while offering the potential for improved sulfur removal capability.

5. By virtue of the low unit cost of gas turbines and the ability to use a low-pressure steam system at relatively high condenser pressure for the bottoming cycle, capital costs of the integrated low-Btu gas/combined-cycle system that are some 10 percent less than for a conventional system are possible.

6. The combined effect of performance and capital cost advantage for a second-generation integrated combined-cycle/low-Btu gasification system results in a cost of coal-derived power as much as 20 percent less than for conventional systems with flue gas desulfurization. These estimates assume 1975 prices and do not include development costs.

7. Currently available gas turbine and gasifier technology do not offer any economic incentive over conventional coal-fired systems. However, anticipated advances in gas turbine technology (2600 F turbine inlet temperature) and gasifier performance (BCR two-stage slagging unit) offer improved performance, better emission control, and lower cost then conventional systems.

CONCLUSIONS CONT'D

8. Some performance and cost improvement can result from the use of high-temperature sulfur removal systems. However, these processes do not remove ammonia if present in the fuel gas and preclude (due to high temperature) premixing of the air/fuel mixture to reduce nitrogen oxide production.

9. Where ammonia is present in the raw gas, the use of a low-temperature water scrub for its removal negates virtually all of the performance advantage associated with high-temperature cleanup.

10. Significant reductions in the cost of low-temperature cleanup processes and utility load (for the system studied) can be achieved by catalytic conversion of COS to H_2S prior to cleanup.

11. Although fuel availability is uncertain, integrated partial oxidation (e.g., Shell or Texaco process) of residual oil/sulfur removal/combined-cycle systems offers higher performance and lower capital cost then their coal-fired counterparts. There is also a potential for reduced emissions of SO_2, NO_x, and particulates compared to coal-based units.

12. Integrated systems based upon the partial oxidation of coal at atmospheric pressure (using Koppers-Totzek as an example) were not competitive in either cost or performance with those systems operating at pressure.

13. The water-borne and solid effluents from integrated systems can meet proposed 1980 standards using best available technology.

RECOMMENDATIONS

1. The potential economic and performance benefits resulting from the high-temperature cleanup processes warrant early developmental efforts to establish their operating characteristics on a scale large enough to more realistically assess their technical and environmental viability in commercial applications.

2. In order to fully utilize the potential advantages of the high-temperature cleanup processes, such as the CONOCO half-calcined dolomite process, it is recommended that an investigation be undertaken to identify methods of removing fuel-bound nitrogen compounds at elevated temperatures.

3. Experimental verification of the catalytic hydrolyzation of COS under conditions of typical fuel gas streams should be carried out.

4. The performance, cost, and environmental effects of the two generic-type gasifiers not studied in this work, i.e., pressurized fluid bed and molten salt gasifiers, should be investigated. This would allow comparable assessments to be made of the potential of the basic gasifier types, e.g., fixed bed, entrained flow, fluid bed and molten salt types.

5. Particle size distribution in the raw fuel gas from the various gasifiers should be experimentally obtained under a variety of operating conditions. Only when these data are available will it be possible to make realistic estimates of turbine requirements and particulate removal system units.

6. Although investigations of integrated power systems carried out under other sponsorship, e.g., Energy Research and Development Administration and the Electric Power Research Institute, have resulted in conclusions similar to those resulting from studies carried out under the EPA and its predecessor organizations, consideration should be given to better future coordination of efforts to ensure truly comparable results.

7. Future work in gasification should recognize the specific needs of power generation via low-Btu gas and establish the practicality of operation under conditions favorable to the performance of generating plants.

8. The ability to utilize high-temperature fuels without excessive NO_x production is dependent on the ability to premix the air and fuel or to provide very rapid mixing in the primary combustion zone to avoid thermal NO_x production. Further analytical and test work is needed to establish the limits of fuel temperature that are consistent with allowable NO_x production.

INTRODUCTION

The prior investigations carried out for the EPA under the first three phases of this Contract, number 68-02-1099, produced the major conclusion [1] that integrated power systems consisting of coal gasifiers/sulfur cleanup process/combined-cycle power systems have the potential for generation of electric power at costs competitive with or, in some cases, less than those of conventional coal-fired stations with flue gas desulfurization (FGD). Those integrated systems having a high-temperature sulfur removal process, i.e., a process projected to operate at or near gasifier exit temperatures, had higher performance and lower costs than the integrated systems using commercially available low-temperature cleanup systems.

These results are in general agreement with those of other investigations. The NASA, with the cooperation of ERDA, EPRI, NSF, and the Office of Management and Budget (OMB), is sponsoring the Energy Conversion Alternative Study (ECAS), a multiphase effort being carried out by teams headed by General Electric and Westinghouse. At the end of the Phase I screening study of many alternative energy conversion systems, both contractors had identified the integrated low-Btu gas/combined-cycle power system as having the greatest potential attractiveness.[2,3] Similiarily, an EPRI-sponsored study[4] described the attractive performance of the integrated power systems.

While the integrated low-Btu gas/combined-cycle power system is undeniably attractive, there are several areas in which the studies of Phases 1, 2, and 3 indicated a need for expansion or where further empirical verification or analytical definition is required. These are addressed in the Phase 4 work which is reported here. One of the needed areas of expansion is the inclusion of gasifiers other than the fixed-bed and two-stage entrained flow types considered in the earlier phases. Since it appears that development of advanced gasifiers, characterized by the absence of tar in the off-gas and by ability to operate with a wide variety of coals, may be the pacing technology, it would be worthwhile to investigate processes which have this capability. One such process is the Koppers-Totzek (K-T) single-stage atmospheric pressure gasifier using oxygen and steam rather than air and steam as the suspension media. An investigation of this process would put into perspective its applicability to integrated systems as well as identifying the effluents from an integrated system having an oxygen-blown gasifier. A second gasifier type, somewhat similar to the K-T process is the partial oxidation gasification process widely used in the refinery industry for production of H_2 from liquid feed. This process is sometimes called the Texaco process or the Shell process, since both of these energy companies have developed variations of it. A prior study[5] had identified the partial oxidation process using coal as being most attractive for use with combined-cycle power systems, but integration of the gasification cleanup and power system was minimal. Additional data in the depth necessary for this study exist only for an oil-based process, thus a system based upon the use of heavy residual oil was selected for evaluation. This has the added benefit of allowing the environmental effects of oil-based systems to be placed in context with the coal-based systems.

A second area requiring more detailed investigations was that of sulfur cleanup. The processes identified in the earlier phases, i.e., the low-temperature physical absorption (Selexol), the high-temperature iron oxide (Bureau of Mines) and the high-temperature half-calcined dolomite (CONOCO, formerly CONSOL), were representative of their respective genre but suffered from some shortcomings in their application to the overall system. These processes were further refined by appropriate modifications to reduce utility requirements and to better utilize the heat available from the processes. These modifications achieved as much as 10 percent increase in system efficiency.

The third, and perhaps most significant area needing further investigation, was that of system effluents. The prior work had quantified the major system air effluents, but had not attempted to detail the water and solid effluents. Thus, a more in depth analysis of this area was carried out in this Phase 4 program.

Thus, this study was conducted to broaden the coverage of fuel processes, to refine the integration of the gasification/cleanup/power system, and to further identify the potential environmental intrusion of these systems. Section I of this report contains the description of the operating characteristics of the atmospheric pressure, oxygen-blown, entrained-flow coal gasifier (the K-T process) and a single-stage, pressurized partial oxidation of residual oil gasifier (Shell/Texaco process). This section also contains a brief review of the sulfur and particulate cleanup systems, both low- and high-temperature, associated with the gasification processes. In Section 2, the selection criteria for cleanup systems are reviewed and their applications to the K-T and partial oxidation gasifier are analyzed. Detailed flow sheets of the integrated gasifier/cleanup system for the additional gasifiers using both low- and high-temperature cleanup are included. Section 3 contains descriptions of methods to improve system performance. Here are described modifications to the cleanup processes for those gasifiers previously studied as well as a discussion of the effort to develop a computer model of an entrained-flow gasifier for purposes of evaluating performance and effluents. In Section 4, the performance and cost of the integrated power systems are presented and comparison to previous results, where applicable, are given. Lastly, definition of the effluents from the integrated power systems is given in Section 5, and the status of cleanup technology is identified.

Throughout the report, reference is made to the Bureau of Mines (BuMines) stirred bed gasifier and sintered iron oxide cleanup system. During the initial phases of this contract, that gasifier was selected as being representative of fixed (as opposed to air entrained) bed gasifiers. Since that time, the Morgantown Energy Research Center, where the gasifier is under development, has become a part of ERDA. However, for the sake of consistency with the previous Phase Report[(1)] the name "BuMines Gasifier" or BuMines Iron Oxide Cleanup System", have been retained and are used in this report.

SECTION I

REVIEW OF GASIFICATION AND CLEANUP SYSTEMS

SUMMARY

The review of individual systems presented in this section is intended to complement the data presented in Ref. 1. Characteristics of the Koppers-Totzek oxygen-blown, atmoshperic pressure gasifier and a pressurized air-blown redisual fuel oil gasifier (Shell or Texaco) are presented. By virtue of their high operating temperaure, nitrogen compounds are virtually eliminated from the resultant product gas. This is especially helpful if used with a high-temperature cleanup process. While high-temperature cleanup processes tend to be quite efficient, one of the associated major problem areas that has been identified is the lack of a suitable high-temperature, ammonia removal process. As a result, nitrogen compounds are passed through to the combustor where the major portion form nitric oxide.

Cleanup systems are reviewed and the B&W Iron Oxide system is discussed in some detail. Also, potential solutions for two problem areas associated with high-temperature cleanup systems are examined. These are particulate and nitrogen compound removal. In the case of particulates, a system consisting of cyclones and filters is selected for use with high-temperature sulfur removal systems. While no suitable high-temperature ammonia removal system has been identified, an iron oxide sulfur removal system could potentially act as a catalyst for ammonia decomposition. However, it was found that catalysts presently available for ammonia decomposition would be poisoned by the sulfur compounds present in the gas stream.

Throughout the report, reference is made to gasifier efficiency as a rough means of comparison. It is important to note that these efficiencies are not used in cycle calculations because both gasifier input and output are a combination of chemical and sensible (or latent) heat and it is not possible to account for the differences in temperature

level or availability in a single parameter such as efficiency. This is especially true when the gasifier is mated with a combined-cycle generating system and sensible heat, unless used to heat fuel to the gas turbine, can only be utilized at steam cycle efficiency which is about 30 percent as opposed to combined cycle efficiency which is on the order of 50 percent. The other factor that is omitted from efficiency is auxiliary power which can be significant when considering systems such as the K-T where it is necessary to produce oxygen for use in the gasifier.

Nevertheless, the efficiency numbers do provide a means of preliminary comparison and where used, they are as defined here:

1. Cold Gas Efficiency

$$Y = \frac{\text{Chemical heating value of Gas}}{\text{Chemical heating value of coal}}$$

2. Hot Gas Efficiency

$$Y = \frac{\text{Chemical plus sensible (above 80 F) heating value of gas}}{\text{Chemical heating value of coal}}$$

GASIFICATION SYSTEMS

This section contains a review of an atmospheric pressure, oxygen-blown coal gasifier (Koppers-Totzek) and a pressurized air-blown residual oil gasifier (Shell/Texaco). Process descriptions are included and operating characteristics are defined for the coal gasification and oil gasification systems. The gasifiers were evaluated with respect to their output for a fixed input of coal or oil, and their thermal efficiency. The first generation gasifier, typified by the fixed-bed type (e.g., Bureau of Mines or Lurgi) has off-gases containing condensible tars, phenols, and other organics. One second-generation gasifier has been investigated previously. This was the entrained-flow, BCR two-stage gasifier. While this gasifier operated at a temperature high enough to crack tars etc., the fuel-bound nitrogen compounds were not cracked and considerable amounts of these compounds would pass through the high-temperature sulfur cleanup processes and could result in high NO_x emissions from the power system. Thus, it is of great interest to investigate other second generation gasifiers which have the potential for low fuel-bound nitrogen production. While both the K-T and partial oxidation gasifiers are commercially available, they can be considered to be "second generation" in that they produce no condensible tars.

Coal Gasification System - Koppers-Totzek

Process Selection - The Koppers-Totzek process was selected for review and for integrationinto a power plant. This process was chosen because: (1) process operating data and information on effluents are available; (2) the process is commercially proven; and (3) the process has low carryover of fuel bound nitrogen. The process is flexible with respect to feeds, and a prior study[6] has indicated that the gasification portion is relatively clean.

Process Description

A schematic diagram of the Koppers-Totzek (K-T) gasifier is shown in Fig. 1. The K-T gasifier can be operated on coal of different ranks. Depending on the rank, the coal is dried to between two percent and eight percent moisture content and pulverized to about 70 percent through 200 mesh. The coal is conveyed with nitrogen from storage to the gasifier service bins. Controls regulate the intermittent feeding of coal from the service bins to the feed bins, which are connected to variable speed coal screw feeders. The pulverized coal is continuously discharged into a mixing nozzle where it is entrained in oxygen and low-pressure steam. Moderate temperature and high burner velocity prevent the reaction of the coal and the oxygen until entry into the gasification zone.

The oxygen, steam, and coal react in the gasifier at a slight positive pressure and at 3300F, to produce intermediate-Btu (300 Btu/SCF) fuel gas. The overall gasification process is endothermic primarily due to the steam-carbon reaction which requires about 5000 Btu/lb C:

$$C + H_2O \rightarrow CO\ (g) + H_2\ (g) \qquad (1)$$

A portion of the coal feed is burnt with oxygen to provide this heat:

$$C + O_2 \rightarrow CO_2\ (g) \qquad (2)$$

The carbon and volatile matter of the coal are gasified, and the coal ash is converted into molten slag. Approximately 50 percent of this slag drops into a water quench tank and is carried from the tank to the plant disposal system as a granular solid, while the remainder is entrained in the gas exiting the gasifier. Low-pressure steam for the gasifier reaction is produced in the gasifier jacket from the heat passing through the refractory lining.

FIG. 1

THE KOPPERS – TOTZEK GASIFIER

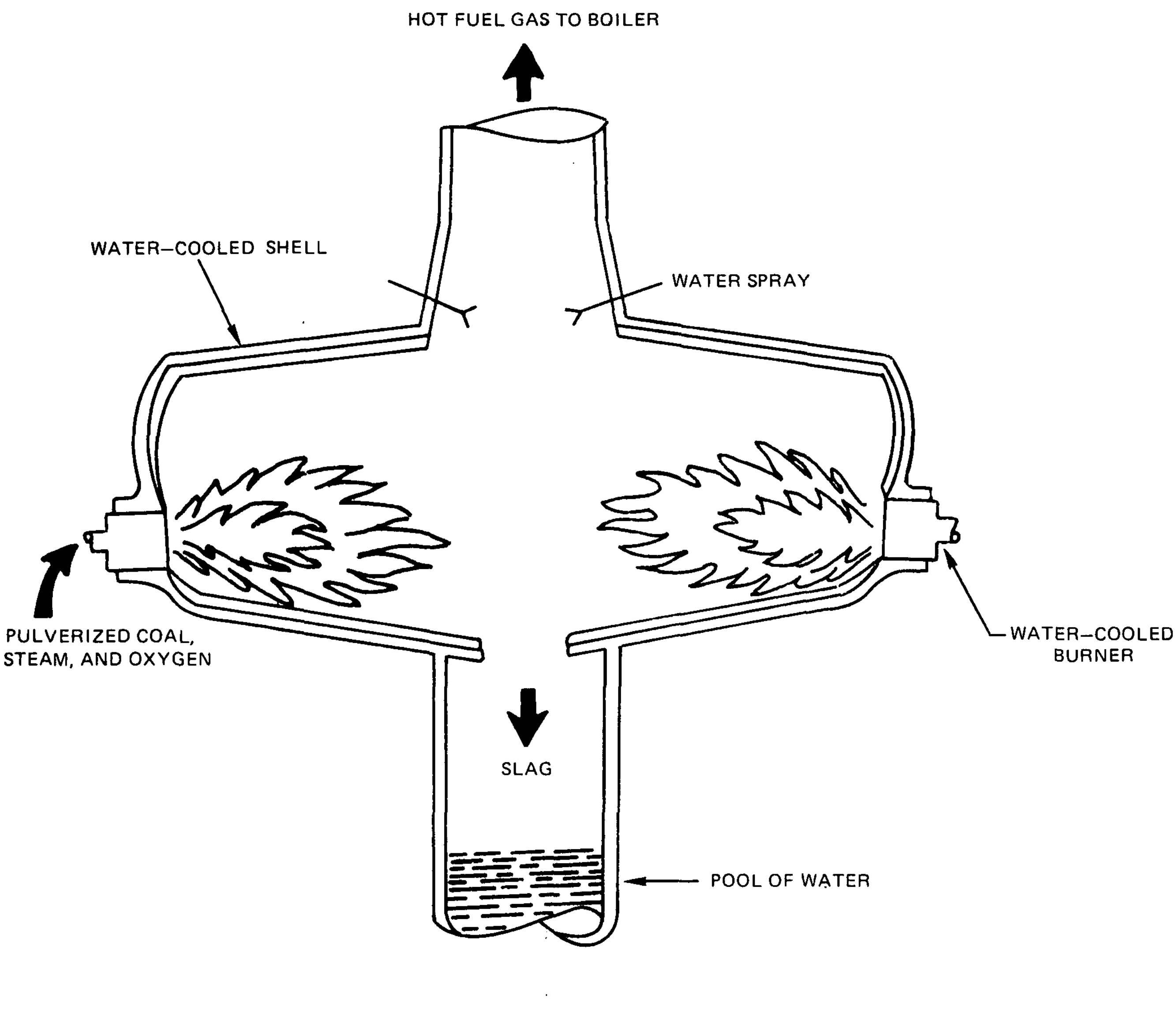

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Table 1[7] shows typical gasification data for eastern and western coals. The cold gas efficiency $\frac{\text{(chemical heating value of gas)}}{\text{(chemical heating value of coal)}}$ of this process is from 70 to 77 percent. Additional energy is recovered as high-pressure steam from the available sensible heat in the gas giving a hot gas efficiency in excess of 90 percent. Very little heat is required for gasifier steam, and oxygen is fed at low temperature. The gasifier performance is greatly affected by the power cycle (discussed in Section 4) and the need to make oxygen.

Oxygen Plant

The oxygen required for the gasification process is produced in an on-site oxygen plant. Gaseous oxygen for gasification can be supplied by an oxygen plant based on the low-pressure (100 psig) air separation cycle principle. In this process, air is compressed to about 100 psig, cooled by heat exchange with counter-current flow of cold oxygen and waste gas streams, and finally distilled in high- and low-pressure distillation columns. Product oxygen is removed as gas from the low-pressure column at a typical purity of 99.5 percent. The capacity of the biggest single-train oxygen plants to date is about 2000 tons/day[8]. The utility requirements for a typical 2000 tons/day oxygen plant[9] are given in Table 2.

The requirements in Table 2 are for. an oxygen plant supplying O_2 at 250 psig. The base-load oxygen compressor can be eliminated sine it is for compressing the product oxygen to 250 psig, but the oxygen for the Koppers-Totzek gasifier is supplies at essentially atmospheric pressure. The power requirement, therefore, drops to 27,983 kW, for a 200o tons/day plant. This is equivalent to approximately 0.17 kWhr/lb of O_2.

Oxygen purity has an insignificant impact on the power requirements. For example, reducing the O_2 purity from 99.5 percent to 98 percent, reduces the power required by about three percent. Further reduction of purity to 90 percent results in about eight percent power reduction from the 99.5 percent purity case.

Operating Characteristics

The major operating characteristics associated with the K-T process are:

1. Versatility -- The process is capable of continuous operation for the gasification of a variety of feedstocks, including all ranks of solid fuels. Coal size is not a limiting factor and caking coals can be handled without pretreatment.

TABLE 1

TYPICAL K-T GASIFIER DATA

TYPE OF FUEL	WESTERN COAL	EASTERN COAL
Gasifier Feed		
Dry feed to Gasifier		
Analysis, Wt%		
C	72.7	69.9
H	5.3	4.9
N	1.1	1.3
S	1.0	1.1
O	9.0	7.1
Ash	8.9	13.7
Moisture	2.0	2.0
	100.00	100.00
Higher heating value of dry feed, Btu/lb	13,135	12,640
Oxygen, tons/ton dried feed @98% purity	0.878	0.849
Process steam, lb/ton dried feed	814	810
Gasifier Products		
Jacket steam, lb/ton dried feed	600	554
High-pressure steam, lb/ton dried feed @900F/900 psig	2760	2675
Raw gas analysis, vol%, dry		
CO	52.55	52.51
CO_2	10.00	10.00
H_2	36.09	35.96
N_2 + argon	1.00	1.15
H_2S	0.34	0.36
COS	0.02	0.02
	100.00	100.00
Dry gas make-SCF/ton dried feed	69,690	66,970
Higher heating value, Btu/SCF, dry	287	286
Heating value of gas/heating value feed, %	76.1	75.8

TABLE 2

UTILITY REQUIREMENTS FOR 2000 TON/DAY O_2 PLANT

Electrical Power	Kw
Main air compressor	27,500
Base load oxygen compressor	8,700
Water wash tower pump	270
Instrument air drier	50
Expander lube oil pump	27
Liquid oxygen circulating pump	18
Main air filter purge blower	18
Lighting, instrumentation, and misc.	100
Total Kw	36,683

Cooling Water

Circulating rate: 16,400 gpm at 50 psig, 85F

Steam

30 psig, saturated plant steam is required intermittently as follows:

Use	Steam requirements
Reactivation rich liquid filters	2000 lb/hr for 8 hr/wk
Reactivation guard adsorber	1000 lb/hr for 8 hr/wk
Plant derime	2500 lb/hr for 60 hr/yr

2. Simplicity of construction and ease of operation -- The only moving parts at the gasifier are screw feeders for solids. Control of the gasifiers is achieved primarily by maintaining CO_2 concentration in the clean gas at a reasonable constatn and predetermined value. Slag fluidity may be visually monitored. Gasifiers display good dynamic response.

3. Moderate capacity -- K-T units are designed for coal feed rates up to 850 tons/day, or for a production of about 45×10^6 SCF/day of 300 BTU/SCF gas. This is equivalent to a nominal 80 MW(e) to 100 MW(e) per unit.

Due to the high operating temperature (3300-3500F), the K-T process produces slag. No condensible hydrocarbons, phenols, pyridines, or other organics are produced. Ammonia and cyanide are produced in amounts well under one volume percent.

A schematic of the K-T process is shown in Fig. 2. A typical composition(7) of the gas including trace impurities at the gasifier outlet is shown in Table 3.

The composition in Table 3 is for a gasifier coupled with a gas quench section in which the gas is sprayed with water. The exit temperature is typically 2200 F but may be varied depending upon the characteristics of the ash carried in the fuel gas stream. The purpose of the quench section is to bring the ash to a temperature below its softening point to avoid sticking to the waste heat boilder surfaces.

Process Selection - Partial Oxidation Oil Gasification System (Shell/Texaco)

The partial-oxidation oil gasification process was also selected because of the availability of data, because it is a proven commercial process, and because of its low fuel nitrogen. The process was originally developed by Hydrocarbon Research, Inc. (HRI) in the 1950's and subsequently commercialized by the Shell Oil Co. and the Texaco Co. A large number of installations operating on this principle produce synthesis gas for ammonia manufacture, methanol synthesis, refinery use, etc. The process operates over a wide range of pressures and hence the synthesis gas could be available at high enough pressure for firing in a combined cycle.

K-T GASIFICATION PROCESS

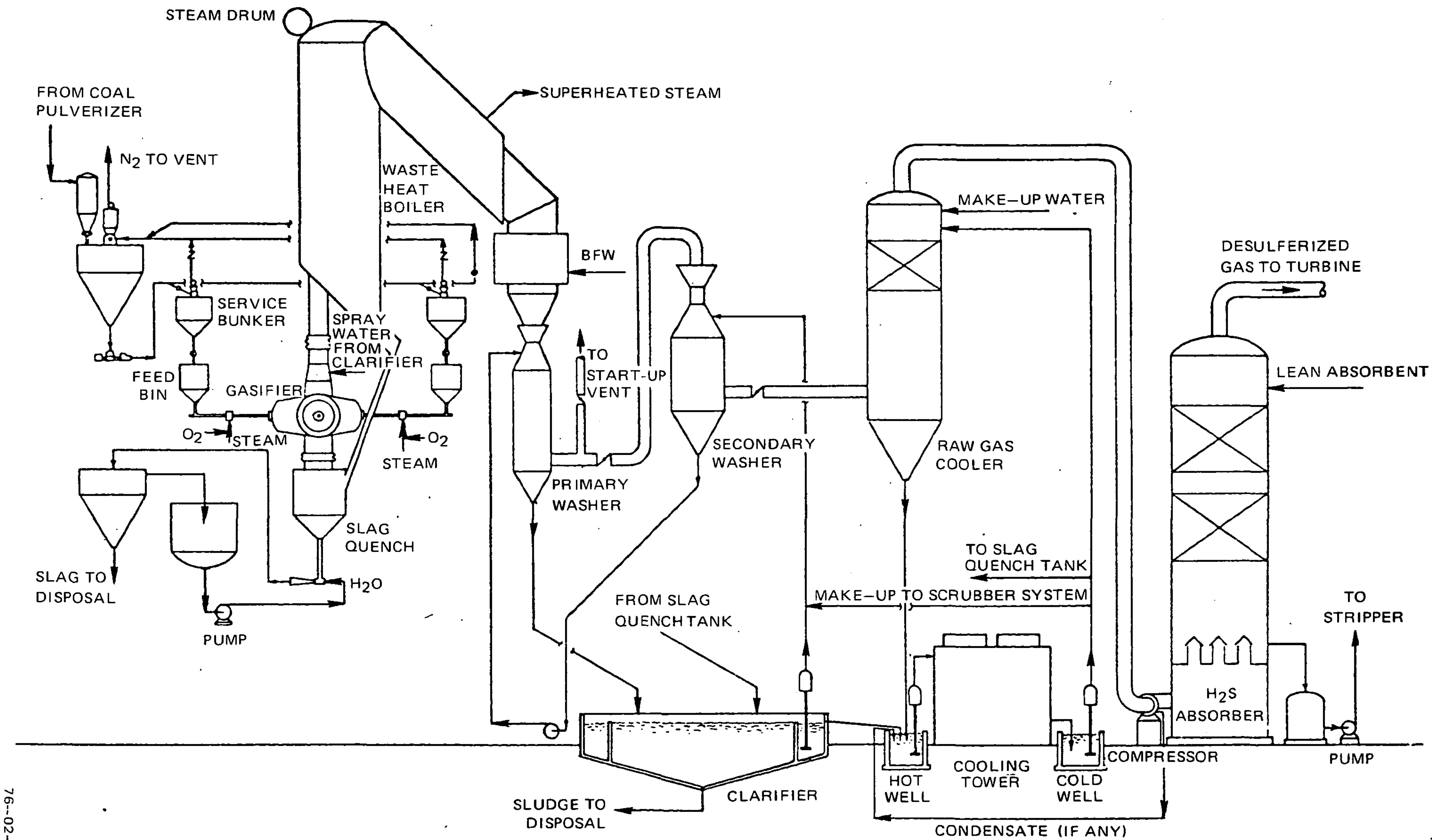

FIG. 2

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TABLE 3

FUEL GAS COMPOSITION FROM K-T GASIFIER

Component	Volume percent
CO	37.36
CO_2	7.13
CH_4	0.08
H_2	25.17
N_2	0.30
H_2S	0.23
COS	178 ppmv
HCN	288 ppmv
NH_3	0.17
H_2O	29.19
Ar	0.32
SO_2	22 ppmv
NO	7 ppmv
Particulates (gr/SCF)	11.57

Process Description

In the partial oxidation scheme, residual fuel oil or sour crude is partially burned in noncatalytic reactors (gasifiers) to provide sufficient heat to maintain a high temperature for the gasification reaction. The gaseous product is composed primarily of hydrogen and carbon monoxide, some carbon dioxide, hydrogen sulfide, small amounts of residual methane and soot. The soot can amount to one to three percent of the feed carbon[10].

The process chemistry can be represented by the following reactions:

$$\mathrm{CnHm} + (\tfrac{n}{2})O_2 \rightarrow n\mathrm{CO} + (\tfrac{m}{2})H_2 \qquad (3)$$

Thermal cracking occurs with partial oxidation of heacy hydrocarbons and forms free carbon.

$$\mathrm{CnHm} \rightarrow n\mathrm{C} + (\tfrac{m}{2})H_2 \qquad (4)$$

Free carbon formation results in reduced gas production. Other reactions that occur are:

$$\mathrm{CnHm} + (n + \tfrac{m}{4})O_2 \rightarrow n\mathrm{CO_2} + (\tfrac{m}{2})H_2O \qquad (5)$$

$$\mathrm{CnHm} + 3\ \mathrm{CO_2} \rightarrow 2n\mathrm{CO} + (\tfrac{m}{2})H_2 \qquad (6)$$

$$\mathrm{CnHm} + (\tfrac{m}{4})O_2 \rightarrow n\mathrm{C} + (\tfrac{m}{2})H_2O \qquad (7)$$

When steam is used in the gasification, the endothermic steam-carbon reaction occurs:

$$\mathrm{CnHm} + n\ H_2O \rightarrow n\mathrm{CO} + (\tfrac{m}{2} + n)H_2 \qquad (8)$$

Some relatively slow secondary reactions that occur are:

$$C + CO_2 \rightarrow 2\ CO \qquad (9)$$

$$C + H_2O \rightarrow CO + H_2 \qquad (10)$$

Normal residence time is insufficient for the completion of reactions (9) and (10); therefore, some soot is always present. For heavy fuel oil, soot may be as high as three percent of the feed carbon. Under the operating conditions (> 2300F) some shift of carbon monoxide to carbon dioxide takes place.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (11)$$

Typical fuel oil and exit gas composition data[11] are shown below:

Heavy fuel oil		Weight %
C		85.70
H		10.73
C		2.65
N_2 + Ash		0.60
O		0.32
	Total	100.00

Gas composition (Dry)		Volume percent
H_2		44.60
CO		48.30
CO_2		4.60
H_2S		0.60
COS		300 ppm
CH_4		0.50
N_2		0.60
Ar		0.80
	Total	100.00
Pressure, atm.		88.0

When the partial oxidation gasifier is used in conjunction with a low-temperature cleanup system, the hot gas is cooled and the heat is recovered in a waste heat boilder. Prior to acid gas removal, the gas is cleaned and it temperature is further reduced in a water scrubber where the soot is removed from the gas in a carbon/water slurry. To recover the carbon, two methods are generally used. One uses an intermediate fluid, naptha, which preferentially wets the carbon and the naptha-carbon mixture can then be separated from the water stream. The naptha-carbon phase is mixed with fresh oil feed and flashed into the naptha stripper. The natpha stripper separates naptha for reuse leaving carbon in the oil feed for recycle to the gasifier. This process was developed for use with very heavy oils where the carbon could not be transferred directly to the oils and has the disadvantage of requiring a considerable amount of steam for naptha stripping. A schematic of another variant of the process as commercialized by Shell is shown in Fig. 3. In this version, soot is recovered from the water slurry in a "pelletizer" and mixed with the feed for recycle to the gasifier. The small amounts of water introduced into the fuel in this process could be troublesome where the oil must be heated to high temperatures causing the water to vaporize. However, operation at pressure offers a potential solution to the problem and may, in fact, be beneficial in that the entrained water may help in the atomization of the heavy oil.

CLEANUP SYSTEMS

Fuel gas cleanup systems consist of particulate removal systems, sulfur removal systems, and systems to remove fuel-bound nitrogen compounds (mostly ammonia). Depending ontheir operating temperature, these can be divided into two broad categories, viz.:

(1) Low-temperature cleanup systems
(2) High-temperature cleanup systems

Low-temperature systems require cooling of the dirty gas to 250 F or below, whereas high-temperature systems require little or no cooling of the dirty gas.

A survey of low- and high-temperature desulfurization processes was done as part of Phases 1 through 3[1] of this contract study. Several low-temperature desulfurization processes are commercially available, and have been widely used for natural gas sweetening, and for treating synthesis gas in the chemical process industry. Ammonia and methanol manufacture are examples of such applications. To facilitate a comparison between the various cleanup processes, a number of criteria were developed. These criteria are:

(1) Type of absorbent
(2) Operating temperature
(3) Operating pressure
(4) Efficiency of sulfur removal

PARTIAL OXIDATION OF RESIDUAL OIL

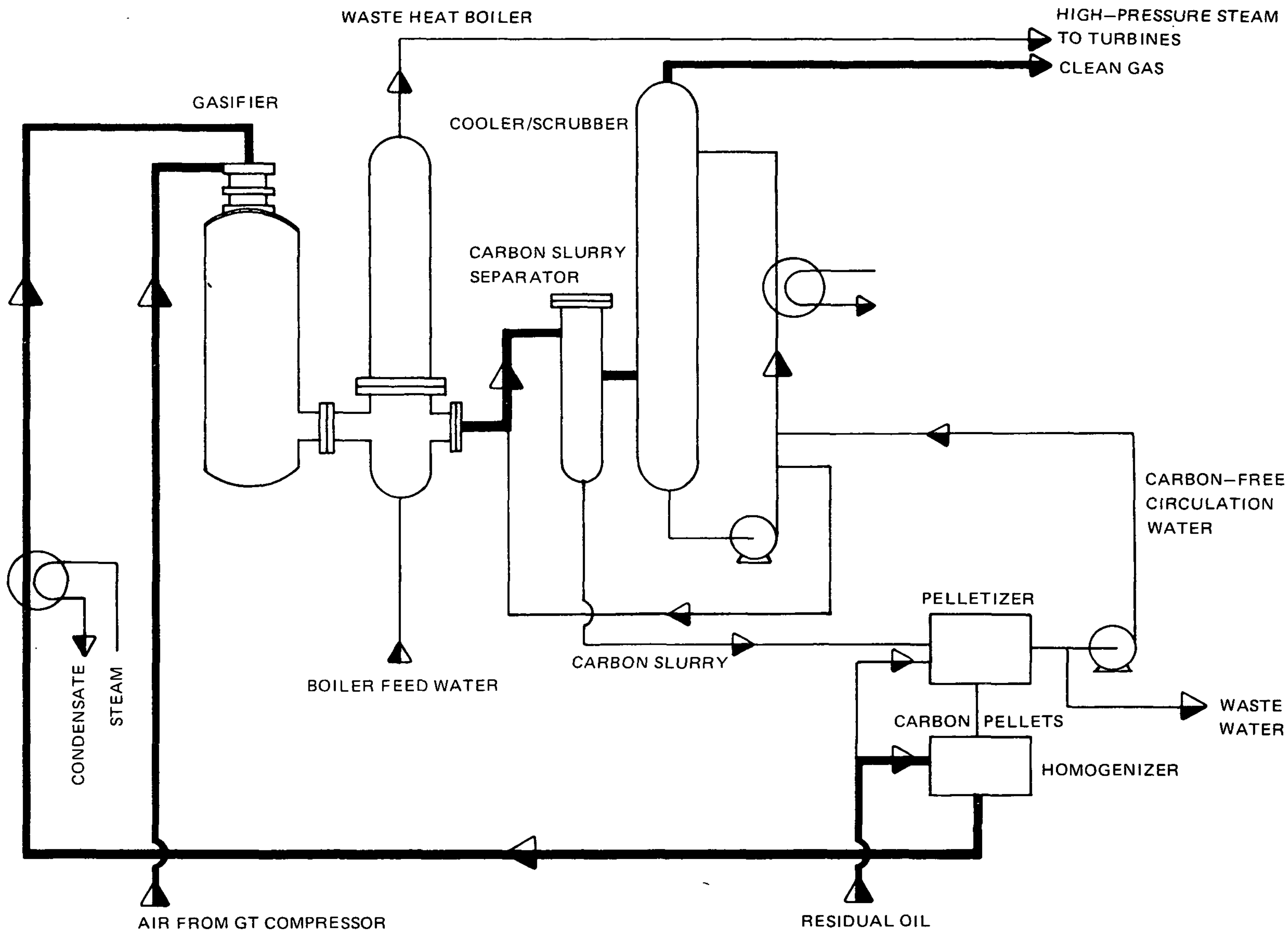


FIG. 3

76–02–191–2

(5) Absorbent characteristics

  (a) life of absorbent
  (b) regenerability
  (c) selectivity toward sulfur compounds over CO_2
  (d) makeup rate

(6) Form of sulfur recovery
(7) Status - commercial, developmental, conceptual

The above criteria were used to compare several desulfurization processes. Tables 4 and 5 are a listing of low- and high-temperature desulfurization processes, respectively. It is seen that the most effective desulfurization processes are those which have a high efficiency of sulfur removal, high selectivity toward H_2S, can handle large volumes of gases (up to 1000 MMSCFD) containing 0.2 to 1.0 volume percent H_2S, are easily regenerable, and have low energy requirements.

Low-Temperature Desulfurization Processes

Several low-temperature processes have been described in the previous Phase Report[1]. For convenience, a listing of various types are given in Table 4 and a brief discussion of the operational characteristics is included.

The processes in Table 4 are best-suited to operate at 250 F or below and hence require cooling of the dirty gas. Low-temperature processes can be subdivided into four categories, according to the principle of operation. These are:

(1) Chemical solvent processes
(2) Physical solvent processes
(3) Direct conversion processes
(4) Dry bed processes

Chemical Solvent Processes - These processes employ aqueous solutions of organic and/or inorganic agents to scrub the "dirty" gas. These agents are capable of forming "complexes" with H_2S, CO_2, and other acid gas components present in the raw gas stream. The "complex" is then decomposed during regeneration at elevated temperatures, thereby releasing the acid gases for further processing and recovery. The regenerated solution is recycled for further absorption. These processes may be subdivided into those based on amine scrubbing solutions, and those based on alkali scrubbing solutions. These processes generally exhibit little or no selective absorption of H_2S over CO_2.

Table 4

Low temperature cleanup processes

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

Process	Absorbent	Type of Absorbent	Temp. °F	Pressure	Efficiency of S Removal		Absorbent Characteristics				Form of Sulfur Recovery	Status
					% H_2S Influent	Effluent H_2S ppm	Life	Regeneration	Selectivity toward	Make up rate		
Chemical solvent type												
1. MEA	Monoethanolamine	Aqueous solution	80 to 120	Insensitive to variation in pressure	99	~100		Thermal	Forms non-regen. comp. with COS, CS_2	50 to 100%	As H_2S gas	Commercial
2. DEA	Diethanol amine	Aqueous solution	100 to 130	Insensitive to variation in pressure	99	~100		Thermal	Absorbs CO_2, does not absorb COS, CS_2	< 5%	As H_2S gas	Commercial
3. TEA	Triethanolamine	Aqueous solution	100 to 150	Insensitive to variation in pressure	99	~100		Thermal	H_2S	< 5%	As H_2S gas	Commercial
4. Alkazid	Potassium dimethyl amino acetate	Aqueous solution	70 to 120	Insensitive to variation in pressure 1 - 80 atm	99	~100		With steam	H_2S		As H_2S gas	Commercial
5. Benfield	Activated potassium carbonate solution	Aqueous solution	150 to 250		99	H_2S + COS ~100	Unlimited No degradation	With steam	H_2S is high		As H_2S gas	Commercial
6. Catacarb	Activated potassium carbonate solution	Aqueous solution	150 to 250	Insensitive to variation in pressure generally > 300 psi	99	H_2S + COS ~100		With steam	H_2S - partial also absorbs COS, CS_2	< 5%	As H_2S gas	Commercial
Physical solvent type												
7. Sulfinol	Sulfolane + Dilsopropanoamine	Organic solvent	80 to 120	High pressure preferred	99	H_2S + COS ~100		Low pressure heating or with steam	H_2S, and also absorbs COS, CS_2 and mercaptans		As H_2S gas	Commercial
8. Selexol	Polyethylene glycol ether	Organic solvent	20 to 80		99	H_2S + COS ~100			H_2S also absorbs COS		As H_2S gas	Commercial
9. Rectisol	Methanol	Organic solvent	< 0		99	~100			H_2S			Commercial
Direct conversion												
10. Stretford	Na_2CO_3 + anthraquinone sulfonic acid	Alkaline solution			99.9	~10			H_2S	50 to 100%	Elemental sulfur	Commercial
11. Townsend	Triethylene glycol	Aqueous solution	150 to 250		99.9	~10			H_2S		Elemental sulfur	
Drybed type												
12. Iron sponge	Hydrated Fe_2O_3	Fixed bed	70 to 100		99	H_2S + COS ~100			H_2S and also towards COS, CS_2 and mercaptans		Elemental sulfur	Commercial

Table 5

High temperature cleanup processes

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

Process	Absorbent	Type of Bed	Temp. °F	Pressure	Efficiency of S Removal		Absorbent Characteristics				Form of Sulfur Recovery	Energy Required		Status
					% H_2S Influent	Effluent H_2S ppm	Life	Regeneration	Selectivity toward	Make up rate		Elec. kw	Other stu	
1. Bureau of Mines	Sintered pellets of Fe_2O_3 (25%) and fly ash	Fixed bed	1000 to 1500	Insensitive to variation in pressure	~95	~350	>174 cycles Wt loss < 5%	With air	H_2S, COS	<5%	As SO_2 gas			Pilot
2. Babcock and Wilcox	Fe_2O_3	Fixed bed	800 to 1200	Insensitive to variation in pressure	~99	~75					As 12-15% SO_2 gas			Experimental
3. CONOCO	Half calcined dolomite	Fluidized bed	1500 to 1800	~200 psia H_2S removal is high at low pressure	~95	~350		10-13% with steam and CO_2	H_2S, COS	1% of circulation rate	As H_2S gas to Claus process	96.360		Pilot
4. Air products	Calcined dolomite	Fixed bed	1600 to 2000	Insensitive to variation in pressure			minimum 5-6 cycles	80-90% with steam and CO_2	H_2S, COS		As H_2S gas to Claus process			Abandoned
5. Battelle Northwest	Molten carbonates (15% $CaCO_3$)	Solution	1100 to 1700	Atmospheric H_2S removal is high at low pressure, 5-6 psig	~95	~350		With steam and CO_2	H_2S, COS, fly ash		As H_2S gas to Claus process			Pilot
6. IGT - Meissner	Molten metal (proprietary)	Splashing contact	900		~98	~150		Electrolytic	H_2S, COS			9830		Conceptual

Physical Solvent Processes - These processes use organic solvents to remove acid gases by physical absorption, rather than by chemical reaction. The extent of absorption is directly proportional to the partial pressure of the acid gas comp nents. These processes are best-suited to high-pressure gas treating where appreciable quantities of acid gases are present. The solvent is then regenerated by heat and/or pressure reduction, thereby releasing a concentrated stream of acid gases and a recyclable solvent. These processes exhibit a selective absorption of H_2S over CO_2. In addition to removing H_2S and CO_2, these processes are all capable of removing COS, CS_2, and mercaptans without solvent degradation.

Direct Conversion Processes - These consist of two types of processes.

(1) Those based on oxidation reduction reactions
(2) Those based on the stoichiometric reaction of H_2S with SO_2 in the presence of a solvent.

In the first type, H_2S is absorbed in an alkaline solution containing oxidizing agents. The H_2S is then oxidized to elemental sulfur by air feeding to the regenerator and the sulfur product is separated from the regenerated solution by froth flotation. Partial removal of COS, CS_2, and mercaptans is also possible.

The second group of direct conversion processes are those in which H_2S is absorbed in a solvent and converted to elemental sulfur by the Claus type reaction with SO_2.

(12)

The solvent are usually aqueous soltuions of organic or inorganic agents.

Dry Bed Processes - These are based on absorption of acid gases by a fixed bed of solid absorbent. Due to their low absorbent loading, they are best-suited to removing small quantities of acid gases. These processes can be subdivided into the historical iron oxide processes and the various molecular sieve processes.

High-Temperature Desulfurization Processes

Several high-temperature desulfurization processes are currently under development. A survey of these processes was made, and these are listed in Table 5. None of the processes has been commercialized;

however, the Bureau of Mines sintered iron-oxide process and the half-calcined dolomite process of the Consolidation Coal Company Coal Development Center, a part of the Continental Oil Company (CONOCO) are relatively advanced in their development and may result in commercialization sooner than the others.

The principle underlying high-temperature desulfurization is the formation of metal sulfides by chemical reaction of the absorbent with sulfur compounds in the gas at high temperatures. The extent of sulfur removal depends on the chemical equilibria for the particular system. All of the high-temperature desulfurization processes with the exception of the IGT-Meissner Process and the Babcock and Wilcox Process, have been described in the Phase Report[1]. The Air Products Process is also discussed here.

IGT-Meissner Process - This process is being developed by the Institute of Gas Technology in conjunction with its U-Gas Process. This process, still in the conceptual stage, utilizes a splashing molten metal-gas contact to remove H_2S from the gas. The contact results in the formation of a metal sulfide which is then decomposed electrolytically to release H_2S and regenerate the molten metal for recycle. The operating temperature is 900 F and a high sulfur removal efficiency (98 percent) is projected. The molten metal absorbent is proprietary. The estimated costs and energy requirements given in Table 5 are preliminary[12]. Further development is being directed toward establishing mass transfer rates.

Babcock and Wilcox Process - This process is similar to the Bureau of Mines process in that it utilizes iron oxide to remove H_2S from the gas at high temperatures. The difference lies in the material used by the two processes. While the Bureau of Mines' process uses a sintered material made from iron oxide and fly ash, the Babcock and Wilcox process starts out with carbon steel and generates an iron oxide scale on the steel surface which is then used as the desulfurization agent. Briefly, the process chemistry is described by the following reactions:

$$Fe/FeO_x + H_2S \longrightarrow FeS_x + H_2O \qquad (13)$$

At some point in time all of the available iron oxide scale is converted to the sulfide scale. At that point, the system is regenerated with air as follows:

$$Fe/FeS_x + Air \longrightarrow Fe/FeO_x + XSO_2 \qquad (14)$$

The overall process accomplishes two things:

(1) It concentrates sulfur from the raw gas to 10 to 13 volume percent SO_2 in the regenerant gas.

(2) It provides SO_2 in the regenerant gas that is either oxidized to sulfuric acid or reduced to elemental sulfur.

A sulfur removal efficiency greater than 90 percent is projected. Absorption can be carried out at temperatures as low as 675 F; however, higher temperatures are desirable for effective regeneration. If regeneration is performed below 1000 F, the sulfide is oxidezed to $FeSO_4$ and not to FeO_x. Also, higher temperatures help activate the surface by developing a thick iron oxide layer over which effective absorption occurs. Hence, operation is usually at temperatures in excess of 1000 F.

The concentration of H_2S in the desulfurized gas increases as the volume of gas desulfurized on a given iron oxide scale increases. Therefore, the hardware design for desulfurization and regeneration is one that[13]:

(1) Has a large number of compartments at various stages of regeneration to give an average H_2S concentration in the fuel gas relatively independent of the regeneration cycle

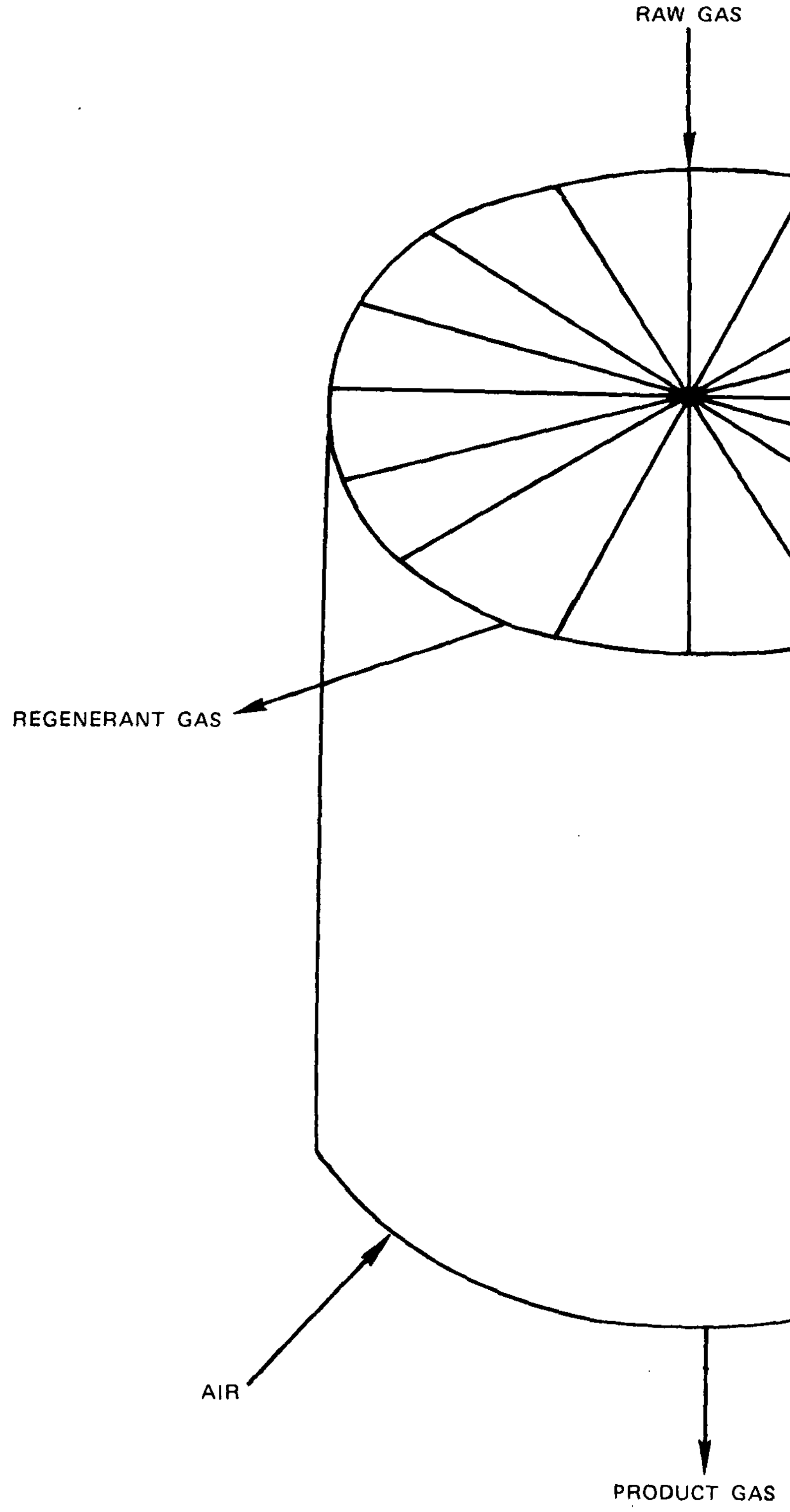
(2) Gives a maximum SO_2 concentration in the regenerant gas

The hardware that has been designed uses a number of compartments for sulfur removal and the so-called countercurrent principle of air regeneration. The desulfurizer uses a modified regenerative type air heater and is referred to as the "regenerative desulfurizer", a schematic of which is shown in Fig. 4. The cylindrical unit is segmented into 16 compartments. Each compartment is filled with carbon-steel plates oriented longitudinally with the gas flow. The vessel itself would be constructed from high alloy steel.

<u>Desulfurization-step</u> - The sulfided iron surface is converted back to the oxide in three of the 16 compartments. The regeneration air passes in and upward in the first compartment to a cross-over, then downward for a second pass, and upward for a third and final pass. At two revolutions per hour, each of the 16 compartments is regenerated twice per hour. Air enters the first regeneration compartment where it contacts a partially regenerated surface accomplished in the second and third pass downstream. At the end of the first pass, the O_2 concentration is

FIG. 4

REGENERATIVE IRON OXIDE DESULFURIZER
(B&W)



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well below 21 percent. During the second pass, the O_2 concentration is further reduced while SO_2 increases. Purging the third (most FeS fouled) compartment with a gas containing a minimum concentration of O_2 and a maximum concentration of SO_2 insures a maximum SO_2 concentration of the final regenerant gas. The regenerant gas should contain 10 to 13 volume percent SO_2.

The effect of reaction temperature on the sulfur concentration in the desulfurized gas is shown in Fig. 5. This may also be represented by the amount of H_2S removed as a function of the temperature. This is referred to as "sulfur pickup" in Fig. 6.

The process concept has been demonstrated on bend scale equipment and a hardware design has been developed. The process has yet to be demonstrated on a large scale.

Air Products Process - This process, now abandoned, employed a fixed-bed of fully calcined dolomite to absorb H_2S from the raw gas. The sulfided dolomite was then regenerated with steam and carbon dioxide before being recycled to the absorber. Poor regenerability of the sulfided dolomite led to the abandonment of this process by the Air Products Company.

Particulate Removal Systems

Particulates of varied sizes, shapes, and composition are a major contributor to air pollution, are a healt hazard, and are the target of statutory limitations. In addition to their effect on human healt, particulates adversely affect pollution control efforts by fouling catalysts used for SO_2 reduction, sulfur recovery, NH_3 decomposition, etc. Particulates in fuel used for firing gas turbines may cause erosion/corrosion of turbine blades. The need for particulate removal from gas streams where they are present in significant quantities cannot be overemphasized.

Only particulates from fixed-bed, fluidized bed, and entrained bed coal gasification are considered here. The primary differences between the three gasification methods lie in:

(1) The manner in which the coal feed is supported
(2) The rate of gas flow (superficial velocity)
(3) Temperature
(4) Feed size

FIG. 5

SULFUR CONCENTRATION VS TEMPERATURE

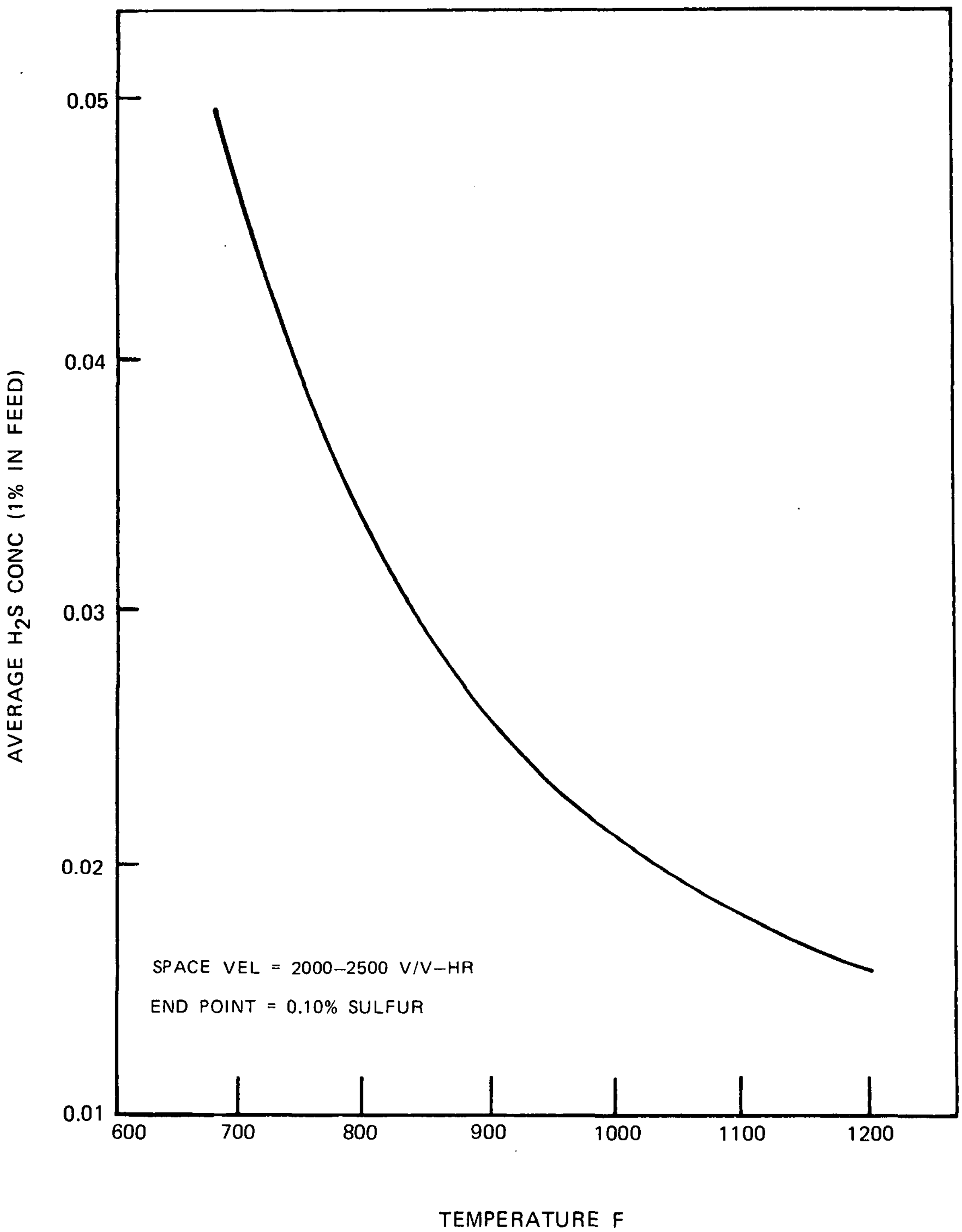

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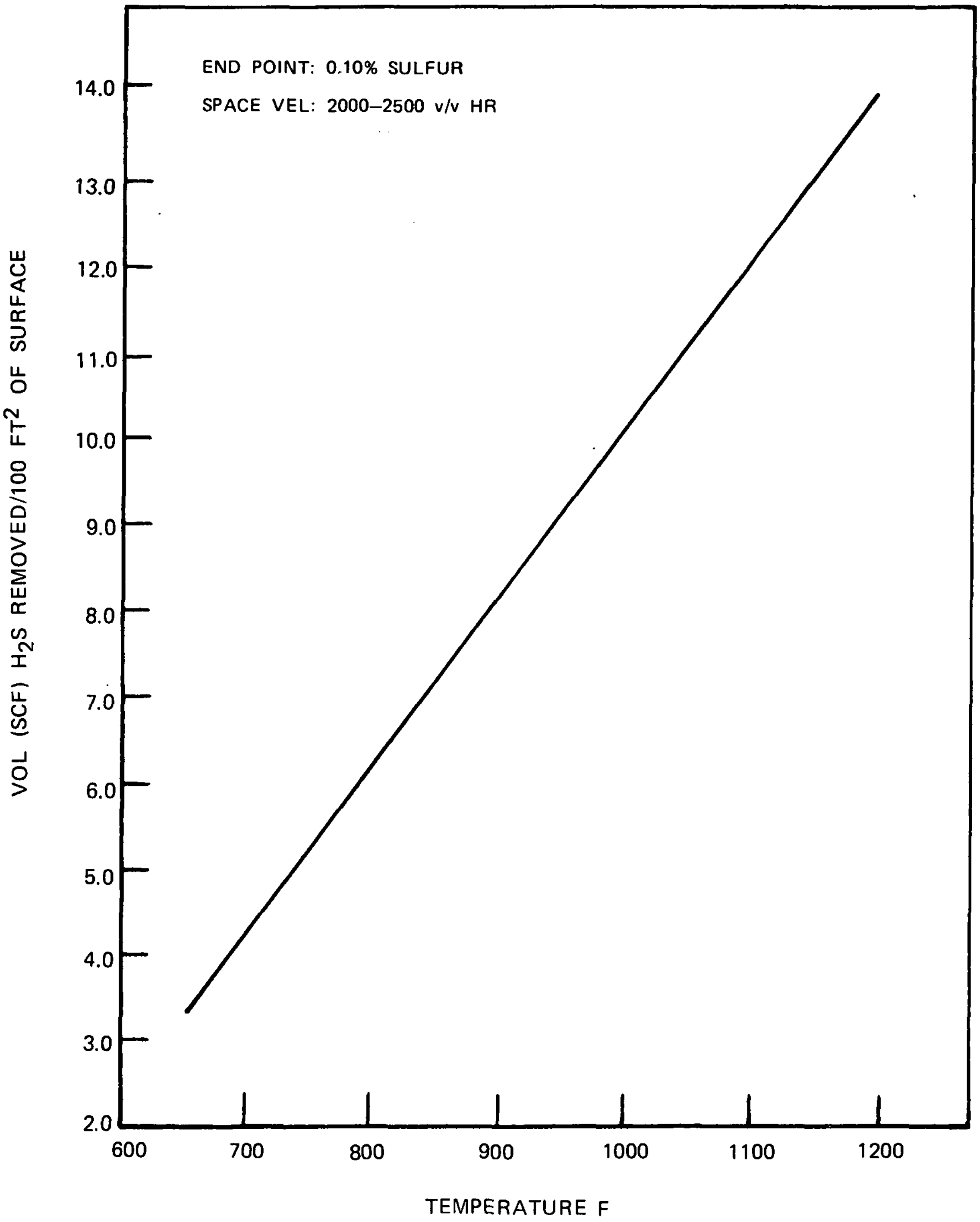
FIG. 6

REMOVAL OF H_2S AS A FUNCTION OF TEMPERATURE



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Gas flow rate is the least in a fixed bed and greatest in an entrained bed. The maximum temperature that can be used in any particular bed depends on the caking properties of the coal fed, the surface area of the coal particles, etc. The surface area is much higher in fluidized and entrained beds than it is in fixed-beds, and therefore, higher temperatures can be employed. Temperatures can generally be raised as the fluidizing/entraining velocity is raised, and hence, are highest in entrained beds and lowest in fixed-beds. Fixed-beds use coarser feeds, whereas fluidized and entrained beds use finer feeds.

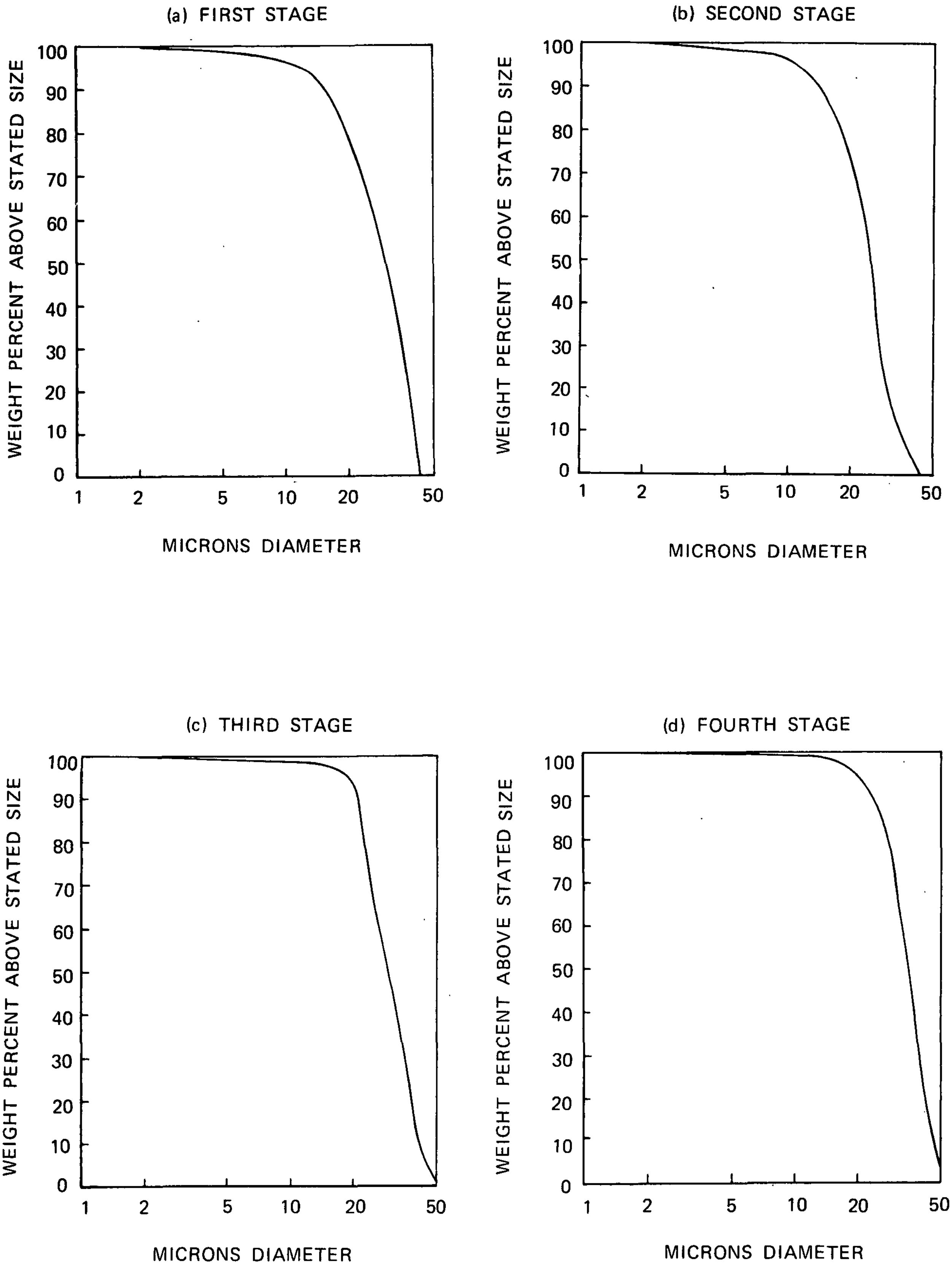
Considering the three types of beds, individually, and using temperature, gas flow rates, and feed size as parameters, the following qualitative analysis can be made of the particulate quantity and size distribution from each.

Fixed Beds - With relatively low gas flow rates, the coarser (heavier) particles tend to settle down and the finer particles are carried away by the gas. These gasifiers operate at temperatures (up to 1500 F) that are lower than ash slagging temperatures. Therefore, the ash does not slag and agglomerate. This leads to a higher ash loading in the gas than if the ash were to slag and agglomerate. The coarse feed (~ 1/5"), on the other hand, tends to reduce particle entrainment to some extent. The net effect of the three factors, therefore, would be to yield a fairly high particulate loading of finer particles comprised of ash and possibly unburned carbon.

Fluidized Beds - Gas flow rates here are higher than for fixed-beds and there is a greater tendency for the bigger particles to be carried away by the gas. Particulate loading is also increased by the finer feed size used in fluidized beds (minus 200 mesh). However, temperature has an opposing effect in gasification, up to a point. The temperatures used in some fluidized bed gasifiers are higher (2000 F) than typical ash softening temperatures, causing the ash to agglomerate. This effect reduces the amount of ash carried over with the gas. The net effect therefore, would be to yield a slightly reduced particulate loading of comparatively larger particles than from a fixed-bed gasifier. This is illustrated by the particle size distribution curves (Fig. 7) for fluidized-bed pyrolysis used in the COED Process[14]. It should be noted that conditions in the four pyrolysis stages to which the curves correspond, change gradually from fixed-bed type conditions in the first stage to fluidized-bed type conditions in the fourth, with a corresponding increase in average particle size going from the first stage to the fourth.

FIG. 7

SIZE DISTRIBUTION OF FINES FROM COED PYROLYSIS



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A quantitative approximation of particulate loading and size distribution for fluidized bed gasification was obtained by Westinghouse researchers using a theoretical model developed by Kunii and Levenspiel[15] and by comparison with the corresponding figures for fluidized bed combustion. Projected operating conditions for fluidized-bed combustion were deduced (by Westinghouse researchers) from experimental data obtained from the National Coal Board (NCB) of England and from EPA contractors. The projected conditions for fluidized-bed combustion and fluidized-bed gasification are given below.

Operating Conditions	Fluidized-Bed Combustion	Fluidized-Bed Gasification
Pressure (atm)	10 to 20	10 to 20
Temperature, F	1600 to 1800	1500 to 1700
Gas flow (lb gas/ lb fuel)	~12.5	~5.5
Projected dust loading prior to gas cleanup (gr/scf)	10 to 30	10 to 30
Projected particle size	10 to 25% <10μ 5 to 15% <5μ	10 to 25% <10μ 5 to 15% <5μ

The projected figures for fluidized-bed gasification were derived by Westinghouse from the corresponding figures for fluidized-bed combustion and the theoretical model of Kunii and Levenspiel taking into consideration the following differences:

(1) The gasification process has less than one-half the gas flow;
(2) Fluidizing velocity in the coal gasification system design is about 4 ft/sec, which is one-fourth to one-half that for fluidized-bed combustion;
(3) Ash will essentially be concentrated and removed in the gasification process as agglomerates, and not carried out of the system in the fuel gas.

Based on a qualitative assessment of the differences in the combustion and gasification systems noted above, it is reasonable that a particulate removal system which is designed to handle the dust loading from a pressurized fluidized bed combustion process that feeds a combined cycle or let-down turbine will be able to cope with that from the fluidized bed gasification process.

Entrained Beds - These have high flow rates and operate at high temperatures (to 3000 F) with fine feed sizes (minus 200 mesh). In this flow regime the entire feed could be carried over as with the BCR two-stage process, and therefore, the particulate loadings could be very high with the particle size distribution proportional to the feed size. Carryover in single-stage systems is not well documented although values for the K-T gasifier after water spraying have been given previously.

Cleanup Requirements - In all three coal gasification systems discussed above, the particle size distribution and particulate loading are affected by several other factors such as the ash content of the coal, the method of coal preparation, the change in particle density due to chemical reactions, attrition in the bed, and description of particles due to their history. The effects of these factors cannot easily be quantified.

Allowable particulate loadings and size distribution that consider gas turbine requirements as well as air pollution emission regulations have to be considered for the design of particulate removal equipment.

As a reference point in considering emission levels, the allowable particulate loading in low (125 Btu/SCF) Btu gas corresponding to current coal standards of 0.1 lb/million Btu of coal is .11 grains/SCF. From an operational standpoint, allowable loadings are significantly less. Based on data presented in Ref. 1, the following tabulation presents current fuel specifications along with a suggested specification for low Btu gas.

	P&WA[1]	P&WA[2]	Westinghouse	GE[1]	Low-Btu Gas
Loading	0.08 lb/10^6 ft^3	0.01 gr/ft^3	0.0004 gr/ft^3	30 ppm	0.0012gr/ft^3
Size		40μ mas	2μ to 10μ		> 2μ

1. Aircraft derivative burning methane
2. Projected for high-temperature turbine

Evaluation Criteria

The criteria used for evaluating different particulate removal systems are given below:

(1) Capability to attain particulate loadings governed by gas turbine specifications at high gas temperatures (1500 to 1800 F) and pressures (10 to 20 atm).

(2) Demonstration of capability: performance, reliability, and life in commercial or pilot plant operation.

(3) Compatibility: pressure drop, operating pressure, and temperature with the coal gasification processes.

(4) Capital, operation, and maintenance costs for a commercial system.

Many low-temperature particulate removal systems are commercially available and descriptions of these are abundant in the literature. Only high-temperature systems have been considered here. Several high-temperature and high-pressure particulate removal systems that satisfy some or all of the above criteria are either available or currently under development. Table 6 lists the different types of high-temperature particulate removal systems and where available, gives the operating conditions and efficiencies attainable with each.

It has been stated previously[1] that the tolerance of the gas turbine for particulates is not well documented. The consensus in the industry that barring significant changes in design philosophy, particulates of $< 2\mu$ can be accepted. It is assumed that particles of this size and smaller will remain in the gas stream rather than impinge on turbine surfaces.

Unfortunately, from an applications standpoint it is the particulates in the 1μ range which cause the visible emissions problem. Thus, it is possible to meet turbine requirements with respect to particle size, yet have a power system which appears to be "smokey".

The application of the devices given in Table 6 to the removal of particulates from the high-temperature, high-pressure fuel gas stream, while not fully defined, does give hope that at least turbine specifications and, hopefully, environmental regulations can be met. It would appear that the use of several stages of cyclones, followed by the

Table 6

High temperature particulate removal systems

Type of removal system	Manufacturer	Capacity ACFM	Collection efficiency %	Minimum particle size with efficiency > 50%, μ	Maximum operating temp. °F	Maximum operating pressure atm	Maximum collection efficiency %	Applicable dust loading range grains/SCF	Pressure drop in. W.G.	Status
Mechanical Collectors										
Cyclones	Buell Ducon	50,000 58,000	80-90 80-90	5-10 5-10	1400 1500	2 10	90-95 90-95		4-40 4-40	Commercial Commercial
Tornado	Aerodyne	30,000	93-97	0.5	1500	10	98	< 30	30	Commercial
Bed Filters										
Granular	Combustion Power Co.		> 90	2	1400		> 90		10-15	Under Development
	Ducon									Under Development
Panel	C.U.N.Y.									Under Development
Rex	Rexnord	20,000	95-99		> 900	1	> 99	< 40	4-15	Commercial
Sonic Agglomeration Collection Systems										
Alternating Velocity Precipitator	Braxton									Under Development
Scrubbers										
Fused salts	Battelle									Under Development
Filters										
Metal and ceramic	Selas and others		> 99	<0.5	2000	1	> 99			Commercial
Electrostatic Precipitators			> 99	< 0.5	800	1	> 99		< 1	Commercial

Aerodyne-type tornado and finally a metallic or ceramic filter could achieve 95 to 99 percent removal of < 2μ particles. There remains a good deal of testing and development, but this aspect of high-temperature fuel gas cleanup is in a technological state comparable to the more developed high-temperature desulfurization processes such as the iron-oxide process.

In the analyses to follow, it is assumed that a high-temperature cleanup system consisting of cyclones and filters is used. Since the energy consumption of these is quite small, even when used in series (< 1 percent of gasifier exit pressure) and there are little other utility requirements or systems interfaces, the particulate removal device is assumed not to affect performance and is represented only in the cost of equipment.

NO_x CONTROL SYSTEMS

Nitrogen oxides, collectively referred to as NO_x, are an important group of air pollutants. The term NO_x refers primarily to NO (nitric oxide), although similar quantities of NO_2 (nitrogen dioxide) and N_2O (nitrous oxide) may also be formed. These oxides are interconvertible, and the equilibrium between them depends on photochemical reactions, the presence of oxidizing agents, etc. Gas turbines, like other combustion engines form NO_x in the hot combustion zones of engines. There are two known mechanisms responsible for NO_x formation in combustion engines:

(1) Thermal NO_x: NO_x formed by the reaction of atmospheric N_2 and O_2 in the hot combustion zone within the engine. This is the dominant mechanism when relatively clean fuels are burnt in the engine. Removal of NO_x from flue gases is an extremely difficult problem. However, it is possible to control the thermal NO_x formation by several techniques, some of which are:

   (a) Off-stoichiometric combustion by modified combustion chamber design

   (b) Water injection

   (c) Exhaust gas recirculation

Each of the above techniques results in a lower peak temperature within the combustion zone, thereby reducing thermal NO_x formation.

(2) NO_x from fixed nitrogen in the fuel: This source of NO_x is important only when nitrogen-bearing fuels such as those derived from coal and residual fuel oil are burned. Dirty fuels may contain organic nitrogen compounds which are oxidized during combustion to NO_x. Gasified fuels, especially those from gasifiers operating below 2000 F, contain combustible nitrogen compunds such as ammonia, hydrogen cyanide, and pyridine. Ammonia is the primary nitrogen compound, while the others are in smaller concentrations. If retained in the gas, these compounds are oxidized during combustion to NO_x. These compounds are removed by water scrubbing when a low temperature cleanup system is used. However, when a high-temperature cleanup system is used, these nitrogen compounds are carried through to the turbine. To prevent this carry-through, ammonia and other nitrogen compounds must be removed from the gas at elevated temperatures.

A potential method to remove ammonia is to decompose it into stable elemental nitrogen and hydrogen, at elevated temperatures. The decomposition of ammonia is governed by the following reaction:

$$2NH_3 \underset{k2}{\overset{k1}{\rightleftharpoons}} N_2 + 3H_2 \qquad (15)$$

The equilibrium constant k_1 increases as the temperature increases and the total pressure decreases. Temperature has a greater effect than pressure as is verified by the fact that k_1 is practically constant over the pressure range, 1 to 50 atmospheres. Hence the higher the temperature, the greater is the decomposition of ammonia into nitrogen and hydrogen. The equilibrium percentage of ammonia in a 3:1 hydrogen-nitrogen gas mixture is shown as a function of pressure and temperature in Fig. 8[16].

The equilibrium constants for ammonia formation, $k_p = \frac{k_1}{k_2}$ are tabulated below[17] for a range of temperatures and pressures.

	Pressure, atm		
Temp. F	10	30	50
660	0.0266	0.0273	0.0278
750	0.0129	0.0129	0.0130
840	0.00659	0.00676	0.0069

EQUILIBRIUM PERCENTAGE OF NH_3 IN A 3:1 HYDROGEN–NITROGEN GAS MIXTURE

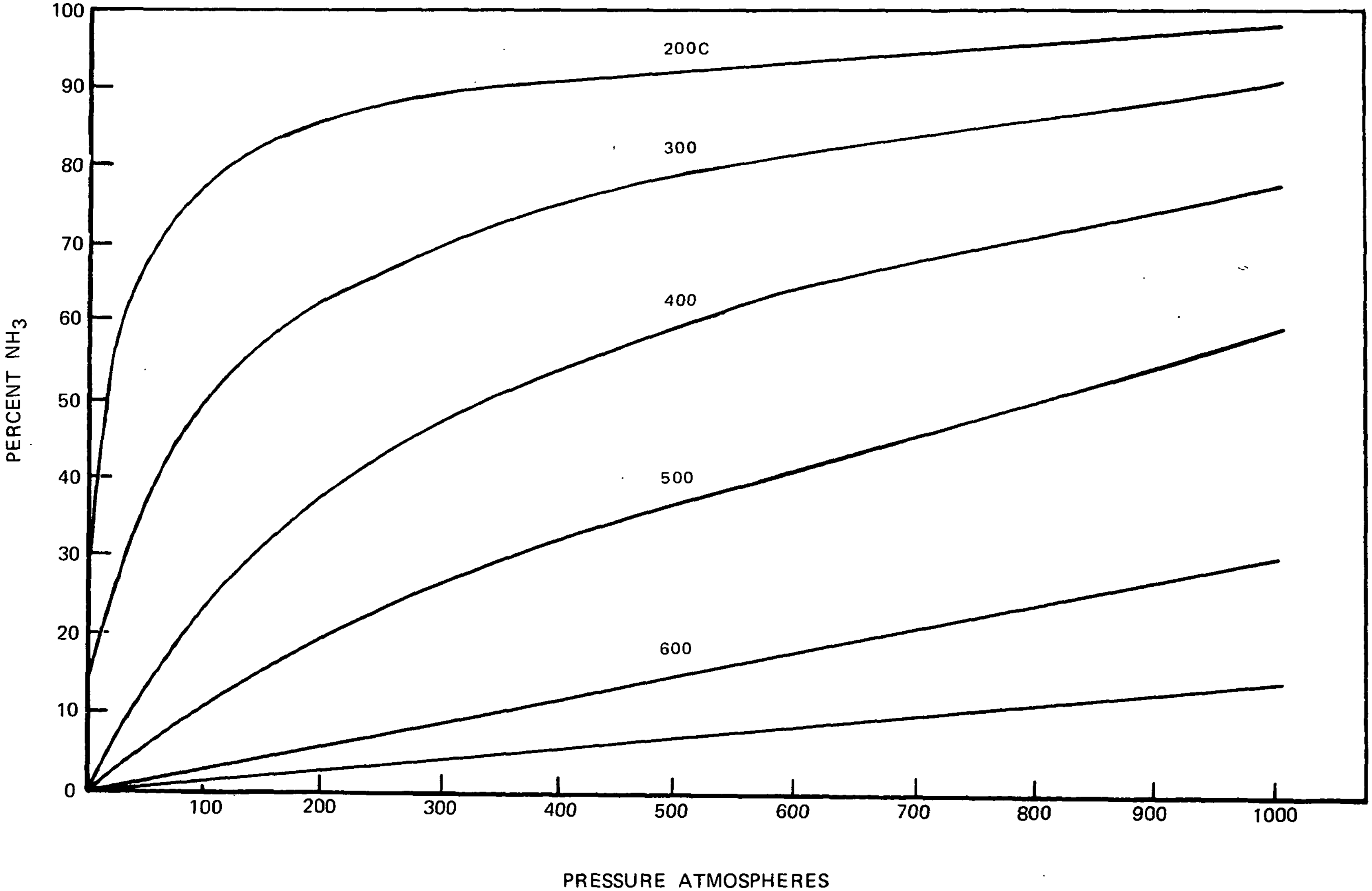


FIG. 8

76–02–4–1

The equilibrium constant for ammonia formation is seen to be very low at high temperatures and low pressures. Under the conditions at the exit of the BCR gasifier (1750 F, 475 psia) the ammonia concentration is 4260 ppm[17]. If allowd to equilibrate, the ammonia composition is reduced to 460 ppm while the temperature, due to other reactions, is reduced to approximately 1600 F. If the only reaction were ammonia decomposition, the temperature change would be much less and the resultant equilibrium ammonia concentration would be even lower (on the order of 200 ppm). This suggests that low equilibrium concentrations, although thermodynamically favored, are not kinetically feasible. Therefore, the kinetics must be aided by a catalyst.

A literature search yielded considerable recent work in the development of catalysts for ammonia decomposition. General Motors[18] and Ford Motor Co.[19] have addressed the ammonia decomposition problem with the goal of ridding automotive exhausts of poisonous nitric oxide, by first reducing it to ammonia and further decomposing the ammonia to elemental nitrogen and hydrogen. Research in this direction led to the development of several catalysts suitable for ammonia decomposition. Among these are Ni, Pt, W, Mo, Re and Ru. Of these catalysts, a Cu-Ni-Al_2O_3 catalyst was seen to have the highest activity for ammonia decomposition. The extent of ammonia decomposition over Cu-Ni-Al_2O_3 catalyst as a function of temperature, is shown in Fig. 9.

All the above catalysts proved to have a serious drawback. They are poisoned by even trace quantities of sulfur compounds present in the feed gas[20]. The poisoning is due to the formation of a metal-sulfide which deactivates the catalyst. Generally the metal/metal-sulfide equilibrium favors the formation of the metal-sulfide at low temperatures and favors its decomposition at high temperatures. As an example, the poisoning by sulfur compounds of Ni catalyst used in methanation reactions is shown in Fig. 10. The poisoning effect is seen to diminish only at high temperatures ($\sim$ 2000 F). Effectively this is the temperature above which, for example, a Cu-Ni-Al_2O_3 catalyst could be used to decompose ammonia. It is impractical, however, to use the catalyst at this temperature for two reasons:

(1) As such high temperatures, sintering would significantly reduce the activity of the catalyst.

(2) In all the gasification systems considered in this study where fuel gas ammonia is significant, fuel gas temperatures approaching 2000 F are unattainable. Gasifiers that operate at temperatures in excess of 2000 F will probably not produce appreciable amounts of ammonia.

AMMONIA DECOMPOSITION OVER Cu–Ni–Al_2O_3 CATALYST (8.1% Cu, 9.2% Ni)

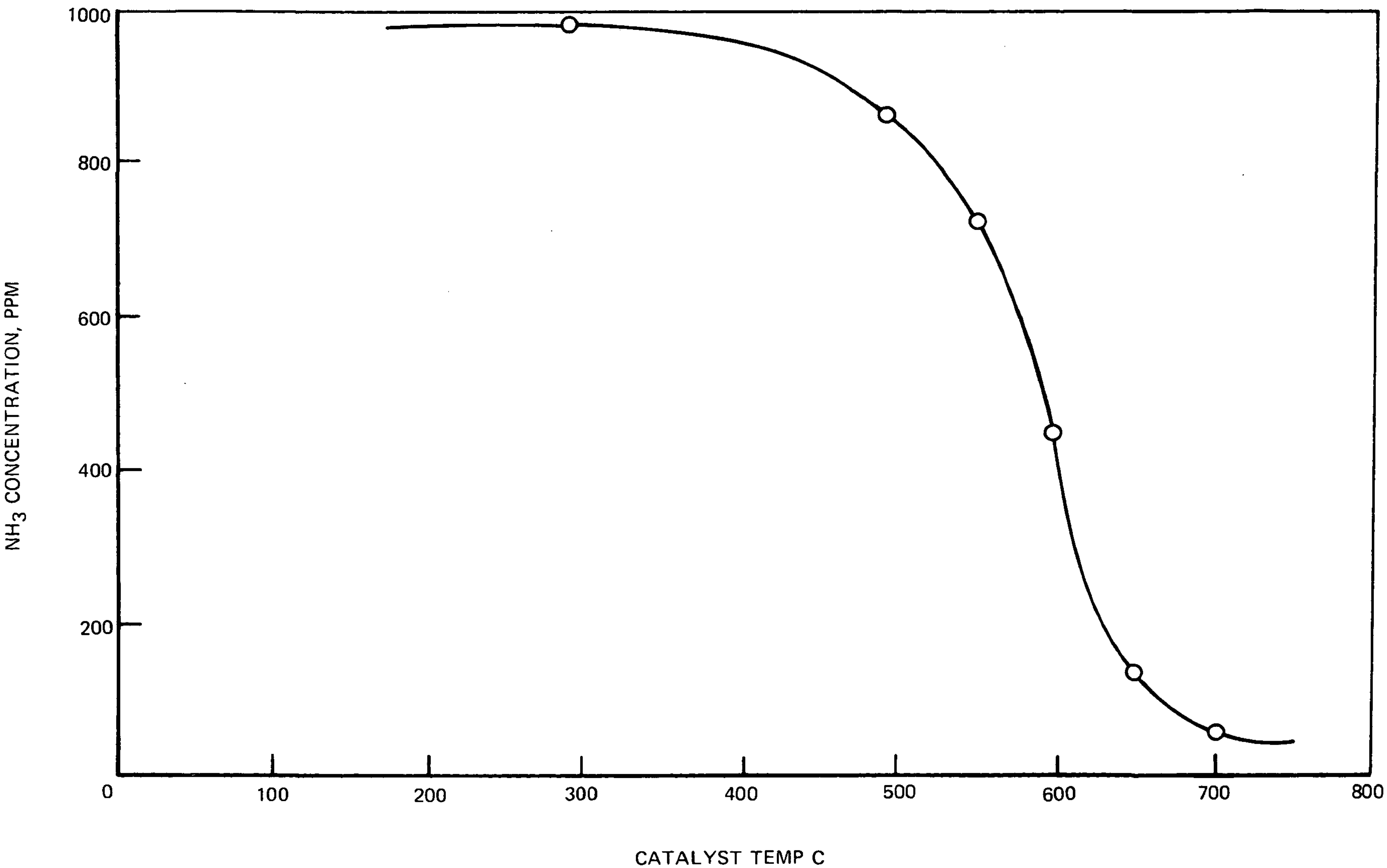
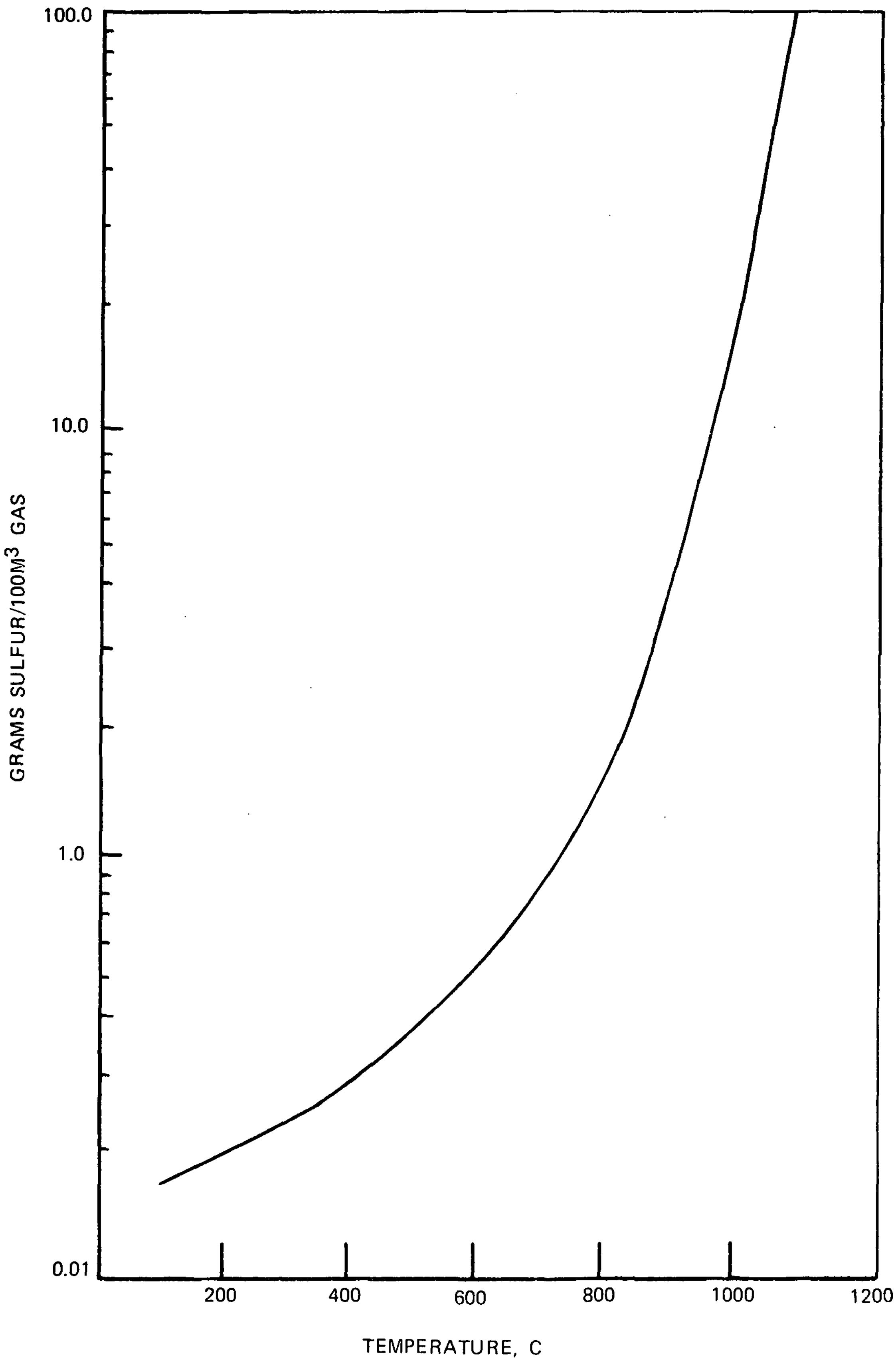


FIG. 9

76–02–4–5

POISONING OF Ni – CATALYSTS USED FOR ADJUSTMENT OF EQUILIBRIUM: $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$



76–02–4–7

The only commercial catalyst potentially capable of decomposing ammonia is an iron oxide catalyst composed of five percent Fe_2O_3 mounted on high-temperature, fired inert alumina spheres. This catalyst could simultaneously remove H_2S from the gas stream, thus combining the ammonia and sulfur removal operations in a single step. However, the operating conditions necessary for this catalyst are not known and must be determined before the catalyst becomes acceptable[21]. An iron oxide system thus has the potential for catalyzing the ammonia decomposition while removing sulfur compounts. Unfortunately, no data concerning ammonia levels across an iron oxide bed were found to be available. It is hoped that future testing will include provision for this measurement.

SECTION 2

EVALUATION OF INTEGRATED GASIFICATION AND CLEANUP PROCESSES

SUMMARY

The results of the integration of the Koppers-Totzek and the residual oil gasifier with selected cleanup systems are presented in this section. Those systems that were selected for integration are:

Koppers-Totzek/Selexol Cleanup
Oil Gasifier/Selexol Cleanup
Oil Gasifier/CONOCO Cleanup

For each of these, a flow sheet, mass balances, utility summary and equipment list are presented. For the K-T gasifier, the results of a preliminary evaluation comparing it in combination with high- and low-temperature cleanup systems are also given. It was determined that there was no advantage to be gained from the combination of the K-T gasifier and high-temperature (B&W iron oxide) cleanup.

Before describing the integration analysis, it will be instructive to briefly review the selection criteria for the cleanup systems as previously described in Ref. 1.

SELECTION CRITERIA

The primary factors considered in selecting cleanup systems include the efficiency of pollutant removal, effect on power system performance, cost considerations, and estimated time of availability for commercial application.

Low-Temperature Desulfurization Systems Selection

The following factors developed in Ref. 1 were considered in selecting low-temperature desulfurization systems most likely to be applicable to treating fuel gas:

(1) Sulfur removal capabilities, not only with respect to H_2S but also other sulfur compounds such as COS and CS_2.

(2) Selective absorption of sulfur compounds over carbon dioxide. The latter need not be removed from low-Btu fuel gas intended for use in advanced power cycles, and therefore its absorption is undesirable since it represents an increased operating load on the cleanup system.

(3) Type of absorbent insofar as the treated fuel gas may contain entrained or volatilized solvent which could be detrimental to downstream system components such as turbine blades, etc.

(4) The system's tolerance to other contaminants present in the raw fuel gas such as ammonia, cyanides, phenols and tars.

(5) Overall energy requirements and operating costs.

An arbitrary ranking technique was used to rank the cleanup systems. Based on the ranking, it appeared that the Benfield chemical solvent process and the Selexol and Rectisol physical solvent processes were fairly comparable, and ranked somewhat higher than the others. Therefore, these were evaluated for integrated system performance using data obtained from process licensors.

High-Temperature Desulfurization Systems Selection

In selecting the most applicable high-temperature desulfurization systems, the following factors were developed in Ref. 1:

(1) Operating temperature

(2) Capability for removing sulfur compounds, COS, CS_2, as well as H_2S.

(3) The form in which the sulfur is regenerated, e.g., H_2S, SO_2, or elemental sulfur. Elemental sulfur is the preferred form since it can be stored without significant pollution problems.

(4) Regenerability of the absorbent without substantial loss of activity.

(5) Overall energy requirements and operating costs.

From a qualitative comparison based on the above factors, the Bureau of Mines, and the Babcock and Wilcox processes appear well suited for use with first-generation gasifiers. These processes are suited for sulfur removal at temperatures below 1500 F, preferably around 1000 F, which is the operating range for first-generation fixed-bed gasifiers. Off-gas from a high-temperature, second-generation gasifier would require cooling to the operating temperature of the iron oxide process and this would represent a lower thermal efficiency than for integrated systems using the dolomite-based processes such as the CONOCO process. A disadvantage of the iron oxide process is the regeneration of sulfur as sulfur dioxide. In order to convert this to elemental sulfur, part of the sulfur dioxide must be reduced to hydrogen sulfide, and this step consumes fuel. The IGT-Meissner process, when developed, should be applicable to first-generation-type gasifiers, since its operating temperature is 900 F. The efficiency of sulfur removal is estimated at 98 percent, and it is selective toward both H_2S and COS over CO_2.

Second-generation gasifiers can employ the CONOCO dolomite process which has an operating temperature of 1500 F and above. The Battelle molten salt process also operates at temperatures around 1500 F, but its sulfur removal capability is questionable, particularly in the high-pressure range.

SYSTEM EVALUATION

After the selection of standard cleanup systems was made, the evaluation of integrated gasifiers and cleanup systems was considered. Of the low-temperature desulfurization systems selected earlier, the Selexol process was chosen for detailed evaluation of the integrated system. This selection was somewhat arbitrary since both the Benfield and Rectisol processes showed comparable sulfur removal to the Selexol process and preliminary estimates of overall system performance were essentially the same.

A comparison of integrated high- and low-temperature gas purification system was of interest in assessing the relative advantage of high-temperature cleanup systems in conjunction with gasifiers. For each of the entrained-flow gasifiers, viz coal-based Koppers-Totzek and the oil-based partial oxidation, two standard cleanup systems were selected for detailed evaluation of the integrated systems; a low-temperature and a high-temperature system. The Selexol process was the representative low-temperature desulfurization process, and the CONOCO half-calcined dolomite and the Babcock and Wilcox (B&W) iron oxide processes were selected as the representative high-temperature desulfurization process. While the B&W and the Bureau of Mines iron oxide processes operate on similar principles, the B&W process appears to be in a more advanced engineering state and was selected for consideration. This will allow identification of significant differences, if any, between the B&W and Bureau of Mines process.

As part of the detailed evaluation, heat and mass balances, utilities requirements, investment cost estimates, and definition of pollutant streams were developed for the various combinations of gasification and cleanup systems selected. The evaluations were based on a coal feed rate of 8400 tons/day and an oil feed rate of 6000 tons/day which roughly corresponds to a 1000-Mw COGAS power station output.

The two coal gasification/cleanup-system combination considered were:

(1) Koppers-Totzek/Selexol

(2) Koppers-Totzek/Babcock and Wilcox

A preliminary comparison of these two systems showed that there is nothing to be gained from the use of the high-temperature B&W cleanup system with the K-T gasifier and a combined-cycle power system. This is due to the need to cool the gas prior to compressing it to the required burner inlet pressure. Therefore, the results of that preliminary comparison are presented and only the K-T/Selexol system is described in detail with a complete mass balance.

Comparison of K-T/Selexol and K-T/B&W Cleanup System

For this comparison the gasifier capacity was taken to be 350 tons per hour of Illinois No. 6 coal having the following analysis and heating value:

	C	H	S	O	N	Ash	H_2O
Wt. %	67.4	5.1	3.8	9.6	1.2	8.7	4.2

HHV = 12,200 Btu/lb

The gasifier inputs were 0.832 lb O_2/lb coal, 0.34 lb steam/lb coal, and the raw gas temperature was taken to be 2730 F. It was assumed that all the nitrogen in the coal evolved as elemental nitrogen because at the peak temperature (3300 F) and pressure (1 atm) in the gasifier, the equilibrium constant for ammonia formation is very small. Furthermore, the sulfur in the coal reacted to give H_2S and COS, of which the latter constituted about six volume percent (of the total sulfur) in accordance with the chemical equilibrium for the hydrolysis reaction:

$$COS + H_2O \rightarrow CO_2 + H_2S \tag{16}$$

The following assumptions were made for the purpose of determining the gasifier output:

(1) Approximately 10 volume percent of the dry product gas is CO_2.

(2) All the convertible carbon in the coal goes to CO and CO_2.

(3) At the conditions present in the K-T gasifier, i.e., 3300 F, 1 atm, the CO shift reaction and methanation are not favored, and are therefore negligible.

(4) Illinois No. 6 coal has a carbon conversion of 97 percent.

The above assumptions are based on actual observations on K-T gasifiers.[7]

Coal at 160 F, 98 percent O_2 at 230 F, and low-pressure steam at 250 F are fed to the entrained-flow K-T gasifier operating a 1 atm. Raw gas leaves the gasifier at 2730 F. After a water quench, gas containing 0.9 lb/1000 scf of particulates is cooled in a waste heat boiler in which high-pressure steam is generated for subsequent use in the power cycle, as shown in Fig. 11 for the K-T/Selexol system. For comparison purposes, it was assumed that the hot gas was used to regenerate the high-pressure clean gas out of the Selexol system to give a clean product gas temperature of 1000 F. In the case of the B&W iron oxide system, cool down is not necessary prior to the desulfurization step but is required prior to compression of the product gas. In the Selexol system, both cool down and compression must be done before desulfurization since the solvent is sensitive to both temperature and partial pressure of the acid gas. In any event, both systems do require cool down and subsequent regeneration to achieve a product gas temperature of 1000 F. The heat recovered from the gas was therefore assumed to be about equal in each case.

KOPPERS–TOTZEK GASIFIER WITH SELEXOL CLEANUP

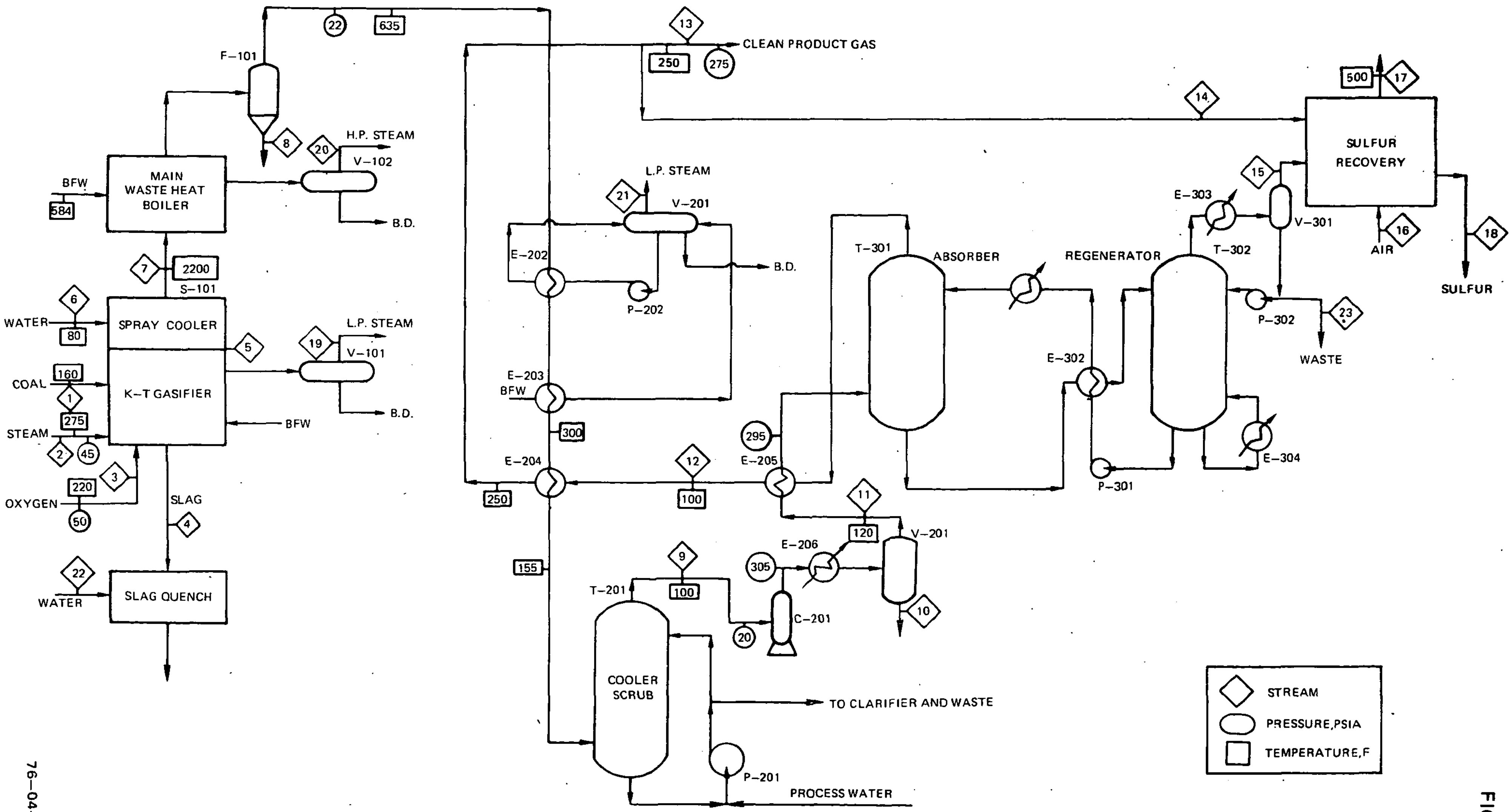


FIG. 11

76-04-334-3

The characteristics of the two systems are compared in Table 2. The overall heating value of the product gas is slightly higher for the Selexol system. This is due to the higher quantity of fuel required for sulfur recovery from the B&W iron oxide regenerator off gas which is in the form of SO_2 at relatively low concentration. Product gas volumetric flow rate differs significantly due to the loss of water vapor and removal of some CO_2 in the Selexol cleanup system. It is interesting to note that the cool down and compression step following the B&W cleanup will not produce a similar reduction in water vapor. Because the iron oxide calalyzes the water gas shift reaction, much of the water vapor is consumed by that process and the product gas is quite rich in hydrogen. While desirable from a combustion standpoint, this means that a higher volume of gas must be compressed. Another undesirable effect of the shift reaction is that the lower heating value of the hydrogen is significantly less than the CO that it replaces. While both effects are estimated to represent less than 1 percent of the total system output, they are certainly in the wrong direction. Thus, while there appears to be little performance difference between the high- and low-temperature systems, any performance advantage is in favor of the low-temperature system. Since a preliminary system performance evaluation showed neither to be competitive with other integrated systems, it was judged that nothing constructive would result from further consideration of the K-T/B&W system.

Koppers-Totzek/Selexol-Process Description

A schematic flow sheet for the K-T/Selexol system is shown in Fig. 11. The material balance is given in Table 8, a utilities summary in Table 9 and an equipment list in Table 10.

Gasifier performance was based on Koppers-Totzek data for a West Virginia Pittsburgh seam coal. To make the sulfur removal process comparable to the other systems studied, the sulfur content of the coal was increased to 3.8 percent. This had only a minor effect on the output gas composition other than to increase the sulfur compounds. Cold gas efficiency was given as 76 percent.

Coal input was taken to be 350 tons per hour with the following composition:

	C	H	S	O	N	Ash	H_2O
wt percent	74.8	5.0	3.8	6.1	1.3	7.0	2.0

HHV = 13,600 Btu/lb

Table 7

COMPARISON OF K-T GASIFIER WITH HIGH AND LOW TEMPERATURE CLEANUP

	FEATURE	K-T/B&W	K-T/Selexol
1.	Tons/day of Illinois No. 6 coal fed to gasifier	8400	8400
2.	Raw gas temperature at gasifier exit, °F	2730	2730
3.	Raw gas pressure at gasifier exit, atm	~ 1	~ 1
4.	Cleanup system inlet temperature, °F	1000	100
5.	Efficiency of sulfur removal	~ 97%	~ 99%
6.	H_2S content of product gas, ppm	270	140
7.	Product gas volume, mscfd	769	524
8.	Product gas temperature, °F	1000	1000
9.	Product gas pressure	~ 1 atm	250 psia
10.	Chemical heating value of product gas (HHV) - MMBtu/hr	6186	6377
11.	Overall cold gas efficiency	72%	74%

Table 8

MATERIAL BALANCE FOR K-T/SELEXOL SYSTEM (FIG. 11)

STREAM		1		2		3		4	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
H_2O	18.016			244652	13579.7				
CO	28.01								
H_2	2.016								
CO_2	44.01								
O_2	32.0					590569	18455.3		
N_2	28.016					10551	376.6		
COS	60.076								
H_2S	34.082								
TOTAL		700000		244652	13579.7	601120	18831.9		
Ash		48720						24360	
Carbon		523950							

STREAM		5		6		7		8	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
H_2O	18.016	140815	7816.1	170370	9456.6	311185	17272.7		
CO	28.01	1028841	36731.2			1028841	36731.2		
H_2	2.016	46951	23289.2			46951	23289.2		
CO_2	44.01	205271	4664.2			205271	4664.2		
O_2	32.0								
N_2	28.016	19847	708.4			19847	708.4		
COS	60.076	3160	52.6			3160	52.6		
H_2S	34.082	25960	761.7			25960	761.7		
TOTAL		1470845	74023.4	170370	9456.6	1641215	83480.		
Ash		24360				24360		24360	
Carbon		26198				26198		26198	

Table 8

MATERIAL BALANCE FOR K-T/SELEXOL SYSTEM (FIG. 11)

STREAM	M.W.	9 LB/HR	9 MOL/HR	10 LB/HR	10 MOL/HR	11 LB/HR	11 MOL/HR	12 LB/HR	12 MOL/HR
H_2O	18.016	73179	3962	64497	3580	6882	382	104	5.8
CO	28.01	1028841	36731.2			1028841	36731.2	1025435	36609.6
H_2	2.016	46951	23289.2			46951	23289.2	46880	23253.8
CO_2	44.01	205271	4664.2			205271	4664.2	172242	3913.7
O_2	32.0								
N_2	28.016	19847	708.4			19847	708.4	19802	706.8
COS	60.076	3160	52.6			3160	52.6	2109	35.1
H_2S	34.082	25960	761.7			25960	761.7	130	3.8
TOTAL		1401409	70169.3	64497	3580	1336912	66589.3	1266702	64528.6
Ash									
Carbon									

STREAM	M.W.	13 LB/HR	13 MOL/HR	14 LB/HR	14 MOL/HR	15 LB/HR	15 MOL/HR	16 LB/HR	16 MOL/HR
H_2O	18.016	104	5.8			1459	81.0		
CO	28.01	1021486	36468.6	3949	141.	3406	121.6		
H_2	2.016	46699	23164.2	181	88.6	71	35.4		
CO_2	44.01	171577	3898.6	665	15.1	33030	750.5		
O_2	32.0							23827	744.6
N_2	28.016	19726	704.1	76	2.7	45	1.6	78476	2801.1
COS	60.076	2103	35.0	6	0.1	1051	17.5		
H_2S	34.082	130	3.8			25831	757.9		
TOTAL		1261825	64280.1	4877	248.5	64893	1765.5	102303	3545.7
Ash									
Carbon									

Table 8

MATERIAL BALANCE FOR K-T/SELEXOL SYSTEM (FIG. 11)

STREAM	M.W.	17 LB/HR	17 MOL/HR	18 LB/HR	18 MOL/HR	19 LB/HR	19 MOL/HR
H_2O	18.016	17366	963.9			148097	82203
CO_2	44.01	46026	1045.8				
O_2	32.0	3971	124.1				
N_2	28.016	78596	2805.4				
SO_2	64.066	2492	38.9				
TOTAL		148451	4978.1			148097	82203
Sulfur	32.066			23617	736.5		

STREAM	M.W.	20 LB/HR	20 MOL/HR	21 LB/HR	21 MOL/HR	22 LB/HR	22 MOL/HR	23 LB/HR	23 MOL/HR
H_2O	18.016	1873070	103967	191705	10640.8	530080	29422.7	5319	295.2
CO_2	44.01								
O_2	32.0								
N_2	28.016								
SO_2	64.066								
TOTAL									
Sulfur	32.066								

Table 9

SUMMARY OF UTILITIES FOR K-T/SELEXOL SYSTEM

	Gasification (1)	Heat Recovery and Fuel Gas Compression	Acid Gas Removal	Sulfur Recovery	Total
Steam, Lb/Hr					
@ 65 psia	96555	(191705)	95150		-0-
@ 1370 psia		(1902770)		(51120)	(1,953,890)
Cooling Water, GPM	5800(2)		33250		33,250
Power, kW	21000	99534	12100	3	132,637
BFW, Lb/hr @125F	151060 (2)	195540			346,600
@584F	99220 (2)	1940820		52140	1,992,960
Stm. Cond., lb/hr			(95150)		(95150)
Process Water, lb/hr	530080				530,080
Chemicals $/day			65		65

(1) Includes Coal Processing
(2) Oxygen Plant Consumption

TABLE 10

EQUIPMENT LIST FOR K-T/SELEXOL SYSTEM (FIG.11)

Section 100 - Gasification

Item	Description
S-101	Gasifier and Main Heat Recovery
F-101	Cyclone Separator
V-101	LP Steam Drum
V-102	HP Steam Drum

Section 200 - Heat Recovery & Gas Compression

Item	Description
C-201	Fuel Gas Compressor - Intercooled
E-201	Main Fuel Gas Regenerator
E-202	LP Waste Heat Boiler
E-203	LP Waste Heat Economizer
E-204	Auxiliary Regenerator
E-205	Low Temperature Regenerator
E-206	Aftercooler
P-201	Process Water Pump
P-202	LP Boiler Recirculating Pump
V-201	Condensate Knock-Out Drum

Section 300 - Acid Gas Removal

Item	Description
E-301	Lean Solvent Cooler
E-302	Rich/Lean Solvent Exchanger
E-303	Selexol Stripper OVHD Condenser
E-304	Selexol Stripper Reboiler
P-301	Selexol Stripper BTMS Pump
P-302	Selexol Stripper Reflux Pump
T-301	Selexol Scrubber
T-302	Selexol Stripper
V-301	Selexol Stripper OVHD Accumulator

Oxygen used in the gasifier was .844 lb O_2/lb coal and steam was .35 lb/lb coal. Hot gases leave the gasifier at 2630 F and are water quenched to 2200 F to solidify the ash prior to entry into the waste heat boiler. Feedwater is supplied to the boiler at saturation temperature. The feedwater heating is done in the main gas turbine waste heat boiler as determined in the course of integrated system optimization. Steam raised in the low pressure boiler (E-202) combined with that raised in the gasifier jacket is sufficient to supply the requirements of both gasifier and Selexol system. The gasifier steam requirement shown in Table 9 represents the difference between gasifier input and that raised in the gasifier jacket. The hot gas leaves the low-pressure boiler at 300 F and is used to regenerate the clean gas to 250 F for delivery to the power system. Prior to compression, the gases are further cooled and scrubbed. The compressed gas is sent to the Selexol system for H_2S removal.

As is shown in Appendix A, the gasifier exit temperature of 2730 F agrees quite well with the result of an equilibrium calculation. Thus, the assumption of 6 percent of sulfur compounds as COS appears to be justified. This is important in the sizing of the Selexol system as the solvent has a relatively low capacity for COS. In the preliminary comparison, the system was sized for COS removal resulting in removal of a significant amount of CO_2 from the fuel gas and increasing the utility requirements. With the system sized only for H_2S removal, the resultant sulfur in the product gas is approximately 600 ppmv. While this exceeds our general study guideline of 500 ppm, this value was established for air blown gasifiers with product gas heating value in the 100-150 Btu/scf range. For the K-T gas an equivalent guideline would be 1000 ppmv. Therefore, the sulfur removal system was sized for H_2S only resulting in reduced size and utilities. Because of the higher concentration of H_2S in the Selexol off gas, this also results in an improvement in the sulfur recovery section. The H_2S concentration in the gas to the Claus plant is only 0.4 percent of the total gas produced.

Another result of the relatively low fuel gas mass flow rate is to minimize the effect of fuel gas regeneration. Cycle studies showed that while possible, regeneration to 1000 F was not sufficiently attractive to warrant the changes that would be required in the basic K-T system.

OIL GASIFICATION PROCESSES

The two oil gasification/cleanup process combinations considered were:

(1) Partial Oxidation/Selexol
(2) Partial Oxidation/CONOCO

For each case study, the gasifier capacity was taken to be 250 tons/hour of Venezuelan residual fuel oil (RFO) having the analysis, physical properties, and heating value given in Table 11.

The gasifier input was 6 lb air/lb oil. The temperature of the exit gas was taken to be 2500. The sulfur in the fuel oil is converted to H_2S and COS. Steam may be used to control the reaction temperature, but is not essential to the gasification process itself. From the chemical equilibrium of the hydrolysis reaction:

$$COS + H_2O \rightarrow CO_2 + H_2S. \qquad (17)$$

The COS is approximately five volume percent of the total sulfur.

Oil Gasification /Selexol-Process Description

Residual fuel oil at 250 F and air at 600 F are fed to the oil gasifier with an air/oil ratio of 6.0. Entrained gasification of the oil occurs at about 2600 F and 400 psia to give a raw gas containing soot (up to three percent of the carbon in the feed). The gas is cooled to 1200 F in a waste heat boiler to generate 1370 psig saturated steam which is sent to the power system. The gas then passes through cyclones and a series of heat exchangers in which it is cooled by exchanging its heat with clean product gas. The gas is then scrubbed with water to remove traces of soot. It is then desulfurized in the Selexol absorber, where 96 percent of the acid gases are removed. The desulfurized gas with a residual sulfur content of about 110 ppmv is reheated in heat exchangers by the incoming raw gas, and is delivered to battery limits at 1000 F, and 275 psia. Including the sensible heat used to raise the high-pressure steam generated in the waste heat boiler, the overall thermal efficiency of the gasifier/cleanup-system becomes 91 percent.

The carbon slurry from the water wash is fed to a "Pelletizer"[22] in which the carbon is recovered from the slurry and mixed with the oil to form a carbon-oil slurry. While this system is normally used only for oils that can be fired at temperatures below 100 C[23], it was selected over the alternative naphtha extraction process because of its low utility requirements. Available data on the naphtha based soot recovery process showed the steam required for naphtha stripping to be equivalent to the heating value of the recovered carbon. In the peletizer, the carbon is wet by the fuel oil forming pellets that are then homogenized into the main fuel stream. Where the oil must be at elevated temperature, the small quantities of water that are introduced by the process can cause

TABLE 11. PROPERTIES OF VENEZUELAN RESIDUAL FUEL OIL

Composition, weight % (ash free)	
Carbon	86.43
Hydrogen	10.78
Sulfur	2.59
	98.8
Ash Content, weight %	0.20
Metals(1), ppm	
Vanadium	425.3
Nickel	47.2
Iron	19.0
Sodium	8.0
Copper	0.3
Chromium	0.2
	500.0
Viscosity, SSU @ 212 F	250
Viscosity, SSU @ 100 F	3700
Net Heating Value, Btu/gal	142,000
Net Heating Value, Btu/lb	17,300
Gross Heating Value, Btu/gal	150,000
Gross Heating Value, Btu/lb	18,300
Flash, F (Pensky-Martens Closed Cup)	175
API Gravity, deg	12
Density, lb/gal	8.229
Characterization Factor	10-12
Stoichiometric Air/Fuel Ratio	13.8

(1) Metals content based on crude and adjusted to RFO specifications

foaming. However, operation at pressure would alleviate these problems (although it has not been done commercially) and appears to be the most desirable approach.

The rich Selexol solvent is regenerated with steam to give an off-gas containing 39 percent H_2S. This is converted to elemental sulfur in a vapor phase Claus plant. About one percent of the product guel gas is used to provide fuel for the Claus plant.

A schematic flow sheet of the oil gasifier/Selexol system is given in Fig. 12. The material balance is given in Table 12, a utilities summary in Table 13, and an equipment list in Table 14.

Oil Gasifier/CONOCO-Process Description

Raw gas from the gasifier is cooled in a waste heat boiler to 1650 F. High-pressure steam is generated for use in the power system. The gas then goes through a high-temperature particulate removal system, where most of the soot is removed. After particulate removal, the gas enters the high-temperature desulfurization system. In the fluidized-bed desulfurizer, the gas contacts a half-calcined dolomite acceptor at 450 psia. The acceptor enters with 75 percent of the calcium as CaS, and leaves with 88 percent of the calcium as CaS. Approach to equilibrium for the CO shift and sulfur absorption reactions is assumed to be 100 percent. The overall reactions occurring during desulfurization are slightly endothermic, so that the treated gas exits at 1600 F and contains 60 ppmv total sulfur. This exceptionally low level is directly attributable to the characteristics of the oil gasifier. By using no steam and minimizing CO_2 production the gas phase absorption products (CO_2 and H_2O) exist at very low concentration and thereby favor the absorption.

Sulfided acceptor plus fresh dolomite, equal to one percent of the circulating solids, is transported to the fluidized-bed regenerator by the regeneration gas. Regeneration is carried out at 1300 F with an 85 percent approach to H_2S equilibrium and the gas exits the regenerator with a molar ratio of carbon dioxide to steam equal to 2.0. About 14 percent of the CaS is converted and the regenerated solids are recycled by gravity to the desulfurizer. The off-gas from the regenerator contains 6.4 percent H_2S by volume and after cooling to 380 F, is fed to a liquid-phase sulfur recovery unit.

PROCESS FLOW DIAGRAM OIL GASIFIER/SELEXOL CLEANUP SYSTEM

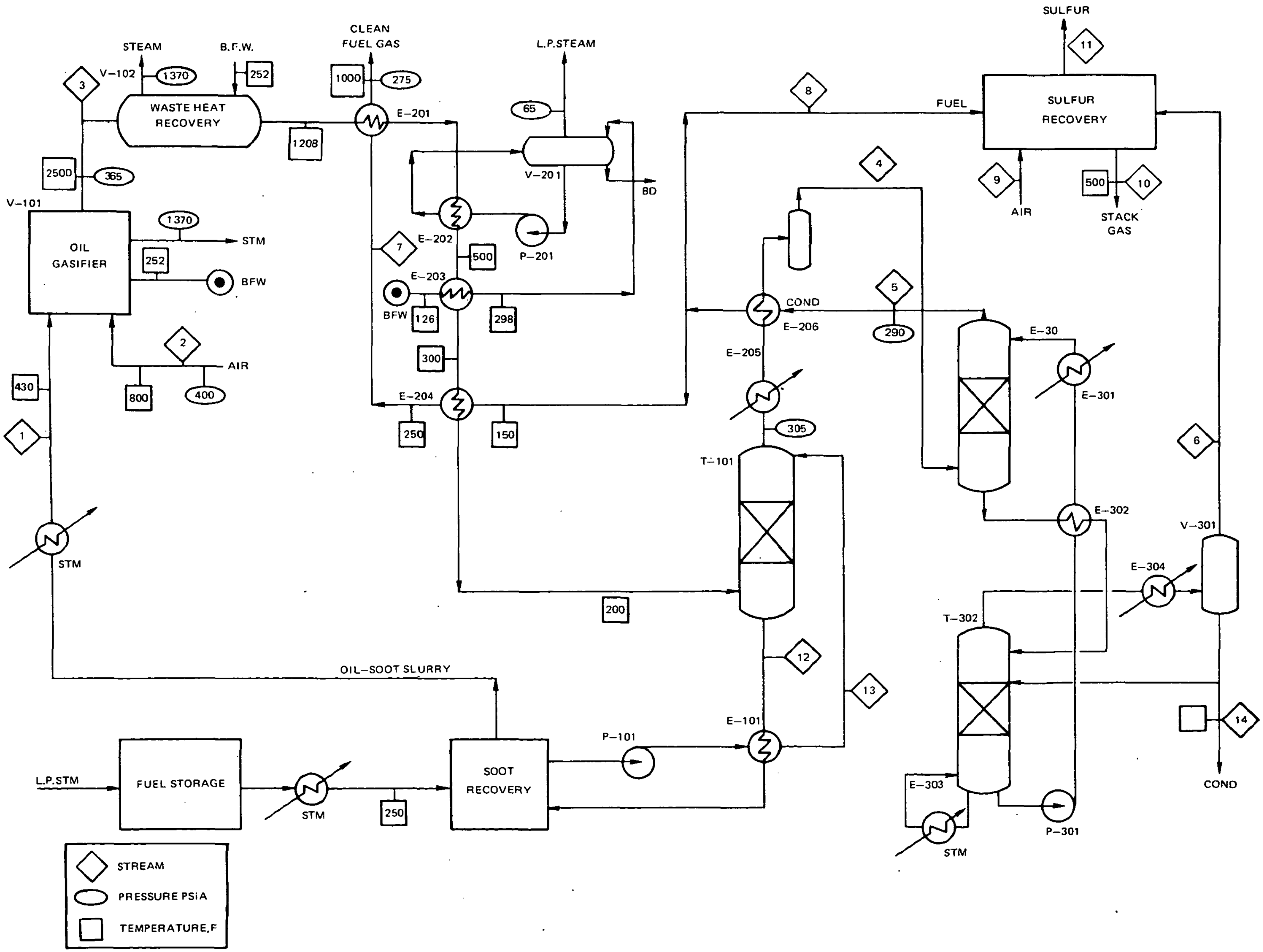


FIG. 12

76-04-334-1

TABLE 12

MATERIAL BALANCE FOR OIL GASIFIER/SELEXOL SYSTEM

(See Figure 12)

Stream		1		2		3		4		5	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
H_2O	18.016					90503	5025.5	14261	791.6	234	13
CO	28.01					937013	33452.8	937013	33452.8	933907	33341.9
H_2	2.016					43059	21358.8	43059	21358.8	42994	21326.3
CO_2	44.01					109556	2489.3	109556	2489.3	91919	2088.6
O_2	32.0										
N_2	28.016					2263916	80808.0	2263916	80808.0	2258938	80630.3
A_r	39.944					40536	1014.8	40536	1014.8	40536	1014.8
CH_4	16.042					46	2.9	46	2.9	46	2.9
NH_3	17.032					148	8.7	148	8.7	51	3.0
COS	60.076					1216	20.2	1216	20.2	811	13.5
H_2S	34.082					13007	381.6	13007	381.6	61	1.8
				3000000		3499000	144560.6	3422758	140328.7	3369497	138436.1
Oil		500000									
Soot		8640				8640					

TABLE 12

MATERIALS BALANCE FOR OIL GASIFIER/SELEXOL SYSTEM

(See Figure 12)

		6		7		8		9		10	
		LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
H_2O	18.016	1457	80.9	234	13.					9929	551.1
CO	28.01	3106	110.9	931744	33264.7	2162	77.2				--
H_2	2.016	66	32.5	42894	21277.	99	49.3				--
CO_2	44.01	17635	400.7	91708	2083.8	211	4.8			26419	600.3
O_2	32.0	--	--		--		--	13616	425.5	2269	70.9
N_2	28.016	4978	177.7	2253714	80443.8	5225	186.5	44316	1581.8	54519	1946.0
A_r	39.944	--	--	40443	1012.5	92	2.3	795	19.9	887	22.2
CH_4	16.042	--	--	46	2.9		--				--
NH_3	17.032	97	5.7	51	3.0		--				--
COS	60.076	403	6.7	811	13.5		--				--
H_2S	34.082	12944	379.8	61	1.8		--				--
NO	30.008	--	--							177	5.7
SO_2	64.066	--	--							1236	19.3
		40686	1194.9	3361707	138116.	7789	320.1	58727	2027.2	95430	3215.5

		11		12		13		14		15	
		LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
Sulfur	32.066	11775	367.2								
H_2O	18.016			500000	27753	500000	27753	14027	778.6	76242	4231.9
Soot	12.01			8640	719.4						

Table 13

SUMMARY OF OIL GASIFIER/SELEXOL CLEANUP SYSTEM
UTILITIES CONSUMPTION

	Oil Gasification	Heat Recovery	Acid Gas Removal	Sulfur Recovery	Total
STEAM, lb/hr					
@ 65 psia	132000	(296000)	194450	(30475)	-0-
@ 1370 psia	60600	(1710900)*			1650300
COOLING WATER, gpm	36600		67910		104510
POWER, kW	17565		24710	2.	42277
BFW, lb/hr		301900		31100	333000
STEAM COND., lb/hr	(192600)		(194450)		(378050)
PROCESS WATER lb/hr					
CHEMICALS, $/day			130		130

*Includes gasifier jacket steam

Table 14

OIL GASIFIER/SELEXOL SYSTEM
EQUIPMENT LIST

Section 100. Gasification & Soot Recycle

Item	Description
V-101	Oil Gasifier
V-102	Heat Recovery Unit
T-101	Water Scrubber
P-101	Recirculating Pump
E-101	Regenerator

Section 200. Heat Recovery

Item	Description
V-201	LP Steam Drum
E-201	Main Fuel Gas Regenerator
E-202	L.P. Boiler
E-203	L.P. Economizer
E-204	Aux. Fuel Gas Regenerator
E-205	Air Cooler
E-206	Aux. Fuel Gas Regenerator
P-201	L.P. Boiler Recirculating Pump

Section 300. Acid Gas Removal

Item	Description
E-301	Selexol Solvent Cooler
E-302	Rich/Lean Solvent Exchanger
E-303	Selexol Stripper Reboiler
E-304	Selexol Stripper OVHD Condenser
P-301	Selexol Stripper BTMS Pump
T-301	Selexol Absorber
T-302	Selexol Stripper
V-301	Selexol Stripper OVHD Accumulator

Section 400. Sulfur Recovery

Spent dolomite, withdrawn from the regenerator via a lock hopper, is treated before discharge to the environment. This stream, containing 75 percent of the calcium as CaS, is slurried with water in a hydrocyclone. The slurry is then processed in a three-stage counter current reactor system where CO_2 is used to convert all the calcium to the carbonate form, thereby rendering the stream suitable for discharge to a sludge pond. The H_2S generated in the spent dolomite system is compressed and fed to the sulfur recovery along with the regenerator off-gas.

The liquid-phase Claus reactor operates at 310 F and converts 90 percent of the H_2S feed to elemental sulfur. Sulfur is produced by the reaction of H_2S with a solution of H_2SO_3. One third of the sulfur that is produced is burned are subsequently absorbed by contact with water to replenish the H_2SO_3 used in the reactor. The overhead gases from the reactor are recycled to the dolomite regenerator. Thus, with this system the only sulfur emission from the processing system is that part of the SO_2 not absorbed by contact with the lean solution from the reactor and the apparent conversion efficiency of H_2S is in excess of 99 percent.

Makeup CO_2 is required for acceptor regeneration and treating of spent dolomite. Because of the low CO_2 content of the fuel gas, the use of a slipstream from the gas turbine exhaust was selected as the source of CO_2. Approximately 1.4 percent of the exhaust stream is fed to an amine recovery system. The product CO_2 is compressed and used for makeup.

Product fuel gas is delivered to battery limits at 1600 F and 395 psia. Heating value of the gas is 122 Btu/scf (HHV) and cold gas efficiency is approximately 73 percent. Because virtually all of the sensible heat is recoverable and because hot gas efficiency does not account for gasifier air and fuel preheat or other utility requirements, the hot gas efficiency is slightly in excess of 100 percent.

A schematic flow sheet for the oil gasifier/CONOCO system is given in Fig. 13. The material balance is given in Table 15, a utilities summary in Table 16, and an equipment list in Table 17.

PROCESS FLOW DIAGRAM OIL GASIFIER/CONOCO CLEANUP SYSTEM

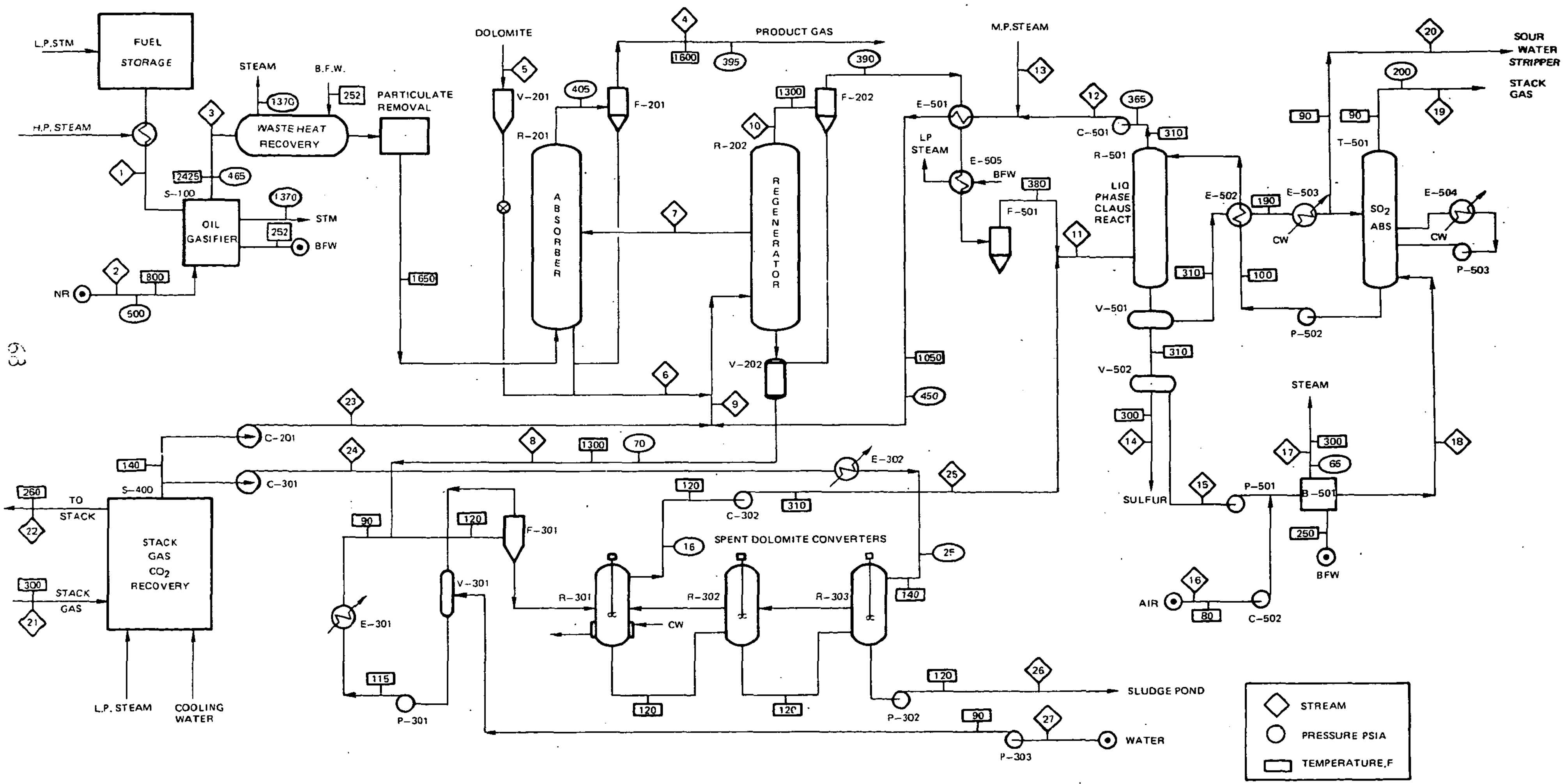


FIG. 13

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Table 15

MATERIAL BALANCE FOR OIL GASIFIER/CONOCO CLEANUP SYSTEM
(See Fig. 13)

Stream	M.W.	1 LB/HR	1 MOL/HR	2 LB/HR	2 MOL/HR	3 LB/HR	3 MOL/HR	4 LB/HR	4 MOL/HR
H_2O	18.016					90503	5025.5	68223	3786.8
CO	28.01					937013	33452.8	891886	31841.7
H_2	2.016					43059	21358.8	46307	22969.9
CO_2	44.01					109556	2489.3	198582	4512.2
O_2	32.0			69559	2173.7				
N_2	28.016			226387	8080.6	2263916	80808.0	2263917	80808.0
Ar	39.944			4054	101.5	40536	1014.8	40535	1014.8
CH_4	16.042					46	2.9	47	2.9
NH_3	17.032					148	8.7	148	8.7
COS	60.076					1216	20.2	90	1.5
H_2S	34.082					13007	381.6	245	7.2
				3000000	10355.8	3499000	144560.6	3509980	144953.7
Oil		5000000							

Stream	M.W.	5 LB/HR	5 MOL/HR	6 LB/HR	6 MOL/HR	7 LB/HR	7 MOL/HR	8 LB/HR	8 MOL/HR
$CaCO_3 \cdot MgCO_3$	184.01	5557.1	30.2	5557	30.2				
$CaCO_3 \cdot MgO$	140.41			3652	350.8	104451	743.9	1039.0	7.4
$CaS \cdot MgO$	112.46			300605	2673	256397.6	2279.9	2564.1	22.8
Inerts	100	530	5.3	53600	536	53070	530.7	530	5.3
		60871	35.5	363414	3590	413918.6	3554.5	4133.1	35.5

Table 15 (Cont'd.)

Stream	M.W.	9 LB/HR	9 MOL/HR	10 LB/HR	10 MOL/HR	11 LB/HR	11 MOL/HR	12 LB/HR	12 MOL/HR
H_2O	18.016	772004.6	2378.5	36179.7	2008.2	36264.4	2012.9	19496.9	1082.2
CO_2	44.01	191729.6	4356.6	176761.8	4016.4	177347.1	4029.7	177347.1	4029.7
H_2S	34.082	1489.4	43.7	14110	414	14887.0	436.8	1489.4	43.7
		965223.6	6787.7	227051.5	6438.6	213611.5	6479.4	198333.4	5155.6

Stream	M.W.	13 LB/HR	13 MOL/HR	14 LB/HR	14 MOL/HR	15 LB/HR	15 MOL/HR	16 LB/HR	16 MOL/HR
H_2O	18.016	22359.6	1241.1					7004.8	218.9
O_2	32							22799.4	813.8
N_2	28.016							407.4	10.2
Ar	39.944							30211.6	1042.9
		22359.6	1241.1						
S	32.066				390.7		199		

Stream	M.W.	17 LB/HR	17 MOL/HR	18 LB/HR	18 MOL/HR	19 LB/HR	19 MOL/HR	20 LB/HR	20 MOL/HR
H_2O	18.016	25039	1398.5			54.0	3.0	23795.5	1320.8
O_2	32.0			636.8	19.9	636.8	19.9		
N_2	28.016			638748.6	813.8	638748.6	813.8		
Ar	39.944			407.4	10.2	407.4	10.2		
SO_2	64.066			12749.1	199	153.8	2.4		
		25039	1389.8	652541.9	1042.9	640000.6	849.3	23795.5	1320.8

Table 15 (Cont'd.)

Stream	M.W.	21 LB/HR	21 MOL/HR	22 LB/HR	22 MOL/HR	23 LB/HR	23 MOL/HR	24 LB/HR	24 MOL/HR
H_2O	18.016	6521.8	362.0	128175.2	394.9	994.5	55.2	201.8	11.2
CO_2	44.01	21626.5	491.4	4326.2	98.3	14382.5	326.8	2917.9	66.3
O_2	32.0	19116.8	597.4	19116.8	597.4				
N_2	28.016	131439.9	4691.6	131439.9	4691.6				
Ar	39.944	2352.7	58.9	2352.7	58.9				
NO	30.088	3	0.1	3	0.1				
SO_2	64.066	6.4	0.1	6.4	0.1				
		181067.1	1509.9	285420.2	5841.2	15377.0	382.0	3119.7	77.5

Stream	M.W.	25 LB/HR	25 MOL/HR	26 LB/HR	26 MOL/HR	27 LB/HR	27 MOL/HR
CO_2	44.01	585.3	13.3				
H_2S	34.082	777.1	22.8				
$H_2O(g)$	18.016	84.7	4.7				
$CaCO_3 \cdot MgCO_3$	184.01			5557.1	30.2		
Inerts	100			530	5.3		
$H_2O(l)$	18.016			7440.6	413.0	3320321.6	429.3
		1447.1	40.8	13527.7	448.5	3320321.6	429.3

Table 16

SUMMARY OF OIL GASIFIER/CONOCO CLEANUP SYSTEM
UTILITIES CONSUMPTION

	Oil Gasification	Heat Recovery	Sulfur Removal	Spent Dolomite Treating	CO_2 Recovery	Sulfur Recovery	Sour Water Stripper	Total
Steam, lb/hr								
@ 65 psia	132000		(18164)		30660	(22162)	7150	129484
@ 1370 psia	60600	(1099700)*	22360					(1016740)
Cooling Water, gpm	30600			600	2780	3300		37280
Power, kw	17565		145	85	4570	2055	20	24440
BFW, lb/hr			18527			22605		41132
Steam Cond., lb/hr	(192600)				(30660)		(7150)	230410
Process Water, lb/hr								
Chemicals, $/day			800					800

*Includes steam raised in gasifier jacket

Table 17

OIL GASIFIER/CONOCO SYSTEM
EQUIPMENT LIST

Section 100 - Gasifier and Heat Recovery

Section 200 - Desulfurization

Item	Description
Reactors	
R-201	Sulfur Absorber
R-202	Acceptor Regenerator
Vessels	
V-201	Dolomite Feed Hopper
V-202	Spent Dolomite Hopper
Miscellaneous	
F-201	Absorber Cyclone Separator
F-202	Regenerator Ccylone Separator
Compressors	
C-201	CO_2 Makeup Compressor

Table 17 - Continued

OIL GASIFIER/CONOCO SYSTEM
EQUIPMENT LIST

Section 300 - Spent Dolomite Treating

Item	Description
Reactors	
R-301	Acceptor Converter 1^{st} Stage
R-302	Acceptor Converter 2^{nd} Stage
R-303	Acceptor Converter 3^{rd} Stage
Vessels	
V-301	Quench Water Surge
Pumps	
P-301	Quench Water Pump
P-302	Dolomite Slurry Pump
P-303	Make-up Water Pump
Exchangers	
E-301	Quench Water Cooler
E-302	CO_2 Trim Cooler
Compressors	
C-301	CO_2 Blower
C-302	Acid Gas Compressor
Miscellaneous	
F-301	Hydroclone

Section 400 - CO_2 Recovery System

Table 17 - Continued

OIL GASIFIER/CONOCO SYSTEM

EQUIPMENT LIST

Section 500 - Sulfur Recovery

Item	Description
Reactors	
R-501	Liquid Phase Clause Reactor
Towers	
T-501	SO_2 Absorption Column
Vessels	
V-501	Sulfur Separator Drum
V-502	Sulfur Storage Drum
Pumps	
P-501	Sulfur Pump
P-502	Acid Pump
P-503	Acid Circulating Pump
Compressors	
C-501	Recycle CO_2 Compressor
C-502	Air Compressor
Exchangers	
E-501	Recycle CO_2 Reheater
E-502	Feed/Bottoms Exchanger
E-503	Weak Acid Cooler
E-504	SO_2 Absorber Intercooler
E-505	L.P. Boiler
Miscellaneous	
F-501	Electrostatic Precipitator
B-501	Sulfur Burner

SECTION 3

REFINEMENT OF INTEGRATED SYSTEMS

SUMMARY

Based upon the results previously obtained,[1] further refinement of certain integrated systems was judged to be desirable and achievable. The refinements desired were those leading to higher efficiencies, lower emissions, and lower power costs. These were achieved by making appropriate process modifications whereby low-grade heat was better utilized and the utility requirements in different process units were reduced. The process modifications discussed in this section are summarized below:

BuMines/Selexol System - Resaturation of the clean fuel gas results in a higher turbine mass flow rate and better performance.

BuMines/Iron Oxide System - Based on more recent data for operation of the iron oxide cleanup system, significant improvement in the sulfur recovery process can be made resulting in lower utility requirements and decreased equipment cost. Several alternative methods of sulfur recovery are compared.

BCR/Selexol System - Catalytic conversion of COS to H_2S upstream of the cleanup system can permit the use of a smaller Selexol unit, lower solvent flow rate, lower cost and reduced utility consumption.

BCR/CONOCO System - While reducing overall performance, the addition of a water scrub for ammonia and particulate removal results in decreased NO_x emission.

In addition to the process refinements, further performance improvements or at least a better understanding of some of the operating and effluent relationships of entrained-flow gasifiers could result from the development of a computer model of the gasification process. A discussion of the model development and the results of parametric studies using the model are contained in the following section.

REVISED UTILITY REQUIREMENTS FOR AMMONIA REMOVAL

A re-evaluation of the ammonia scrubbing requirement[1] indicated that for a practical system only 33 percent of the original value resulted in a more concentrated ammonia solution (2.14 percent by weight as against 0.85 percent by weight) off the scrubber. This led to a 58 percent reduction in the steam and power requirements for the BuMines/Selexol sour water stripper and a 52 percent reduction for the BCR/Selexol stripper. The overall effect on system performance of those improvements is given in SECTION 4.

FUEL GAS RESATURATION - BUMINES/SELEXOL

It was found that the performance of the integrated system consisting of the BuMines gasifier and Selexol cleanup improved when the fuel gas was resaturated with water vapor before being fired in the gas turbine. The improved turbine performance described in detail in SECTION 4, is attributable to the increased mass flow through the turbine. The amount of water required to resaturate the fuel gas, and the resaturation temperature were determined. The process schematic (Fig. 14) downstream of the water-quench was altered to utilize the heat contained in the gas for the sour water and Selexol stripping operations. The resaturation requirements were found to be:

(1) Saturation temperature: 252°F
(2) Water required: 257, 812 lb/hr
(3) Water circulation rate: 15,850 gpm
(4) Water temperature at the saturator inlet: 252°F
(5) Water temperature at the saturator outlet: 205°F

A revised mass balance is given in Table 18, a revised utilities summary in Table 19 and a revised equipment list in Table 20.

REVISED SO_2 REMOVAL FROM BUMINES/IRON-OXIDE

Previous estimates of the iron oxide performance during regeneration had shown a low (5 percent) concentration of SO_2 in the off-gas. More recent data[24] gives a value for SO_2 concentration in the regeneration off-gas of 12 percent (by volume). This value was used as a basis to evaluate four alternative methods of handling the SO_2 in the off-gas. These alternatives were evaluated in light of the higher SO_2 concentration to determine their effect on the overall plant efficiency and costs. Each of the alternatives was arbitrarily chosen as being representative of the three different categories of SO_2 removal processes:

REVISED PROCESS FLOW DIAGRAM BUMINES/SELEXOL

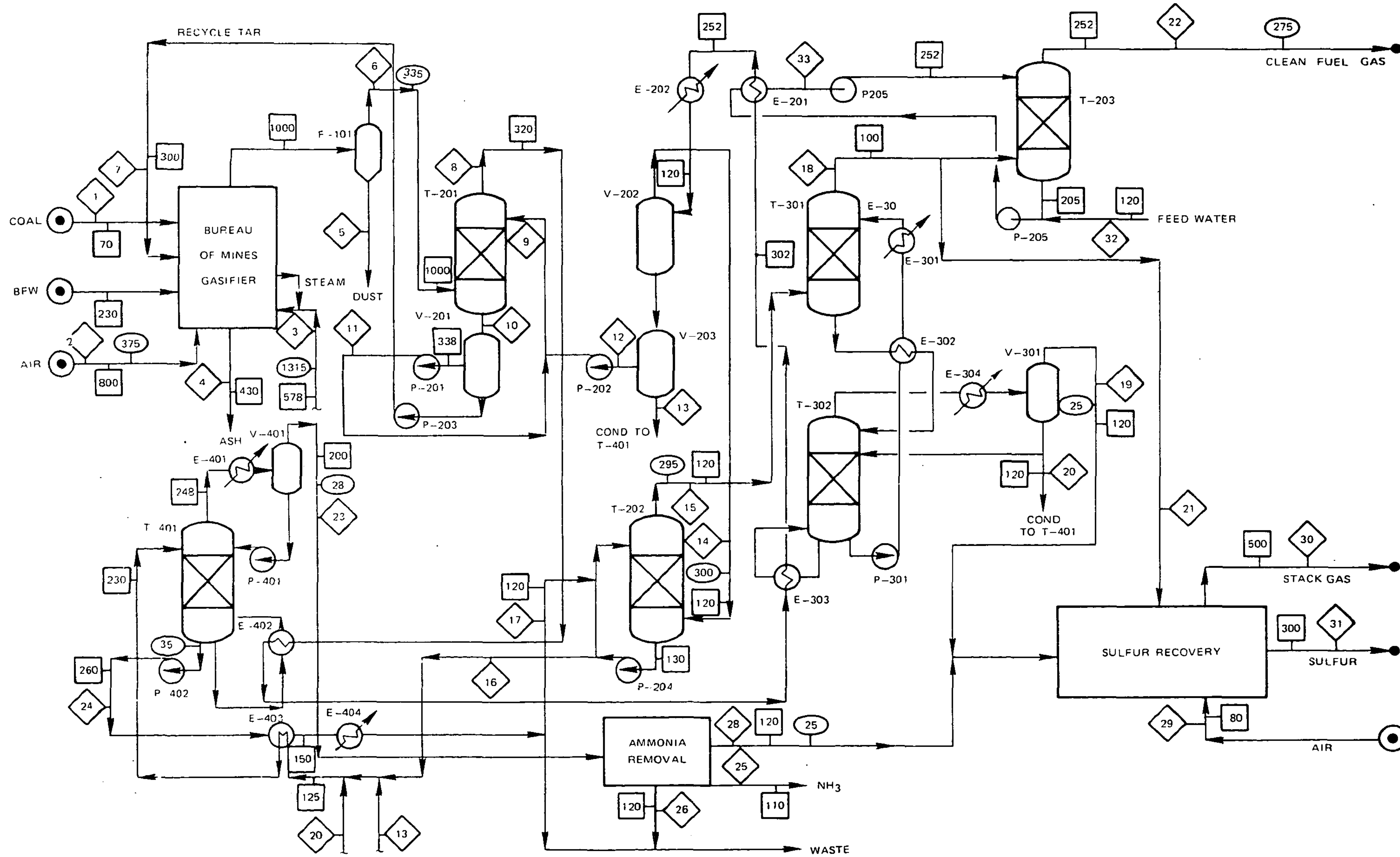

FIG. 14

Table 18

REVISED MATERIAL BALANCE FOR BUREAU OF MINES/SELEXOL SYSTEM
(see Figure 14)

STREAM		1		2		3		4	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
O_2	32.00			491,168	15,349				
N_2	28.02			1,617,932	57,742				
CO	28.01								
CO_2	44.01								
H_2	2.016								
CH_4	16.04								
H_2S	34.08								
COS	60.08								
NH_3	17.03								
H_2O	18.02					283,509	15,733		
TAR	212								
ASH								114,132	
TOTAL		700,000		2,109,100	73,091	283,509	15,733	114,132	

STREAM		5		6		7		8	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
N_2	28.02			1.617,931	57,742			1,617,931	57,742
CO	28.01			743,637	26,549			743,637	26,549
CO_2	44.01			294,691	6,696			294,691	6,696
H_2	2.016			35,772	17,744			35,772	17,744
CH_4	16.04			55.819	3,480			55,819	3,480
H_2S	34.08			27.094	795			27,094	795
COS	60.08			721	12			721	12
NH_3	17.03			13,437	789			13,437	789
H_2O	18.02			176.920	9,818				
TAR	212			77.076	364	77,076	364	805,836	44,719
TOTAL		13,619		3,043,098	123,989	77,076	364	3,594,938	158,526

Table 18 - Continued

MATERIAL BALANCE FOR BUREAU OF MINES/SELEXOL SYSTEM

STREAM	M.W.	9 LB/HR	9 MOL/HR	10 LB/HR	10 MOL/HR	11 LB/HR	11 MOL/HR	12 LB/HR	12 MOL/HR
N_2	28.02								
CO	28.01								
CO_2	44.01								
H_2	2.016								
CH_4	16.04								
H_2S	34.08								
COS	60.08								
NH_3	17.03								
H_2O	18.02	804593	44650	168073	9327	168073	9327	636520	35323
TAR	212			77076	364				
TOTAL		804593	44650	245149	9691	168073	9327	636520	35323

STREAM	M.W.	13 LB/HR	13 MOL/HR	14 LB/HR	14 MOL/HR	15 LB/HR	15 MOL/HR	16 LB/HR	16 MOL/HR
N_2	28.02			1617931	57742	1617931	57742		
CO	28.01			743637	26549	743637	26549		
CO_2	44.01			294691	6696	291742	6629	2993	68
H_2	2.016			35772	17744	35772	17744		
CH_4	16.04			55819	3480	55819	3480		
H_2S	34.08			27094	795	21675	636	5452	160
COS	60.08			721	12	721	12		
NH_3	17.03			13437	789	1618	95	12245	719
H_2O	18.02	167712	9307	9208	511	9136	507	452356	25103
TAR	212								
TOTAL		167712	9307	2798310	114318	2778051	113394	473046	26050

Table 18 - Continued

MATERIAL BALANCE FOR BUREAU OF MINES/SELEXOL SYSTEM

STREAM		17		18		19		20	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
N_2	28.02			1614372	57615	3559	127		
CO	28.01			741173	26461	2465	88		
CO_2	44.01	44	1	244784	5562	46959	1067		
H_2	2.016			35717	17717	54	27		
CH_4	16.04			55322	3449	497	31		
H_2S	34.08	34	1	102	3	21573	633		
COS	60.08			481	8	240	4		
NH_3	17.03	426	25	562	33	1056	62		
H_2O	18.02	452290	25099	180	10	1766	98	7190	399
TOTAL		452794	25126	2692693	110858	78169	2137	7190	399

STREAM		21		22		23		24	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
N_2	28.02	12441	444	1601931	57171				
CO	28.01	5714	204	735459	26257				
CO_2	44.01	1892	43	242891	5519	2949	67	44	1
H_2	2.016	274	136	34553	17581				
CH_4	16.04	433	27	54889	3422				
H_2S	34.08			102	3	5385	158	68	2
COS	60.08			481	8				
NH_3	17.03			562	33	11649	684	596	35
H_2O	18.02			256010	14207	9533	529	617726	34280
TOTAL		20754	854	2927840	124201	29516	1438	618434	34318

Table 18 - Continued

MATERIAL BALANCE FOR BUREAU OF MINES/SELEXOL SYSTEM

STREAM		25		26		27		28	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
N_2	28.02								
CO	28.01								
CO_2	44.01							2949	67
H_2	2.016								
CH_4	16.04								
H_2S	34.08					34	1	5385	158
COS	60.08								
NH_3	17.03	11529	677	119	7	170	10		
H_2O	18.02			9244	513	165442	9181	288	16
TOTAL		11529	677	9363	520	165646	9192	8622	

STREAM		29		30		31	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
O_2	32.00	34304	1072	6848	214		
N_2	28.02	113061	4035	129060	4606		
CO_2	44.01			67379	1531		
SO_2	64.06			2562	40		
NO	30.01			1861	62		
H_2O	18.02			22994	1276		
Sulfur	32.06					24205	755
TOTAL		147365	5107	230704	7729	24205	755

	32		33	
	LB/HR	MOL/HR	LB/HR	MOL/HR
H_2O	255830	14197	7930000	440067

Table 19

REVISED UTILITIES SUMMARY OF BUREAU OF MINES/SELEXOL SYSTEM

	Coal Gasification	Gas Cooling	Sour Water Stripping	Ammonia Recovery	Acid Gas Removal	Sulfur Recovery	Total
STEAM, LB/HR							
@ 65 psia			*	6420	*	(68365)	0
@ 1315 psia	119790			50710			170500
COOLING WATER GPM				7330	37090		44420
POWER, kW	10500	1286	297	1244	20242	4	33573
BRW, LB HR	165355					75060	240415
STM COND., LB/HR				(57130)	(106200)		(163330)
CHEMICAL $/DAY				40	70	26	136

* Heat provided by condensation of water vapor in saturated fuel gas stream.

Table 20

REVISED EQUIPMENT LIST FOR BUREAU OF MINES/SELEXOL SYSTEM

SECTION 100
COAL GASIFICATION AND DUST REMOVAL

F-101 GASIFIER OFFGAS CYCLONE

SECTION 200
GAS SCRUBBING AND TAR REMOVAL

P-201 Quench Water Recycle Pump
P-202 Quench Water Pump
P-203 Tar Recycle Pump
P-204 Gas Scrubber BTMS Pump
P-205 Resaturator Pump
E-201 Fuel Gas Reheat Exchanger
E-202 Gas Cooler

T-201 Quench Vessel
T-202 Water Scrubber
T-203 Resaturator Vessel
V-201 Tar/Water Separator
V-202 Gas/Liquid Separator
V-203 Oil/Water Separator

SECTION 300
SELEXOL ACID GAS REMOVAL SYSTEM

P-301 Selexol Stripper BTMS Pump

E-301 Selexol Solvent Cooler
E-302 Rich/Lean Solvent Exchanger
E-303 Selexol Stripper Reboiler
E-304 Selexol Stripper OVHD Condenser
V-301 Selexol Stripper OVHD Accumulator
T-301 Selexol Absorber
T-302 Selexol Stripper

Table 20 - Continued

EQUIPMENT LIST

SECTION 400
SOUR WATER STRIPPING

P-401 SWS Reflux Pump
P-402 SWS BTMS Pump

E-401 SWS OVHD Condenser
E-402 SWS Reboiler
E-403 Feed/BTMs Exchanger
T-401 Sour Water Stripper
V-401 SWS OVHD Accumulator

SECTION 500
AMMONIA REMOVAL

SECTION 600
SULFUR RECOVERY

(1) Nonregenerable process
(2) Regenerable process producing sulfuric acid
(3) Regenerable process producing elemental sulfur

The processes chosen were:

(1) Reduction of two-thirds of the SO_2 to H_2S followed by Claus plant recovery of elemental sulfur (re-evaluated for 12 percent SO_2).
(2) Lime slurry process for the removal of SO_2 from the gas followed by disposal of the sludge formed (nonregenerable process).
(3) Catalytic oxidation (Cat-Ox) of SO_2 to SO_3 followed by absorption in water to give sulfuric acid (regenerable process producing sulfuric acid).
(4) Reduction of SO_2 (Rsoox) to elemental sulfur using coal as the reducing agent, followed by recovery of the elemental sulfur (regenerable process producing elemental sulfur).

Evaluation of the alternatives must be done on the basis of their effect on overall power system performance and cost. To do this, the energy accounting system presented in the Phase Report[1] was used. While it does not account for changes in the steam cycle caused by the temperature level of the available heat, it does differentiate between the value of energy when used at combined cycle vs. steam cycle efficiency and accounts for all utility requirements. The resultant comparison, while not accurate on an absolute basis, is adequate for the selection process.

Process 1 - Claus Plant

The higher SO_2 concentration in the off-gas eliminates the need for an intermediate step to concentrate the SO_2 in the off-gas. This results in a significant reduction in the steam and power requirements for the sulfur recovery section. Although the SO_2 concentration entering the Claus plant is now lower than the previous value (after the intermediate step to concentrate SO_2) and, therefore, the Claus plant fuel requirement is higher, there is an increase in overall plant efficiency due to the lower utility requirements. The total power plant efficiency gain is almost four points to 36 percent. The capital costs of the sulfur recovery plant are also significantly reduced.

Process 2 - Lime Slurry Process for SO_2 Removal and Disposal

In this process the regeneration off-gas is contacted with a recirculating slurry containing slaked lime and reaction products in two venturi absorbers in series. About 90 percent SO_2 removal is achieved and the calcium sulfite and sulfate solids formed are disposed of. Material balances for this process are given in Table 21. Capital and operating costs[25] are shown in Tables 22 and 23. A schematic is shown in Fig. 15.

The lime scrubbing is done in two stages (called scrubber and absorber in Fig. 15) with a combined SO_2 removal efficiency of 90 percent. A 15 percent (wt) lime solution is used as a make up and the Ca/SO_2 ratio is taken to be 1.1 times stoichiometric. Overall plant efficiency is 37 percent.

Process 3 - Catalytic Oxidation Process

The Cat-Ox process utilizes vanadium pentoxide catalyst to oxidize SO_2 to SO_3 in the off-gas followed by the absorption of the SO_3 to produce nominal 80 percent sulfuric acid. Efficient conversion of SO_2 to SO_3 requires a gas temperature of approximately 850°F to 900°F. This is achievable in the BuMines/iron-oxide system by partially cooling the off-gas from the regenerator before introducing it into the oxidation unit. About 90 percent SO_2 conversion occurs. A high degree of particulate removal is required prior to the catalytic oxidation to minimize fouling of the catalyst. It was assumed that high-efficiency electrostatic precipitators would be introduced upstream of the oxidation unit. The oxidation is exothermic and the sensible heat in the gas is used to produce low-pressure steam before it is sent to the absorber. The recirculating solution is cooled in circulation acid coolers before being recycled or sent to product storage. Material balances, and capital and operating costs[25] are given in Tables 24, 25, and 26. A schematic is shown in Fig. 16.

The material balance in Table 24 is based upon cooling the regenerator off-gas from 1500°F to 890°F prior to passing it through an electrostatic precipitator. It then undergoes catalytic oxidation followed by an absorbtion process in which SO_3 is absorbed by sulfuric acid to gain 80 percent H_2SO_4.

Table 21. MATERIAL BALANCE FOR LIME SLURRY PROCESS
(Stream numbers refer to the flow sheet Fig. 15)

Stream 1 - Cooled regenerator off-gas at 307 F; 20 psia

Component	mols/hr	mol%	lbs/hr
N_2	5,311	83.74	148,708
CO_2	270	4.26	11,880
SO_2	761	12,00	48,704
Total	6,342	100.00	209,292

Stream 2 - Flue gas after first stage scrubber

Component	mols/hr	lbs/hr
N_2	5,311	148,708
CO_2	270	11,880
SO_2	202	12,928
H_2O	625	11,250
Total	6,408	184,766

Stream 3 - Flue gas after second stage absorber

Component	mols/hr	lbs/hr
N_2	5,311	148,708
CO_2	270	11,880
SO_2	76	4,864
H_2O	625	11,250
Total	6,282	176,702

Table 21 (Continued)

Stream No.	4	5	6	7	8	9
Material	Makeup water to absorber	Pone water to absorber	Lime to screw conveyor	Vent from slaker	Grit to disposal	Lime slurry to system
lbs/hr	321059	25943	46787	2694	464	405357

Stream No.	10	11	12	13	14
Material	Lime slurry to absorber	Recycle slurry to absorber	Discharge slurry from absorber	Absorber slurry to scrubber	Makeup water to scrubber
lbs/hr	90348	54007	54338	446900	321059

Stream No.	15	16	17	18	19
Material	Lime slurry to scrubber	Recycle slurry to scrubber	Discharge slurry from scrubber	Used slurry to pump	Used slurry to settling pond
lbs/hr	316219	60001	60009	769573	769573

Stream No.	20	21	22
Material	Settled used slurry	Recycle pond water	Pond water to slaker
lbs/hr	353767	389223	363006

Table 22

LIME SLURRY PROCESS - OPERATING COST

(On-Site Solids Disposal)

	Cost $
* Raw Material	3,602,633
* Labor and Supervision	238,950
* Steam	571,975
* Process Water	37,700
* Electricity	1,297,856
Labor (maint.)	701,802
Analysis	59,850
Total Direct	6,510,766
Average Capital Charges (14.9% of total capital investment)	2,333,717
Overhead	
Plant, 20% of 2,908,133	581,627
Administrative 10% of 238,950	23,895
Total Indirect	2,939,239
Total Annual Operating Cost =	$9,450,005

* Unit Costs: Steam: $0.60/M lb.

Process Water: $0.08/M gal.

Electricity: $0.009/Kwh

Lime: $20.50/ton

Labor and Supervision: $8.00/Man-Hr.

Table 23

LIME SLURRY PROCESS - CAPITAL COST
(On-Site Solids Disposal)

	Investment,$
Lime receiving and storage (bins, feeders, conveyors and elevators)	1,234,176
Feed preparation (conveyors, slakers, tanks, agitators, and pumps)	589,103
Particulate - sulfur dioxide scrubbers and inlet ducts (4 scrubbers including common feed plenum and pumps)	689,300
Sulfur dioxide scrubbers and ducts (4 scrubbers including mist eliminators, pumps, and exhaust gas ducts to inlet of fans)	509,688
Stack gas reheat (4 indirect steam reheaters)	41,609
Fans (4 fans including exhaust gas ducts and dampers between fan and stack gas plenum)	117,170
Calcium solids disposal (on-site disposal facilities including slurry disposal pumps, pond, liner, and pond water return pumps)	5,040,968
Utilities (instrument air generation and supply system, plus distribution systems for obtaining process steam, water and electricity from the power plant)	88,267
Service facilities (buildings, shops, stores, site development, roads, railroads, and walkways)	706,103
Construction facilities	1,023,698
Subtotal direct investment	10,040,082
Engineering design and supervision	903,607
Construction field expense	1,004,008
Contractor fees	502,004
Contingency	1,004,008
Subtotal fixed investment	13,453,709
Allowance for startup and modifications	1,104,409
Interest during construction (8%/annum rate)	1,104,409
Total capital investment	15,662,527

LIME–SLURRY SCRUBBING PROCESS FOR SO_2 REMOVAL FROM BuMINES/IRON–OXIDE REGENERATION OFF–GAS

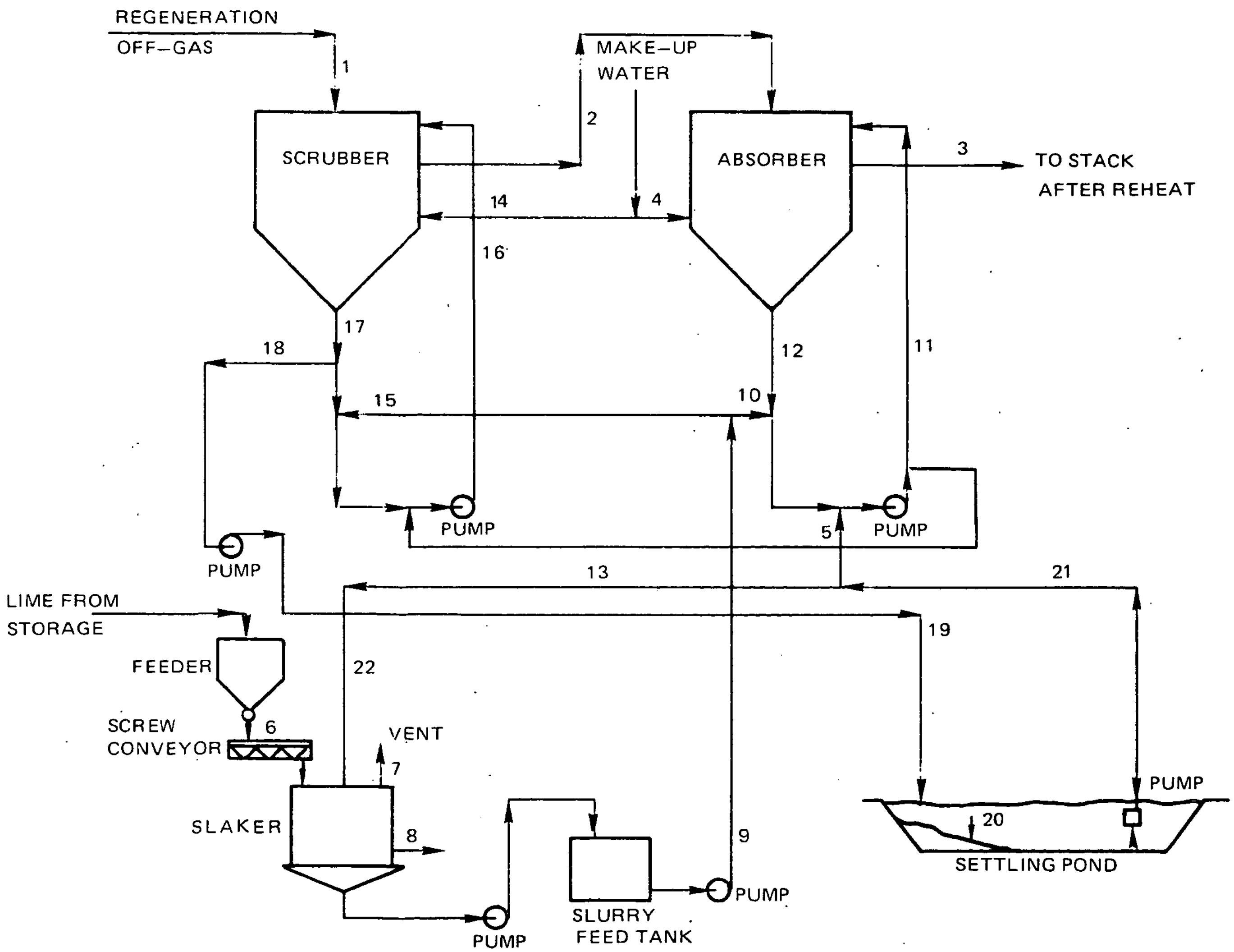

FIG. 15

76–02–32–3

Table 24

MATERIAL BALANCE FOR CAT-OX PROCESS
(see Figure 16)

Stream No.	1	2	3	4
Component	lbs/hr	lbs/hr	lbs/hr	lbs/hr
O_2	121760		110802	110802
N_2	400792	148708	549500	549500
CO_2		11880	11880	11880
SO_2		48704	4870	4870
SO_3			54792	
H_2O				
Total	522552	209292	731844	677052

No	5	6	7	8
Stream	Acid to No. 1 Circ. acid cooler	Acid to No. 2 Circ. acid cooler	Acid to absorber	Acid to product storage
lbs/hr	11680726	1168072	11600112	80614

Table 25

CATALYTIC OXIDATION PROCESS - CAPITAL COST

	Investment,$
Converter and absorber startup bypass ducts and dampers	191,610
Electrostatic precipitators and inlet ducts (4 high temperature electrostatic precipitators including common feed plenum)	2,467,567
Sulfur dioxide converters and ducts (4 converters including catalyst sifter, hopper, storage bin, conveyors, and elevators)	520,107
Heat recovery and ducts (4 steam/air heaters and 4 fluid/air heaters including ducts between economizers and air heaters, and combustion air ducts and dampers between powerhouse and air heaters; investment credit for use of smaller air heaters included)	638,796
Fans (4 ID fans including exhaust gas ducts and dampers between ID fans and stack gas plenum)	506,426
Sulfuric acid absorbers and coolers (2 absorbers including mist eliminators, coolers, tanks, pumps, and ducts and dampers between air heaters and ID fans)	1,983,578
Sulfuric acid storage (storage and shipping facilities for 30 days production of H_2SO_4)	128,207
Utilities (instrument air generation and supply system, and distribution systems for obtaining process steam, water, and electricity from power plant)	28,964
Service facilities (buildings, shops, stores, site development, roads, railroads, and walkways)	269,916
Construction facilities	325,646
Subtotal direct investment	7,060,817
Engineering design and supervision	776,690
Construction field expense	776,690
Contractor fees	353,040
Contingency	706,082
Subtotal fixed investment	9,673,320
Allowance for startup modifications	967,332
Interest during construction (8%/annum rate)	776,690
Total capital investment excluding catalyst	11,417,342
Catalyst	313,232
Total capital investment	11,730,574

Table 26

CATALYTIC OXIDATION PROCESS - OPERATING COST

	Cost $
* Raw material (catalyst)	31,323
* Labor and Supervision	30,766
* Steam	33,899
* Heat credit	(107,540)
* Process water	42,606
* Electricity	215,004
Labor (maint.)	247,129
Analyses	14,003
Total Direct	507,190
Average Capital Charges- (14.9% of total capital investment)	1,747,856
Overhead	
Plant, 20% of conversion costs	95,173
Administrative	124,242
Total Indirect	1,967,271
Total Annual Operating Cost =	$2,474,461

---

* Unit Costs: Steam: $0.70/M lb.

Process Water: $0.07/M gal.

Electricity: $0.01/Kwh

Catalyst: $1.65/liter.

Labor and Supervision: $8.00/Man-Hr.

Heat Credit: $0.60/MM Btu.

CATALYTIC–OXIDATION PROCESS FOR REMOVAL OF SO_2 FROM BuMINES/IRON OXIDE REGENERATION OFF–GAS

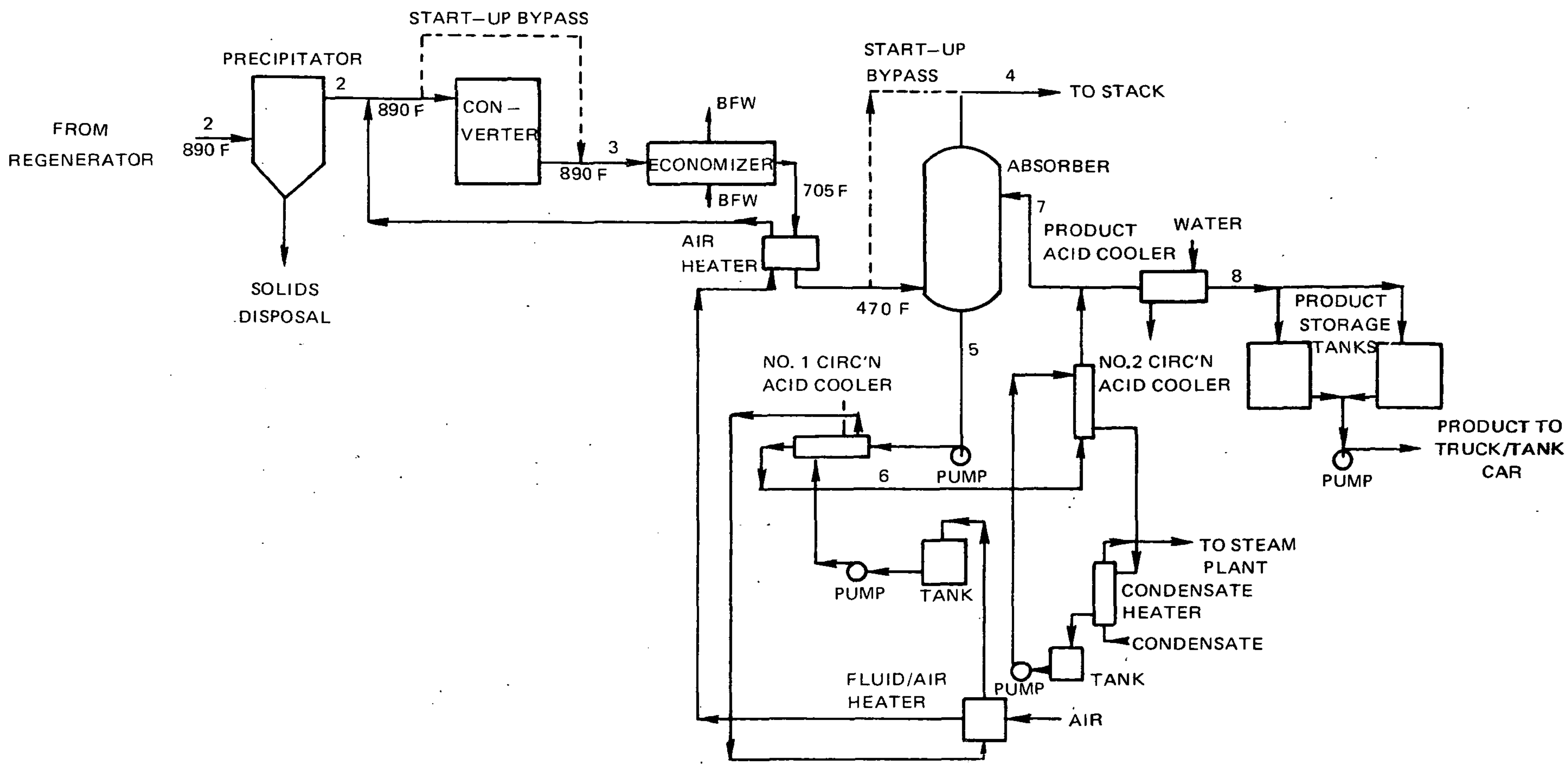

FIG.16

76–02–32–2

Process 4 - Resox Process

This process developed by the Foster-Wheeler Corporation[26] uses coal as a reducing agent to produce elemental sulfur from SO_2 contained in a regeneration off-gas. The SO_2 in the off-gas stream is reduced to elemental sulfur which is then condensed out of the gas stream. Crushed coal is the only material and the only catalyst consumed in the process. At SO_2 conversions of 65 percent or lower, and at temperatures below 1100°F, only elemental sulfur is obtained as the product. At higher temperatures and conversions, H_2S is the favored product. The Resox unit is suited to the BuMines/iron-oxide process and can be located downstream of the iron-oxide absorber/regenerator with partial intermediate gas cooling Different types of coals can be used as the reducing agent.

Process Comparison

Performance and costs for each method are given in Table 27 and a breakdown of capital and power production costs are presented in Table 28. From Table 27 and 28 it is clear that the better performance and lower power cost are due to the increased SO_2 concentration and there is little difference between the various methods of sulfur recovery or disposal (approximately ± 2 percent about the mean cost). It is interesting to note that there is apparently no significant cost of performance penalty associated with recovery of elemental sulfur. Accordingly, the limestone and Cat-Ox processes were not considered further.

For the purposes of this study the Claus plant approach to sulfur recovery was selected for use in the final performance and cost estimates. A revised schematic for this process is shown in Fig. 17, a revised material balance is given in Table 29, a revised utility summary in Table 30, and a revised equipment list in Table 31. However, there is little reason for its selection over the Resox process other than the fact that it is widely used and information is generally more readily available. It is possible that improvements in the Resox could result in higher efficiency or lower cost. The first full-scale plant has only recently been put into operation for the Gulf Power Company in Florida. Certainly, a lower SO_2 concentration or a decreased H_2 content of the fuel gas would be reason to reassess the situation. In this system, reduction of the SO_2 using hydrogen in the fuel gas results in a further dilution of the sulfur bearing stream. This is due to the presence of CO_2 and N_2 in the fuel and results in an equivalent Claus feed gas concentration of seven percent H_2S which is at the lower end of the practical range. However, this can be improved by shifting the CO in the fuel to almost double the H_2 concentration and thereby decrease the amount of diluent added during the reduction process.

Table 27

COMPARISON OF ALTERNATE SULFUR RECOVERY METHODS FOR BUREAU OF MINES/IRON OXIDE PROCESS

	Phase Report[1]	12% SO_2 Feed to Claus Plant	Limestone Slurry SO_2 Removal	Cat-Ox Processing to H_2SO_4	Resox to Elemental Sulfur
New Plant Output - Mw	751.5	841.3	875.7	895.1	890.3
Overall Efficiency	.320	.358	.373	.381	.366
Heat Rate - Btu/kwhr	10,668	9,529	9,155	8,957	9,314
Capital Costs - $\$10^6$					
Sulfur Recovery	10.4	3.0	15.7	11.4	16.1
Total Plant	289.4	282.0	294.7	290.4	295.1
Plant Cost - $/kw	385	335	337	324	331
Power Cost - Mills/kwhr	20.51	17.95	17.87	17.25	17.76

Table 28

POWER COST FOR ALTERNATE SULFUR RECOVERY METHODS BUREAU OF MINES/IRON OXIDE SYSTEM

	Phase Report[1]	12% SO_2 Feed to Claus Plant	Limestone Slurry SO_2 Removal	Cat-Ox SO_2 Processing to H_2SO_4	Resox to Produce Elemental Sulfur
Power System - $/kw	230	206	198	193	194
Gasification & Cleanup - $/kw	155	129	139	131	137
Total - $/kw	385	335	337	324	331
Owning Costs - Mills/kwhr	10.66	9.28	9.33	8.97	9.17
Operation & Maintenance					
Power System	1.31	1.17	1.13	1.10	1.11
G&C	2.14	1.78	1.92	1.81	1.89
Fuel at 60¢/MMBtu	6.40	5.72	5.49	5.37	5.59
Total - Mills/kwhr	20.51	17.95	17.87	17.25	17.76

REVISED PROCESS FLOW DIAGRAM BUMINE/IRON OXIDE SYSTEM

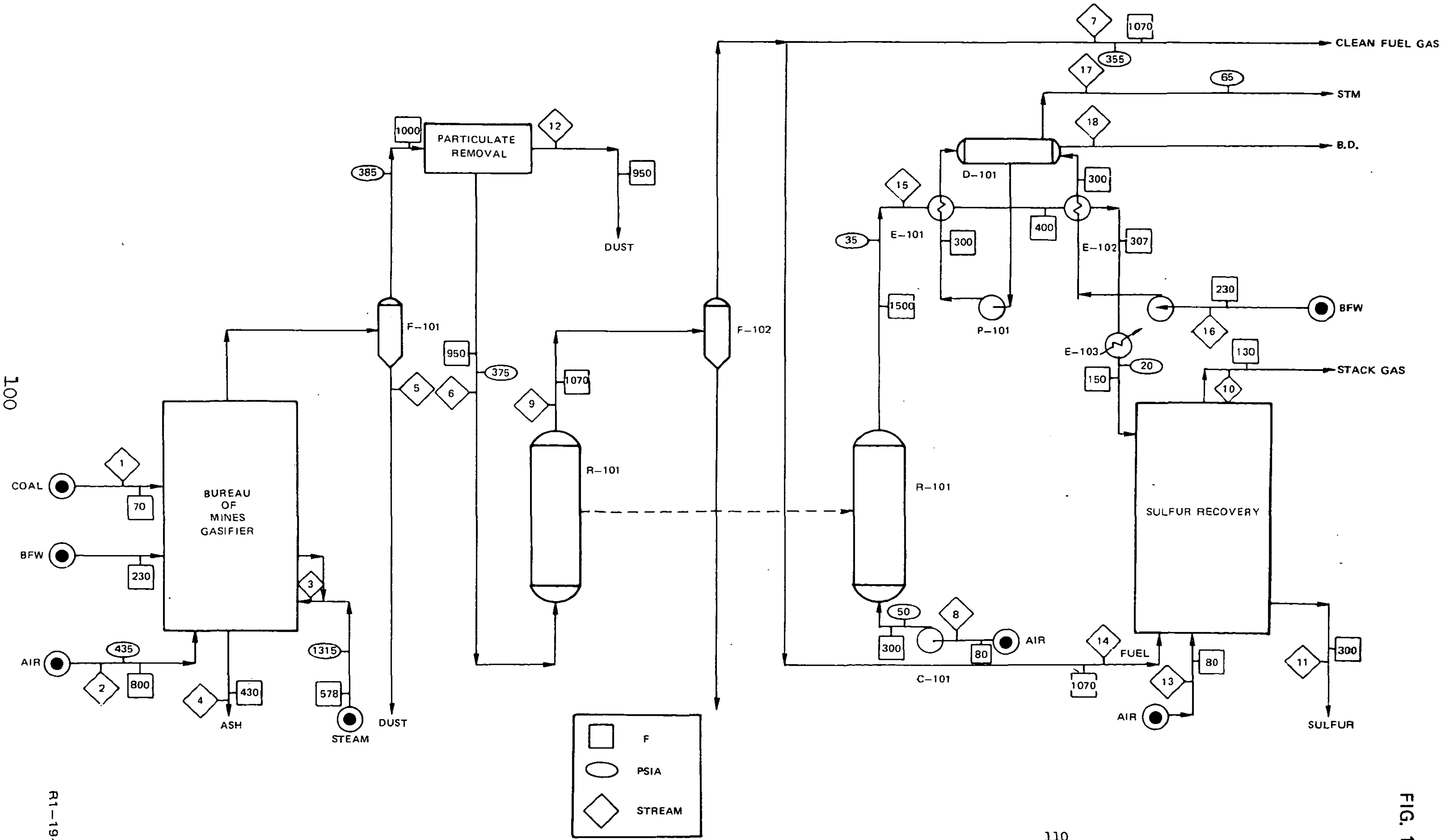

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FIG. 17

Table 29

REVISED MATERIAL BALANCE FOR BUREAU OF MINES/IRON OXIDE SYSTEM

(See Figure 17)

STREAM		1		2		3		4	
	M.W.	lb/hr	mol/hr	lb/hr	mol/hr	lb/hr	mol/hr	lb/hr	mol/hr
O_2	32.00			438,240	13,695				
N_2	28.02			1,443,366	51,512				
CO	28.01								
CO_2	44.01								
H_2	2.016								
CH_4	16.04								
H_2S	34.08								
COS	60.08								
NH_3	17.03								
H_2O	18.02								
TAR	212					244,045	13,543		
ASH								114,132	
TOTAL		700,000		1,881,606	65,207	244,045	13,543	114,132	

STREAM		5		6		7		8	
	M.W.	lb/hr	mol/hr	lb/hr	mol/hr	lb/hr	mol/hr	lb/hr	mol/hr
N_2	28.02			1,443,366	51,512	1,328,736	47,421	148,814	5,311
CO	28.01			639,076	22,816	427,096	15,248		
CO_2	44.01			253,278	5,755	486,882	11,063		
H_2	2.016			27,000	13,393	36,455	18,083		
CH_4	16.04			47,960	2,990	44,158	2,753		
H_2S	34.08			25,867	759	307	9		
COS	60.08			721	12				
NH_3	17.03			11,649	684	10,729	630		
H_2O	18.02			175,136	9,719	69,936	3,881		
TAR	212			73,819	348	67,840	320		
O_2	32.00							45,184	1,412
TOTAL		11,625		2,697,872	107,988	2,472,139	99,408	193,998	6,723

Table 29 - Cont'd

MATERIAL BALANCE FOR BUREAU OF MINES/IRON OXIDE SYSTEM

(See Figure 17)

STREAM		9		10		11		12	
	M.W.	lb/hr	mol/hr	lb/hr	mol/hr	lb/hr	mol/hr	lb/hr	mol/hr
O_2	32.00			8,608	269				
N_2	28.02	1,443,422	51,514	433,525	15,472				
CO	28.01	463,958	16,564						
CO_2	44.01	528,912	12,018	81,551	1,853				
H_2	2.016	39,602	19,644						
CH_4	16.04	47,960	2,990						
H_2S	34.08	341	10						
COS	60.08								
SO_2	64.06			4,612	72				
NH_3	17.03	11,649	684						
NO	30.01			1,621	54				
H_2O	18.02	75,972	4,216	45,032	2,499				
Sulfur	32.06					20,518	640		
Tar	212	73,819	348						
Dust								1,994	
TOTAL		2,685,635	107,988	574,949	20,219	20,518	640	1,994	

Table 29 - Cont'd

MATERIAL BALANCE FOR BUREAU OF MINES/IRON OXIDE SYSTEM

(See Figure 17)

STREAM		13		14		15		16	
	M.W.	lb/hr	mol/hr	lb/hr	mol/hr	lb/hr	mol/hr	lb/hr	mol/hr
O_2	32.00	51,616	1,613						
N_2	28.02	170,025	6,068	114,686	4,093	148,814	5,311		
CO	28.01			36,861	1,316				
CO_2	44.01			42,030	955	11,883	270		
H_2	2.016			3,147	1,561				
CH_4	16.04			3,801	237				
H_2S	34.08			34	1				
COS	60.08								
SO_2	64.06					48,750	761		
NH_3	17.03			920	54				
H_2O	18.02			6,037	335			65,313	3,624
TAR	212			5,936	28				
TOTAL		221,641	7,681	213,452	8,580	209,447	6,342	65,313	3,624

STREAM		17		18	
	M.W.	lb/hr	mol/hr	lb/hr	mol/hr
H_2O	18.02	64,033	3,553	1,280	71
TOTAL		64,033	3,553	1,280	71

Table 30

REVISED UTILITIES SUMMARY FOR
BUMINES/IRON OXIDE SYSTEM

	Gasifier	Sulfur Recovery	Desulfurization	Total
Steam, lb/hr,				
65 psia		(131,280)	(64,030)	(195,310)
1315 psia	27,775			27,775
Power, Kw	10,500	5	8,340	18,845
BFW, lb/hr	218,435	133,900	65,310	199,210
Chemicals, $/Day		26		26

Table 31

REVISED BUREAU OF MINES/IRON OXIDE SYSTEM

EQUIPMENT LIST

ITEM	DESCRIPTION
Pumps	
P-101	Boiler Recycle Pump
P-120	Boiler Feed Water Pump
Reactors	
R-101	Sulfur Absorber/Regenerator (2 Req'd)
Drums	
D-101	Steam Drum
Exchangers	
E-101	Waste Heat Boiler
E-102	Economizer
Compressors	
C-101	Air Compressor
Separators	
F-101	Gasifier Off-Gas Cyclone
F-102	Regenerator Off-Gas Cyclone

CATALYTIC CONVERSION OF COS TO H_2S IN THE BCR/SELEXOL SYSTEM

One of the problems that arise in the integration of the BCR gasifier with a Selexol cleanup system is the high proportion of sulfur assumed to be in the form of COS in the raw gas (≈ 17 percent of S as COS). When the Selexol system is sized for H_2S removal, the relative probabilities of H_2S and COS result in removal of only one third of the COS. Since this yields a product gas having a sulfur content of some 700 ppm, the design of the Selexol system must be tailored to COS removal to meet the basic study guidelines. The net result[1] was seen in the relatively high steam and power utility requirements of the BCR/Selexol system and the relatively large quantity of CO_2 removed from the fuel gas as a result of an increased solvent circulating rate. Equilibrium calculations show that the estimated quantities of COS are well in excess of their equilibrium level and that a suitable catalyst could be used to reduce much of the COS to H_2S according to the reaction:

$$COS + H_2S \rightarrow CO_2 + H_2S \qquad (18)$$

A suitable commercial catalyst was found[27] to be a $CoMo/Al_2O_3$ catalyst. The optimum conditions for the catalytic reduction are:

Catalyst:	Katalco 20-3 $CoMo/Al_2O_3$ spheres
Temperature:	550 - 750 F
Pressure:	Variable
Vessel L/D:	≥ 1
Gas hourly space velocity:	5,000/hr

Greater than 90 percent conversion is expected under these conditions. The estimated catalyst life and cost are:

Expected life:	≥ 1 year
Estimated cost:	$65/cu ft

For the purposes of this study, other species were assumed to remain frozen at the gasifier outlet conditions. Testing would be necessary to verify the validity of that assumption and to be certain that no undesirable reactions are encouraged.

After catalytic conversion, the COS is reduced to less than two percent of the total sulfur with H_2S now becoming the key component. This results in a reduction in solvent flow rate and utilities. The Selexol stripper off-gas now has a higher H_2S concentration, lowering the Claus plant fuel requirement. The following reductions in utilities were identified:

Selexol plant:	Steam:	64 percent
	Power:	59 percent
Claus plant:	Fuel:	55 percent

The COS conversion estimates are based on the use of commercial Katalco 20-3 CoMo/Al_2O_3 catalyst. The recommended temperature for 90 percent or greater conversion is between 550 F and 750 F. Locating the catalytic converter between the fuel gas regenerator and the low-pressure boiler as shown in the revised process flow diagram, Fig. 18 provides a temperature of 645 F in the converter. The original and revised compositions of the gas stream entering the Selexol absorber are given in Table 32. A complete revised mass balance is given in Table 33, the revised utilities in Table 34, and a revised equipment list in Table 35. With the revised Selexol solvent circulation rate, significantly less CO_2 is absorbed resulting in a lower product gas heating value (156.8 Btu/SCF HHV as against 159.2 Btu/SCF).

Cost estimates for the cleanup system were revised and showed a slight savings in capital cost, principally due to the smaller Selexol system. A comparison of costs with and without the catalytic converter is shown below.

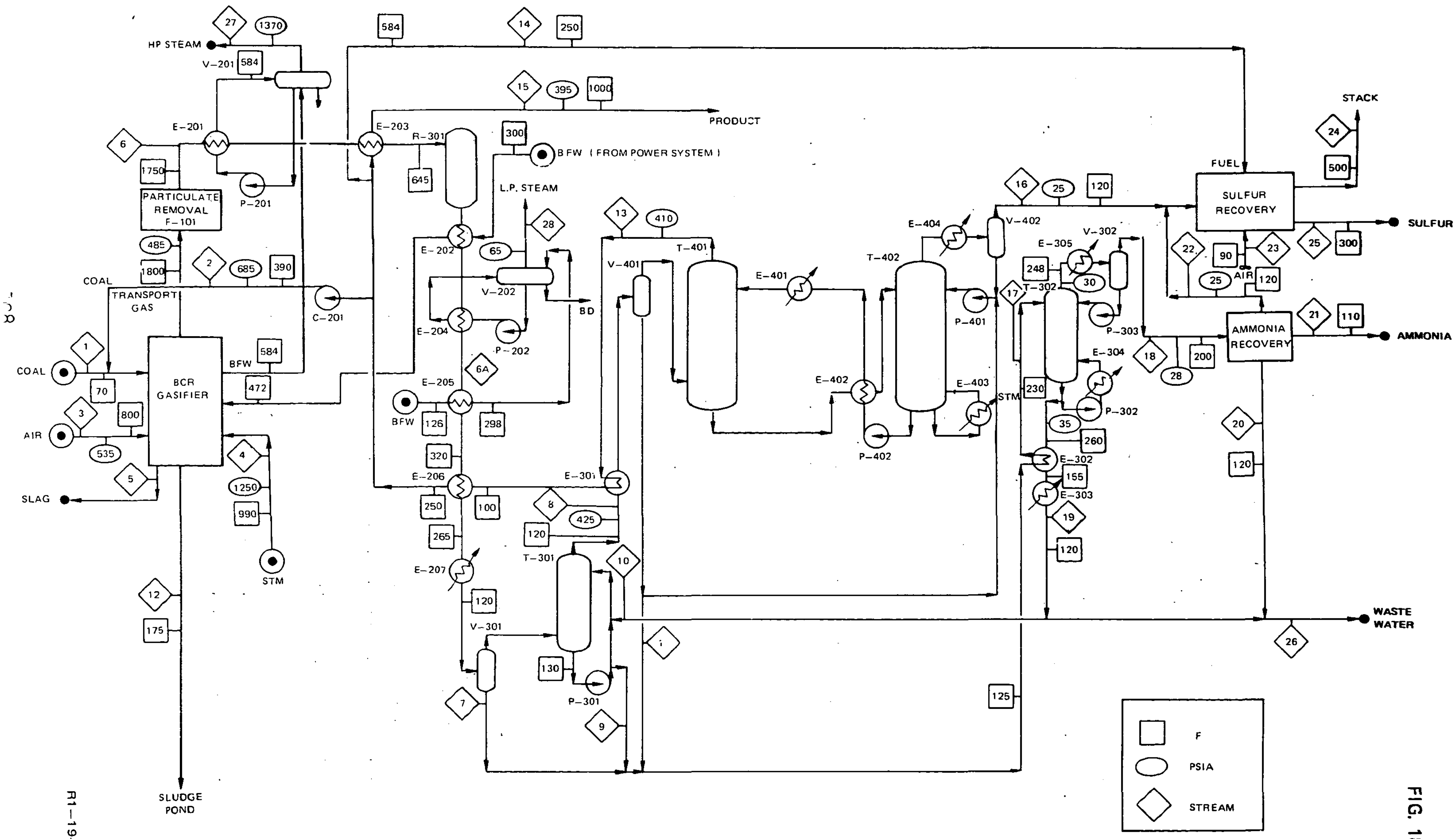
	Capital Cost Without converter ($ million)	Capital Cost With converter ($ million)
Selexol plant	29.72	23.78
Claus plant	2.97	2.97
Catalytic unit	-	0.45
Subtotal	32.69	27.20

The estimates include interest and escalation during construction. Annual operating costs associated with the catalytic unit are estimated to be $40,000. The cold gas efficiency of the combined gasifier and cleanup system increased slightly from 76.4 to 76.9 percent. However, this does not reflect the reduced Selexol utilities which further improve overall system performance as discussed in SECTION 4.

BCR/CONOCO WITH WATER SCRUB

A revised configuration of the BCR/CONOCO system (Fig. 19) incorporating a water scrub for ammonia and particulate removal was investigated. Gas from the CONOCO absorber is passed through a boiler

PROCESS FLOW DIAGRAM BCR/SELEXOL SYSTEM



R1-19-25

FIG. 18

Table 32

RAW GAS COMPOSITION - BCR/SELEXOL SYSTEM

Original Raw Gas Composition

Component	mols/hr	mol%	
N_2	65498.6	46.04	
CO	26151.1	18.38	
CO_2	11751.0	8.26	
H_2	18319.4	12.88	
CH_4	5188.4	3.65	
H_2S	687.1	0.483	4830 ppmv
COS	142.3	0.10	1000 ppmv
NH_3	573.3	0.40	Total 'S' = 5830 ppmv
H_2O	13953.3	9.81	COS = 17.15%
Total	142264.5	100.00	

Assumed Composition After Catalytic Conversion

Component	mols/hr	mol%	
N_2	65498.6	46.04	
CO	26151.1	18.38	
CO_2	11879.07	8.35	
H_2	18319.4	12.88	
CH_4	5188.4	3.65	
H_2S	815.17	0.573	5730 ppmv
COS	14.23	0.01	100 ppmv
NH_3	573.3	0.40	Total 'S' = 5830 ppmv
H_2O	13825.23	9.72	COS = 1.715%
Total	142264.5	100.00	

Table 33

REVISED MATERIAL BALANCE FOR BCR/SELEXOL SYSTEM
USING CATALYTIC COS REMOVAL

(see Figure 18)

STREAM		1		2		3		4	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
O_2	32.00					503392	15731.0		
N_2	28.02			177260	6326.2	1658190	59178.8		
CO	28.01			70672	2523.1				
CO_2	44.01			41928	952.7				
H_2	2.016			3570	1770.6				
CH_4	16.04			7985	497.8				
H_2S	34.08			14	0.4				
COS	60.08			55	0.9				
NH_3	17.03			34	2.0				
H_2O	18.02			23	1.3			396900	22025.5
TOTAL		700000	(coal)	301541	12075.	2161582	74909.8	396900	22025.5

STREAM		5		6		6a		7		8	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
N_2	28.02			1835271	65498.6	1835271	65498.6			1835271	65498.6
CO	28.01			732492	26151.0	732492	26151.1			732492	26151.1
CO_2	44.01			517162	11751.0	522799	11879.1			517591	11760.3
H_2	2.016			36932	18319.4	36932	18319.4			36932	18319.4
CH_4	16.04			83222	5188.4	83222	5188.4			83222	5188.4
H_2S	34.08			23416	687.1	27782	815.2			25004	733.7
COS	60.08			8549	142.3	853	14.2			853	14.2
NH_3	17.03			9763	573.3	9763	573.3			976	57.3
H_2O	18.02			251483	13953.3	249130	13825.2	241446	13398.8	7875	437.0
TOTAL		60900	(slag)	3498245	142264.5	3498245	142264.5	241446	13398.8	3240196	128160.

Table 33 - Continued

STREAM	M.W.	9 LB/HR	9 MOL/HR	10 LB/HR	10 MOL/HR	11 LB/HR	11 MOL/HR	12 LB/HR	12 MOL/HR
N_2	28.02								
CO	28.01								
CO_2	44.01	5259	119.5	36	0.7				
H_2	2.016								
CH_4	16.04								
H_2S	34.08	2795	82.0	17.	0.5				
COS	60.08								
NH_3	17.03	9050	531.4	262.	15.4				
H_2O	18.02	347757	19298.4	347948	19309	1739	96.5	210000	11653.7
TOTAL		364861	20031.3	348258	19325.6	1739	96.5	210000	11653.7

STREAM	M.W.	13 LB/HR	13 MOL/HR	14 LB/HR	14 MOL/HR	15 LB/HR	15 MOL/HR	16 LB/HR	16 MOL/HR
N_2	28.02	1831233	65354.5	20379	727.3	1633594	58301.	4038	144.1
CO	28.01	730075	26064.8	8123	290.	651280	23251.7	2417	86.3
CO_2	44.01	433115	9842.2	4819	109.5	386408	8780.	84416	1918.1
H_2	2.016	36876	18291.9	410	203.5	32896	16317.7	55	27.5
CH_4	16.04	82481	5142.2	917	57.2	73579	4587.2	741	46.2
H_2S	34.08	126	3.7	-	-	112	3.3	24878	730.
COS	60.08	571	9.5	6	0.1	511	8.5	282	4.7
NH_3	17.03	342	20.1	3	0.2	305	17.9	634	37.2
H_2O	18.02	234	13.0	2	0.1	209	11.6	5902	327.5
TOTAL		3115093	124741.9	34659	1388.	2778894	111278.9	123363	3321.6

Table 33 - Continued

STREAM	M.W.	17 LB/HR	17 MOL/HR	18 LB/HR	18 MOL/HR	19 LB/HR	19 MOL/HR	20 LB/HR	20 MOL/HR
N_2	28.02								
CO	28.01								
CO_2	44.01	5259	119.5	5206	118.3	53	1.2		
H_2	2.016								
CH_4	16.04								
H_2S	34.08	2795	82.0	2767	81.2	27	0.8		
COS	60.08								
NH_3	17.03	9050	531.4	8597	504.8	453	26.6	85	5.0
H_2O	18.02	590942	32793.7	7287	404.4	583655	32389.3	7055	391.5
TOTAL		608046	33526.6	23857	1108.7	584188	32417.9	7140	396.5

STREAM	M.W.	21 LB/HR	21 MOL/HR	22 LB/HR	22 MOL/HR	23 LB/HR	23 MOL/HR	24 LB/HR	24 MOL/HR
O_2	32.00					40224	1257.	8029	250.9
N_2	28.02					132507	4729.	156923	5600.4
CO_2	44.01			5206	118.3			115764	2630.4
NO	30.01							1122	37.4
H_2S	34.08			2767	81.2				
SO_2	64.06							2620	40.9
NH_3	17.03	8512	499.8						
H_2O	18.02			232	12.9			29656	1645.7
TOTAL		8512	499.8	8205	212.4	172731	5986.	314114	10205.7

Table 33 - Continued

STREAM	M.W.	25 LB/HR	25 MOL/HR	26 LB/HR	26 MOL/HR	27 LB/HR	27 MOL/HR	28 LB/HR	28 MOL/HR
Sulfur	32.06	24850	775.1						
CO_2	44.01			22	0.5				
H_2S	34.08			10	0.3				
NH_3	17.03			191	11.2				
H_2O	18.02			235707	13080.3	754920	41893.4	469270	26041.6
TOTAL		24850	775.1	235930	13092.3	HP STM		LP STM	

Table 34

REVISED SUMMARY OF BCR GASIFICATION/SELEXOL DESULFURIZATION UTILITIES CONSUMPTION

	Coal Gasification	Heat Recovery	Gas Scrubbing	Acid Gas Removal	Trans. Gas Compression	Sour Water Stripper	Sulfur Recovery	Ammonia Recovery	Total
STEAM, lb/hr									
@ 65 psia		(160479)		108324		130315	(78160)	4780	-0-
@ 1370		(1009100)						37750	(971350)
@ 1250 SPHT	396900								396900
COOLING WATER, gpm	10000			37832				5460	52842
POWER, kw	21000		783	13765	3190	273	5	926	39942
BFW, lb/hr		163690					79725		243415
STM. COND., lb/hr				(108324)		(130315)		(42530)	(281169)
PROCESS WATER lb/hr	210000								210000
CHEMICALS, $/day				100			26	30	156

Table 35

REVISED BCR/SELEXOL SYSTEM

EQUIPMENT LIST

SECTION 100 - GASIFICATION

ITEM	DESCRIPTION
F-101	Particulate Removal System

SECTION 200 - HEAT RECOVERY

ITEM	DESCRIPTION
Vessels	
V-201	HP Steam Drum
V-202	LP Steam Drum
Exchangers	
E-201	HP Waste-Heat Boiler
E-202	HP Economizer
E-203	Main Regenerator
E-204	LP Waste-Heat Boiler
E-205	LP Economizer
E-206	Auxillary Regenerator
E-207	Gas Cooler
Pumps	
P-201	HP Recirculating Pump
P-202	LP Recirculating Pump
Compressors	
C-201	Transport Gas Compressor

Table 35 - Continued

REVISED BCR/SELEXOL SYSTEM

EQUIPMENT LIST

SECTION 300 - GAS SCRUBBING AND SWS

ITEM	DESCRIPTION
Towers	
T-301	NH_3 Scrubber
T-302	NH_3 Stripper
Vessels	
V-301	Condensate Knock-Out Drum
V-302	NH_3 Stripper OVHD Accumulator
Exchangers	
E-301	NH_3 Scrubber OVHD Exchanger
E-302	NH_3 Stripper BTMS Exchanger
E-303	NH_3 Stripper BTMS Cooler
E-304	NH_3 Stripper Reboiler
E-305	NH_3 Stripper OVHD Condenser
Pumps	
P-301	NH_3 Absorber BTMS Pump
P-302	NH_3 Stripper BTMS Pump
P-303	NH_3 Stripper Reflux Pump
Reactors	
R-301	COS Converter

Table 35 - Continued

REVISED BCR/SELEXOL SYSTEM

EQUIPMENT LIST

SECTION 400 - ACID GAS REMOVAL

ITEM	DESCRIPTION
Towers	
T-401	Selexol Scrubber
T-402	Selexol Stripper
Vessels	
V-401	Condensate Knock-Out Drum 2
V-402	Selexol Flash Drum
V-403	Selexol Stripper OVHD Accumulator
Exchangers	
E-401	Lean Solvent Cooler
E-402	Rich/Lean Solvent Exchanger
E-403	Selexol Stripper Reboiler
E-404	Selexol Stripper OVHD Cooler
Pumps	
P-401	Selexol Stripper Reflux Pump
P-402	Selexol Stripper BTMS Pump
Compressor	
C-401	Recycle Gas Compressor

SECTION 500 - AMMONIA RECOVERY

SECTION 600 - SULFUR RECOVERY

FIG. 19

PROCESS FLOW DIAGRAM BCR/CONOCO WITH WATER WASH

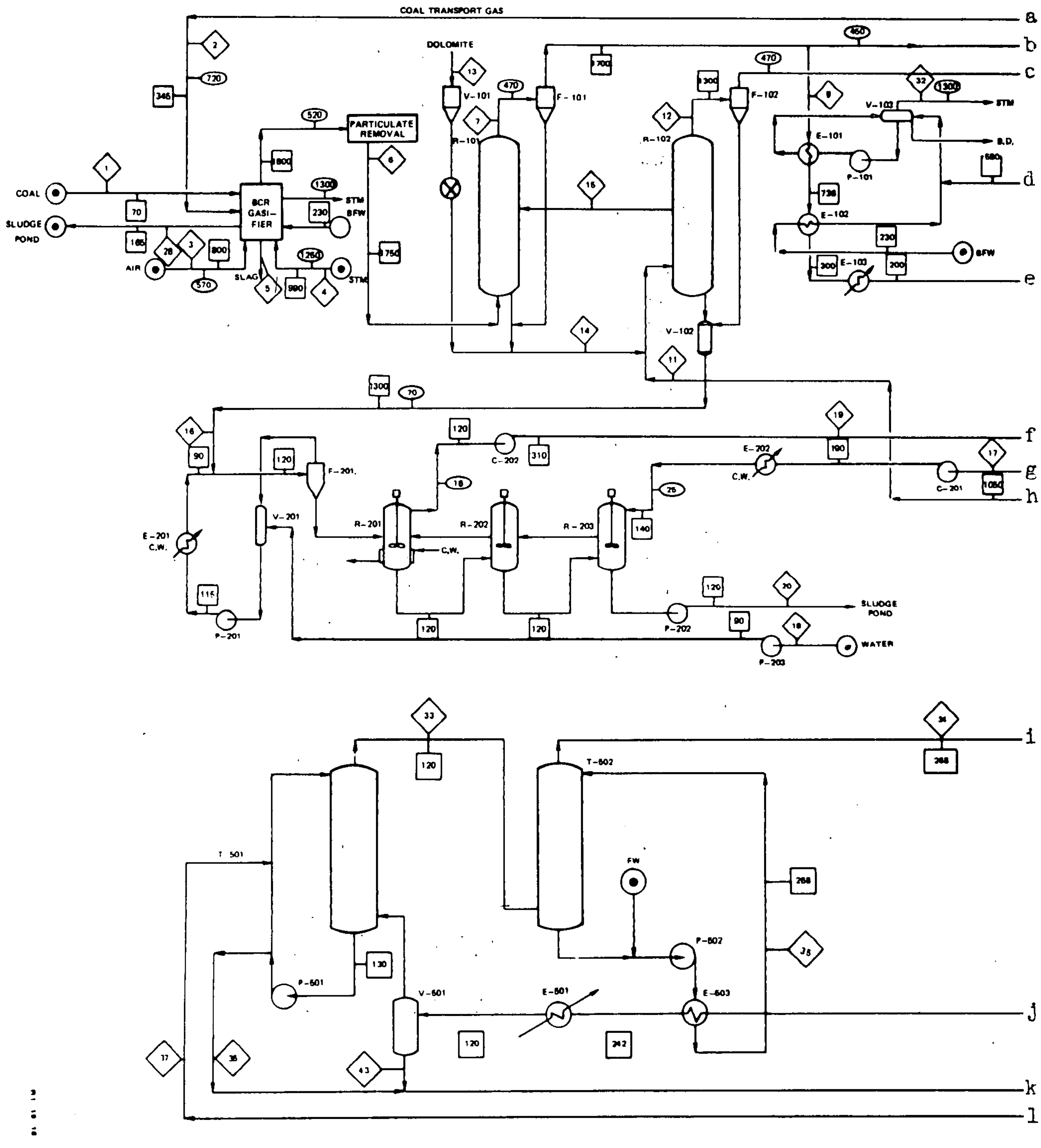
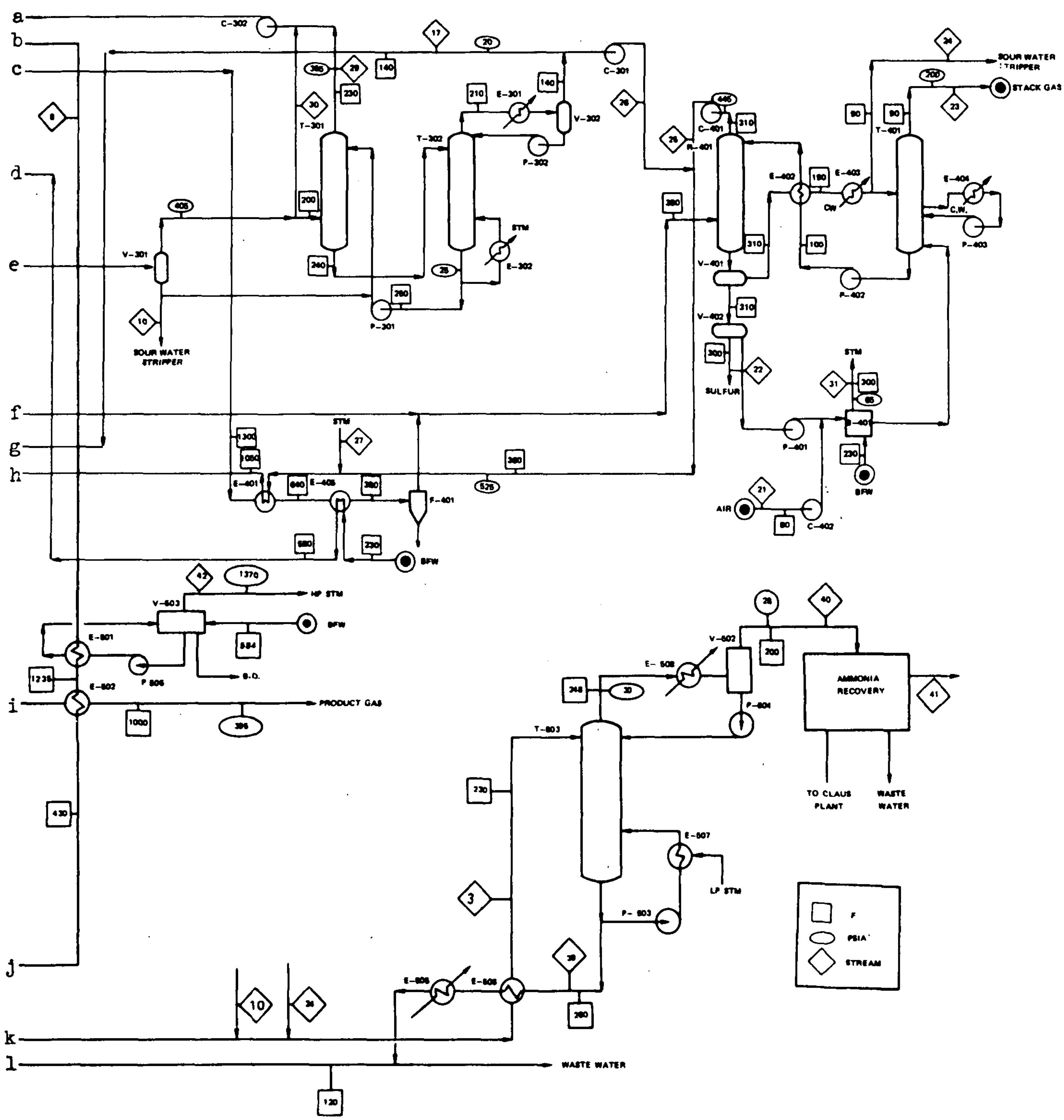


FIG. 19

PROCESS FLOW DIAGRAM BCR/CONOCO WITH WATER WASH



to drop temperature to the desired level at the inlet of a regenerative heat exchanger. An aftercooler is required to further reduce temperature to 120 F for the ammonia scrub and particulate removal process. Resaturation of the fuel gas is incorporated into that block. The gas is then reheated in the cold side of the regenerator prior to being sent to the burner.

Inherent in the addition of the water scrub is the need for process steam in both the sour water stripper and ammonex unit. Also, the regenerator temperature and effectiveness will have an effect on system performance. The resultant reduction in fuel gas mass flow rate due to removal of both ammonia and water vapor also affects performance, with the loss of water vapor having the most significant effect. Because of the relatively inexpensive equipment involved and the availability of low-temperature waste heat, it is apparent that resaturation is desirable.

Regenerator temperature also has a large effect on performance and while materials are available to withstand temperatures in excess of 1600 F, the practical design and operational problems associated with thermal stress, operational life and cost make their use questionable. Therefore, alternate solutions to achieve better performance at more conventional inlet temperatures (1100 F) were considered.

The high-temperature heat available from the fuelgas as it is cooled from 1700 to 1100 F can be used to improve steam cycle characteristics. In essence, it can be used to provide almost all the heat used in vaporizing the steam while the exhaust gas is used for superheating and feedwater heating. As a result, a 300 F stack temperature can be achieved at increased feedwater supply temperatures. If regenerative feedwater heating to 250 F is used, steam cycle efficiency will improve by about 6 percent thereby increasing the utilization of the heat available to the steam cycle and increasing output by 6 percent. This would provide an increase of 0.8 points in overall cycle efficiency allowing the use of a more conventional regenerator without serious performance degradation.

However, in order to more directly allow comparison to the BCR/CONOCO system without the scrubber for ammonia(1), it was decided to keep a consistent steam bottoming cycle for each.

A revised mass balance is given in Table 36, a revised utility summary in Table 37, and a revised equipment list in Table 38.

Table 36

REVISED MATERIALS BALANCE FOR BCR/CONOCO SYSTEM

(see Fig. 19)

STREAM	M.W.	1 LB/HR	1 MOL/HR	2 LB/HR	2 MOL/HR	3 LB/HR	3 MOL/HR	4 LB/HR	4 MOL/HR
O_2	32.00					503395	15731.1		
N_2	28.02			178053	6354.5	1658187	59178.7		
CO	28.01			67395	2406.1				
CO_2	44.01			23537	534.8				
H_2	2.016			3761	1865.7				
CH_4	16.04			7919	493.7				
H_2S	34.08			228	6.7				
COS	60.08			54	0.9				
NH_3	17.03			1003	58.9				
H_2O	18.02			6374	353.7			396900	22025.5
TOTAL		700000 (coal)		288324	12075.0	2161582	74909.8	396900	22025.5

STREAM	M.W.	5 LB/HR	5 MOL/HR	6 LB/HR	6 MOL/HR	7 LB/HR	7 MOL/HR	8 LB/HR	8 MOL/HR
N_2	28.02			1839079	65634.5	1839079	65634.5	1661026	59280.0
CO	28.01			716557	25582.2	696085	24851.3	628693	22445.3
CO_2	44.01			513583	11669.7	584880	13289.7	528252	12003.0
H_2	2.016			37374	18538.8	38850	19270.9	35089	17405.1
$CH_4$1	16.04			81796	5099.5	81796	5099.5	73877	4605.8
H_2S	34.08			23369	685.7	2341	68.7	2113	62.0
COS	60.08			8621	143.5	517	8.6	469	7.8
NH_3	17.03			10371	609.0	10371	609.0	9367	550.0
H_2O	18.02			258373	14338.1	256288	14222.4	231474	12845.4
TOTAL		60900 (slag)		3489123	142301.0	3510207	143054.5	3170360	129204.4

Table 36 - Continued

MATERIAL BALANCE FOR BCR/CONOCO SYSTEM

STREAM	M.W.	9 LB/HR	9 MOL/HR	10 LB/HR	10 MOL/HR	11 LB/HR	11 MOL/HR	12 LB/HR	12 MOL/HR
N_2	28.02	178053	6354.5						
CO	28.01	67392	2406.0						
CO_2	44.01	56628	1286.7			311071	7068.2	282443	6417.7
H_2	2.016	3761	1865.7						
CH_4	16.04	7919	493.7						
H_2S	34.08	228	6.7			2846	83.5	26985	791.8
COS	60.08	48	0.8						
NH_3	17.03	1005	59.0						
H_2O	18.02	24814	1377.0	16142	895.8	70588	3917.2	57824	3208.9
TOTAL		339848	13850.1	16142	895.8	384505	11068.9	367252	10418.4

STREAM	M.W.	13 LB/HR	13 MOL/HR	14 LB/HR	14 MOL/HR	15 LB/HR	15 MOL/HR	16 LB/HR	16 MOL/HR
$CaCO_3MgCO_3$	184.01	10636	57.8	10636	57.8				
$CaCO_3MgO$	140.41			94201	670.9	199775	1422.8	1994	14.2
CaS MgO	112.46			574997	5112.9	490438	4361.0	4903	43.6
INERTS	100	1010	10.1	101750	1017.5	100740	1007.4	1010	10.1
TOTAL		11646	67.9	781584	6859.1	790953	6791.2	7907	67.9

Table 36 - Continued

MATERIAL BALANCE FOR BCR/CONOCO SYSTEM

STREAM	M.W.	17 LB/HR	17 MOL/HR	18 LB/HR	18 MOL/HR	19 LB/HR	19 MOL/HR	20 LB/HR	20 MOL/HR
CO_2	44.01	5580	126.8			1118	25.4		
H_2S	34.08					1486	43.6		
H_2O	18.02	387	21.5	14780	820.2	148	8.2	14234	789.9
$CaCO_3MgCO_3$	184.01							10636	57.8
INERTS	100							1010	10.1
TOTAL		5967	148.3	14780	820.2	2752	77.2	25880	857.8

STREAM	M.W.	21 LB/HR	21 MOL/HR	22 LB/HR	22 MOL/HR	23 LB/HR	23 MOL/HR	24 LB/HR	24 MOL/HR
O_2	32.00	13312	416.0			1210	37.8		
N_2	28.02	43851	1565.0			43851	1565.0		
SO_2	64.06					288	4.5		
H_2O	18.02					101	5.6	48436	2687.9
Sulfur	32.06			23962	747.4				
TOTAL		57163	1981.0	23962	747.4	45450	1612.9	48436	2687.9

Table 36 - Continued

MATERIAL BALANCE FOR BCR/CONOCO SYSTEM

STREAM		25		26		27		28	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
CO_2	44.01	283561	6443.1	27511	625.1				
H_2S	34.08	2846	83.5						
H_2O	18.02	22903	1271.0	1910	106.0	45774	2540.2	210000	11653.7
TOTAL		309310	7797.6	29421	731.1	45774	2540.2	210000	11653.7

STREAM		29		30		31		32	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
N_2	28.02	122414	4363.8	55639	1985.7				
CO	28.01	46334	1654.2	21061	751.9				
CO_2	44.01	5840	132.7	17696	402.1				
H_2	2.016	2586	1282.7	1175	583.0				
CH_4	16.04	5444	339.4	2475	154.3				
H_2S	34.08	157	4.6	72	2.1				
COS	60.08	36	0.6	18	0.3				
NH_2	17.03	690	40.5	313	18.4				
H_2O	18.02	4646	257.8	1728	95.9	48880	2712.5	193530	10739.7
TOTAL		188147	8081.3	100177	3993.7	48880	2712.5	193530	10739.7

Table 36 (Cont'd)

MATERIAL BALANCE BCR/CONOCO

	M.W.	33 LB/HR	33 MOL/HR	34 LB/HR	34 MOL/HR	35 LB/HR	35 MOL/HR	36 LB/HR	36 MOL/HR
N_2	28.02	1661025.6	59280.0	1661025.6	59280.0				
CO	28.01	628692.8	22445.3	628692.8	22445.3				
CO_2	44.01	522970.8	11883.0	522970.8	11883.0			5281.2	120
H_2	2.016	35088.7	17405.1	35088.7	17405.1				
CH_4	16.04	73877.0	4605.8	73877.0	4605.8				
H_2S	34.08	1908.5	56.0	1908.5	56.0			204.5	6.
COS	60.08	468.6	7.8	468.6	7.8				
NH_3	17.03	936.6	55.0	936.6	55.0			8663.2	508.7
H_2O	18.02	8238.7	457.2	12845.4	12845.4	4597561	255136.6	318575.6	17679
TOTAL		2933207.3	116195.2	2937814.0	128583.4	4597561	225136.6	332724.5	18313.7

	M.W.	37 LB/HR	37 MOL/HR	38 LB/HR	38 MOL/HR	39 LB/HR	39 MOL/HR
N_2	28.02						
CO	28.01						
CO_2	44.01					44.0	1.0
H_2	2.016						
CH_4	16.04						
H_2S	34.08					3.4	0.1
COS	60.08						
NH_3	17.03	233.3	13.7	8663.2	508.7	423.5	25.4
H_2O	18.02	318575.6	17679	606389.2	33650.9	600094.8	33301.6
TOTAL		318808.9	17692.7	615052.4	34159.6	600574.7	33328.1

Table 36 (Cont'd)

MATERIAL BALANCE BCR/CONOCO

		40		41		42		43	
	M.W.	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
N_2	28.02								
CO	28.01								
CO_2	44.01	5193.2	118.						
H_2	2.016								
CH_4	16.04								
H_2S	34.08	201.1	5.9						
COS	60.08								
NH_3	17.03	8230.6	483.3	8149	478.5				
H_2O	18.02	6294.4	349.3			916369	50852.9	223235	12388.2
TOTAL		199193.3	956.5	8149	478.5	916369	50852.9	223235	12388.2

Table 37

UTILITIES SUMMARY OF REVISED BCR/ CONOCO SYSTEM WITH WATER SCRUB

	Coal Gasification	Gas Purification	Spent Dolomite Treating	CO_2 Removal	Sulfur Recovery	Ammonia Recovery	Sour Water Stripping	Scrubbing and Resaturation	Total
STEAM, LB/HR									
@ 65 PSIA				58200	(48880)	4780	130315		144415
@ 1300	(135530)	(147819)				(37750)			
@ 1250 SPHT	396900								396900
COOLING WATER, GPM	10000		1120	390	6200				17710
POWER, KW	21000	277	155	4863	3931	926	273	890	30255
BFW, LB/HR	137190	195530			49370			223235	
STM, COND., LB/HR				(58200)			(13680)		(71880)
PROCESS WATER LB/HR	210000								210000
CHEMICALS, $/DAY		1400							1400

Table 38

REVISED BCR/CONOCO WITH WATER SCRUB SYSTEM

EQUIPMENT LIST

SECTION 100 - DESULFURIZATION

ITEM	DESCRIPTION
Reactors	
R-101	Sulfur Absorber
R-102	Acceptor Regenerator
Vessels	
V-101	Dolomite Feed Hopper
V-102	Spent Dolomite Hopper
V-103	HP Steam Drum
Pumps	
P-101	BFW Circulation Pump
Exchangers	
E-101	Waste Heat Boiler
E-102	Economizer
E-103	Gas Cooler
Miscellaneous	
F-101	Absorber Cyclone Separator
F-102	Regenerator Cyclone Separator

Table 38 - Continued

REVISED BCR/CONOCO SYSTEM

EQUIPMENT LIST

SECTION 200 - SPENT DOLOMITE TREATING

ITEM	DESCRIPTION
Reactors	
R-201	Acceptor Converter 1st Stage
R-202	Acceptor Converter 2nd Stage
R-203	Acceptor Converter 3rd Stage
Vessels	
V-201	Quench Water Surge
Pumps	
P-201	Quench Water Pump
P-202	Dolomite Slurry Pump
P-203	Make-up Water Pump
Exchangers	
E-201	Quench Water Cooler
E-202	CO_2 Trim Cooler
Compressors	
C-201	CO_2 Blower
C-202	Acid Gas Compressor
Miscellaneous	
F-201	Hydroclone

Table 38 - Continued

REVISED BCR/CONOCO SYSTEM

EQUIPMENT LIST

SECTION 300 - CO_2 RECOVERY

ITEM	DESCRIPTION
Tower	
T-301	CO_2 Absorber
T-203	CO_2 Stripper
Vessels	
V-301	Water Separating Drum
V-302	Stripper OVHD Accumulator
Pumps	
P-301	Stripper BTMS Pump
P-302	Stripper Reflux Pump
Compressors	
C-301	CO_2 Blower
C-302	Transport Gas Compressor
Exchangers	
E-301	Stripper OVHD Condenser
E-302	Stripper Reboiler

Table 38 - Continued

REVISED BCR/CONOCO SYSTEM

EQUIPMENT LIST

SECTION 400 - SULFUR RECOVERY

ITEM	DESCRIPTION
Reactors	
R-401	Liquid Phase Clause Reactor
Towers	
T-401	SO_2 Absorption Column
Vessels	
V-401	Sulfur Separator Drum
V-402	Sulfur Storage Drum
Pumps	
P-401	Sulfur Pump
P-402	Acid Pump
P-403	Acid Circulating Pump
Compressors	
C-401	Recycle CO_2 Compressor
C-402	Air Compressor
Exchangers	
E-401	Recycle CO_2 Reheater
E-402	Feed/Bottoms Exchanger
E-403	Weak Acid Cooler
E-404	SO_2 Absorber Intercooler
E-405	BFW Preheater
Miscellaneous	
F-401	Electrostatic Precipitator
B-401	Sulfur Burner

Table 38 - Continued

REVISED BCR/CONOCO SYSTEM

EQUIPMENT LIST

SECTION 500 - AMMONIA REMOVAL AND HEAT RECOVERY

ITEM	DESCRIPTION
Towers	
T-501	NH_3 Scrubber
T-502	Fuel Gas Saturator
T-503	NH_3 Stripper
Vessels	
V-501	Condensate Kock-Out Drums
V-502	NH_3 Stripper OVHD Accumulator
V-503	H.P. Steam Drum
Exchangers	
E-501	H.P. Boiler
E-502	Regenerator
E-503	Resaturation Water Heater
E-504	Gas Cooler
E-505	NH_3 Stripper BTMS Cooler
E-506	NH_3 Stripper BTMS-Feed Exchanger
E-507	NH_3 Stripper Reboiler
E-508	NH_3 Stripper OVHD Condenser
Pumps	
P-501	NH_3 Absorber BTMS Pump
P-502	Resaturator Circulating Pump
P-503	NH_3 Stripper BTMS Pump
P-504	NH_3 Stripper Reflux Pump

GASIFIER MODELING

One of the major limitations of this and prior studies has been the lack of data on the operational characteristics of coal gasifiers. While there are numerous gasifier installations, these are for the most part providing feedstock for chemical plants and are generally run at constant conditions. Also, much of the development work has been directed toward substitute natural gas with the resultant emphasis on methane production in the gasifier. It is quite likely that a gasifier designed for methane production will not produce optimum performance in a low-Btu gas fired combined-cycle power generating system. Also, when used in conjunction with a power system, it will be desirable to operate at other than design point conditions, i.e. at different air/coal, steam/coal or pressure levels. Thus, it was apparent that a gasifier model should be developed to indicate the trends in operation at alternate design conditions.

The initial approach was based on the use of a chemical equilibrium model developed nearly 20 years ago as a tool to analyze rocket combustion. That approach described in Appendix A, can be used in an equilibrium calculation considering in excess of 100 species. A simplified approach (limited to 10 species) was used to model an oil gasifier. The results of that analysis are presented in SECTION 4 showing the effect of gasifier parameters on system performance and supporting the need for a model capable of predicting gasifier performance at alternate operating conditions.

Although the equilibrium approach is applicable to several gasifier types, for example, the oil and Koppers Totzek gasifiers, it was found to be unsuitable for the upper stage of the BCR two-stage gasifier. This type gasifier requires a more complicated approach to account for the nonequilibrium conditions that are encountered in, for example, the devolatilization stage of the BCR gasifier. The BCR model is described in Appendix B while results of a series a parametric variations of the model are given in the following paragraphs.

Parametric Study of the BCR Two-Stage Gasifier

A series of parametric variations of the major operating variables of the BCR two-stage gasifier were made in order to see if there were operating regimes away from the reference design point, i.e., the set of operating conditions which were selected for use in this study, which might offer advantages to the overall integrated low Btu coal gasifier combined-cycle system. It was found that some flexibility in design exists. By decreasing steam while increasing air flow, a slightly different operating point results with the product gas having less chemical but more sensible energy. The limitations on the choices of operating conditions are due to chemical kinetics limitations on gasifier operation.

Variations were made on the design point data from the BCR-Selexol integrated system. The operating data are summarized in Table 39. Coal is input at ambient temperature (70 F) carried by a transport gas in a fixed volume/lb coal ratio. The transport gas temperature is fixed at the reference design point temperature of 370 F. The transport gas composition is equal to the gasifier product gas composition with the sulfur compounds (H_2S) removed and varies for each case. Steam temperature is fixed at 1250 F, and all the parametric variations were calculated for minimum steam input (no steam into Stage 2). The air temperature was fixed at the reference design point of 800 F. The air and steam flows are calculated by the gasifier model to satisfy energy and mass flow balances and to meet the specified Stage 1 and 2 temperatures. The solids output from Stage 2 of the gasifier is assumed to be recycled to Stage 1 without mass or energy loss by means of a series of cyclone separators. The Stage 1 char conversion is conservatively assumed at 60 percent. No operating data on Stage 1 exists since this stage has not been operated. With these assumptions, the Stage 1 and Stage 2 temperatures were varied over broad ranges both at the design point pressure (500 psia) and at a higher and lower pressure. The intent was to identify trends for the resultant changes in gasifier operation under the major variations in operating conditions.

Figures 20 and 21 show the results of variations of Stage 1 and 2 operating temperatures on the gasifier product gas chemical energy (HHV-Btu/scf) and the resultant requirements in steam and air. Design point (T_1 = 2800 F, T_2 = 1800 F) is indicated by an X. It should be noted that Figs. 20 and 21 should be plotted on a 3-dimensional curve since Fig. 20 has various air/coal ratios and Fig. 21 has various steam/coal ratios. The trends, however, are clear enough so that the curves as shown present the parametric dependences. Figures 20 and 21 show that in general, lowering the Stage 2 temperature (product gas temperature) T_2 increases the product gas chemical energy and lowers the steam and air requirements. Thus, there is a trade-off between sensible and chemical energy in the gasifier product gas, with the lower steam and air requirements generally favoring chemical energy (HHV). Raising the Stage 1 temperature T_1 for the same product gas temperature

Table 39

SUMMARY OF BCR OPERATING CONDITIONS

Coal Temperature	70 F
Steam Temperature	1250 F
Air Temperature	800 F
Transport Gas Temperature	370 F
Air Composition (mole fraction)	
Oxygen	21%
Nitrogen	79%
Transport gas moles/lb coal	.0173
Withdrawal	0%
Stage 1 char conversion fraction (YC)	60%
Stage 1 Temperature (variable)	2400 - 3400 F
Stage 2 Temperature (variable)	1400 - 2400 F
Pressure	14.7, 500, 1000 psia

BCR TWO–STAGE AIR BLOWN GASIFIER. STEAM/COAL VERSUS PRODUCT GAS HHV FOR DIFFERENT OPERATING CONDITIONS, P=34 atm (500 PSIA)

- – – – CONSTANT STAGE 1 TEMPERATURE, T_1
- ——— CONSTANT STAGE 2 TEMPERATURE, T_2 (PRODUCT GAS TEMPERTURE)
- (shaded) BOUDOUARD CONSTANT K=10
- X DESIGN POINT T_1=2800 F, T_2=1800 F

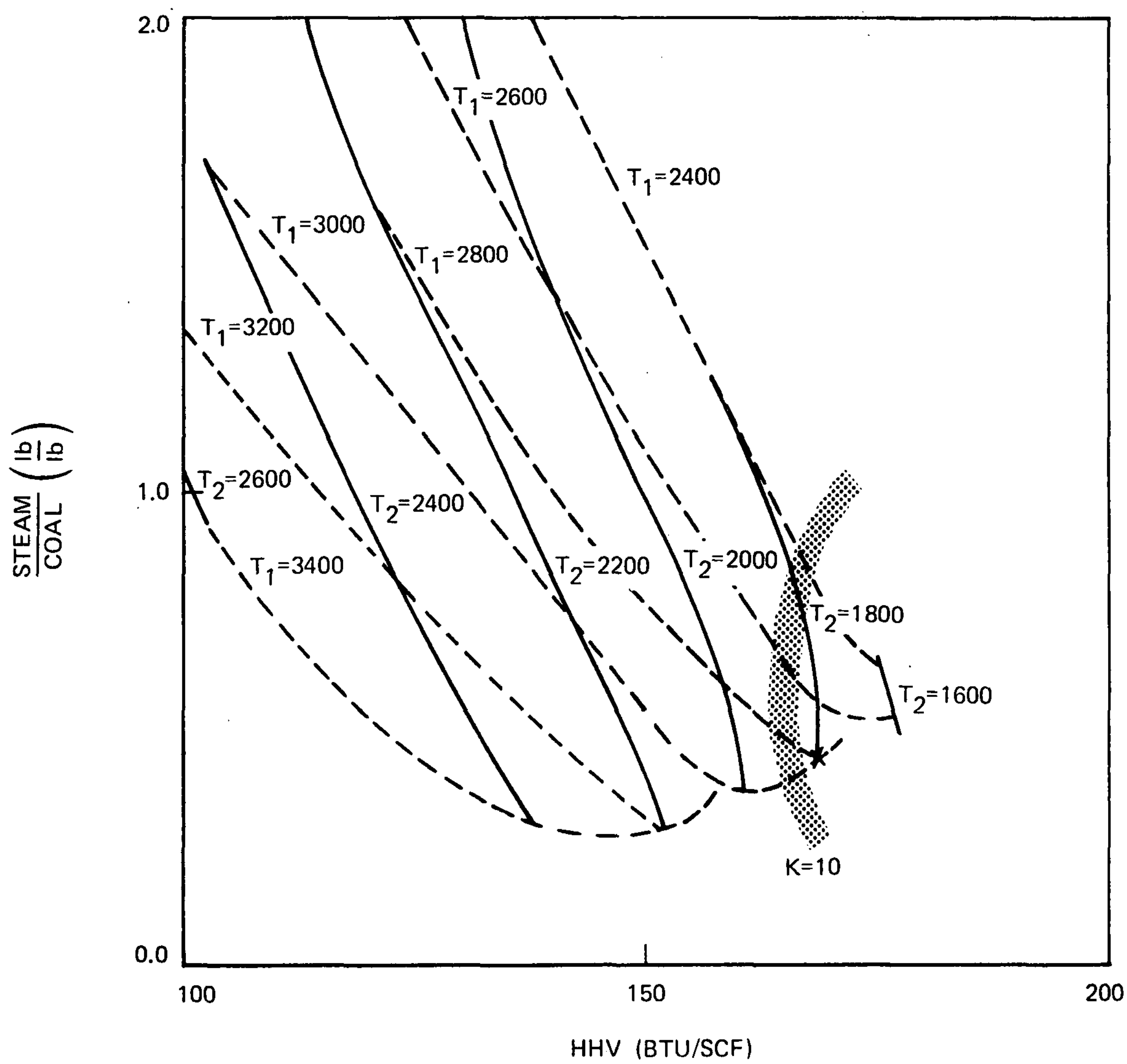


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FIG. 21

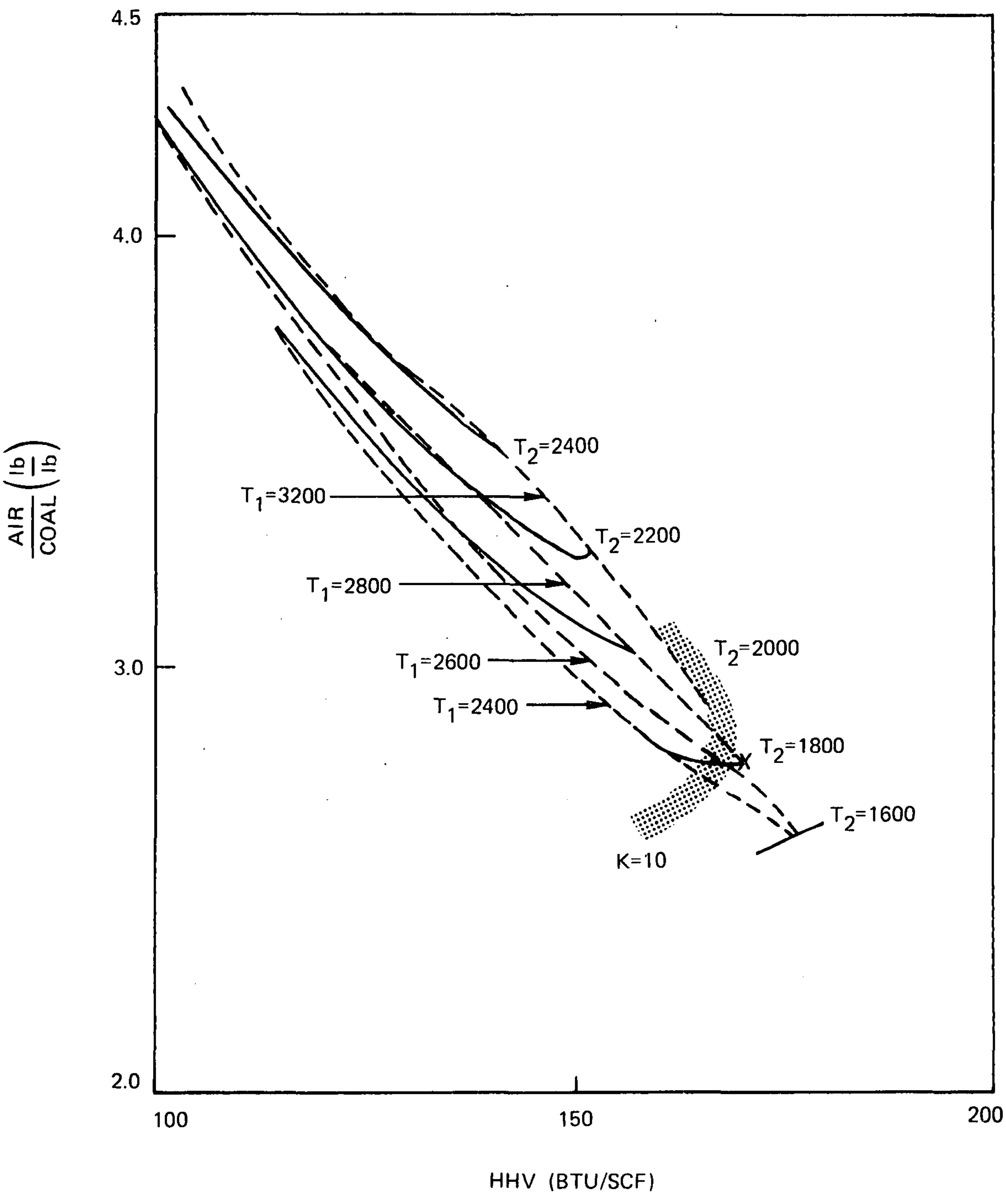
BCR TWO–STAGE AIR BLOWN GASIFIER. AIR/COAL VERSUS GAS HHV FOR DIFFERENT OPERATING CONDITIONS. P=34 (500 PSIA)

- - - - CONSTANT STAGE 1 TEMPERATURE, T_1

——— CONSTANT STAGE 2 TEMPERATURE, T_2 (PRODUCT GAS TEMPERATURE)

░░░ BOUDOUARD CONSTANT K=10

X DESIGN POINT T_1=2800 F, T_2=1800 F



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T_2 raises chemical energy (HHV) and lowers steam and air requirements, in general. Since all three are favorable, higher Stage 1 temperatures are favorable. However, because of kinetic limitations, many of the T_1 and T_2 combinations shown in Figs. 20 and 21 cannot be produced in a gasifier. The limitations are discussed in APPNEDIX B but are not thoroughly understood yet, although much research is being done. The computational approach to the second stage reaction uses a set yield of CH_4 (YCH_4) and CO and/or CO_2 (YCO) as a fraction of the carbon in the feed. This is combined with the assumption of equilibrium for the water gas shift reaction. As is discussed in Appendix B, the methane yield is based on empirical data relating YCH_4 to the partial pressure of hydrogen in the second stage. The parameter, YCO, is varied to achieve the closest approach to equilibrium of the Boudouard reaction ($2\,CO \rightleftarrows CO_2 + C$) as suggested by BCR. The Boudouard Constant, K, is defined as:

$$K = \frac{[X_{CO2}/\rho\,(X_{CO})^2]\ \text{CALCULATED}}{[X_{CO_2}/\rho\,(X_{CO})^2]\ \text{equilibrium}}$$

Values of K greater than 1 indicate that the calculated carbon monoxide concentration is less than the equilibrium value. Thus, each point represents the minimum value of K that can be achieved within the constraints that have been imposed. While it is not known if there is a limiting value of K, the reference design point (K = 5) falls to the right of the area showing K = 10 on the curves. Points having K higher than 10 (to the left of K = 10) are relatively far removed from the design point and may not be kinetically possible. Further research is needed to determine if this or other parameters may be used to identify the kinetic limits on gasifier operation.

In order to assess the variations of gasifier operations at different pressures, data were obtained for 1 atm and 68 atm (1000 psia). It should be noted that use of the model for the 1 atm case is not realistic ($YCH4 = .08 =$ constant was assumed, for example) for actual gasifier operation, but trends may nevertheless be deduced.

Figures 22 and 23 show the variation of steam and air requirements against product gas chemical energy (HHV) for various operating temperatures T_1 and T_2 at 1 atm. In summary, the steam and air requirements are somewhat worse (higher) than in the 500 psia case and the Boudouard

BCR TWO-STAGE AIR BLOWN GASIFIER. STEAM/COAL VERSUS PRODUCT GAS HHV FOR DIFFERENT OPERATING CONDITIONS, P=1 atm (14.7 PSIA)

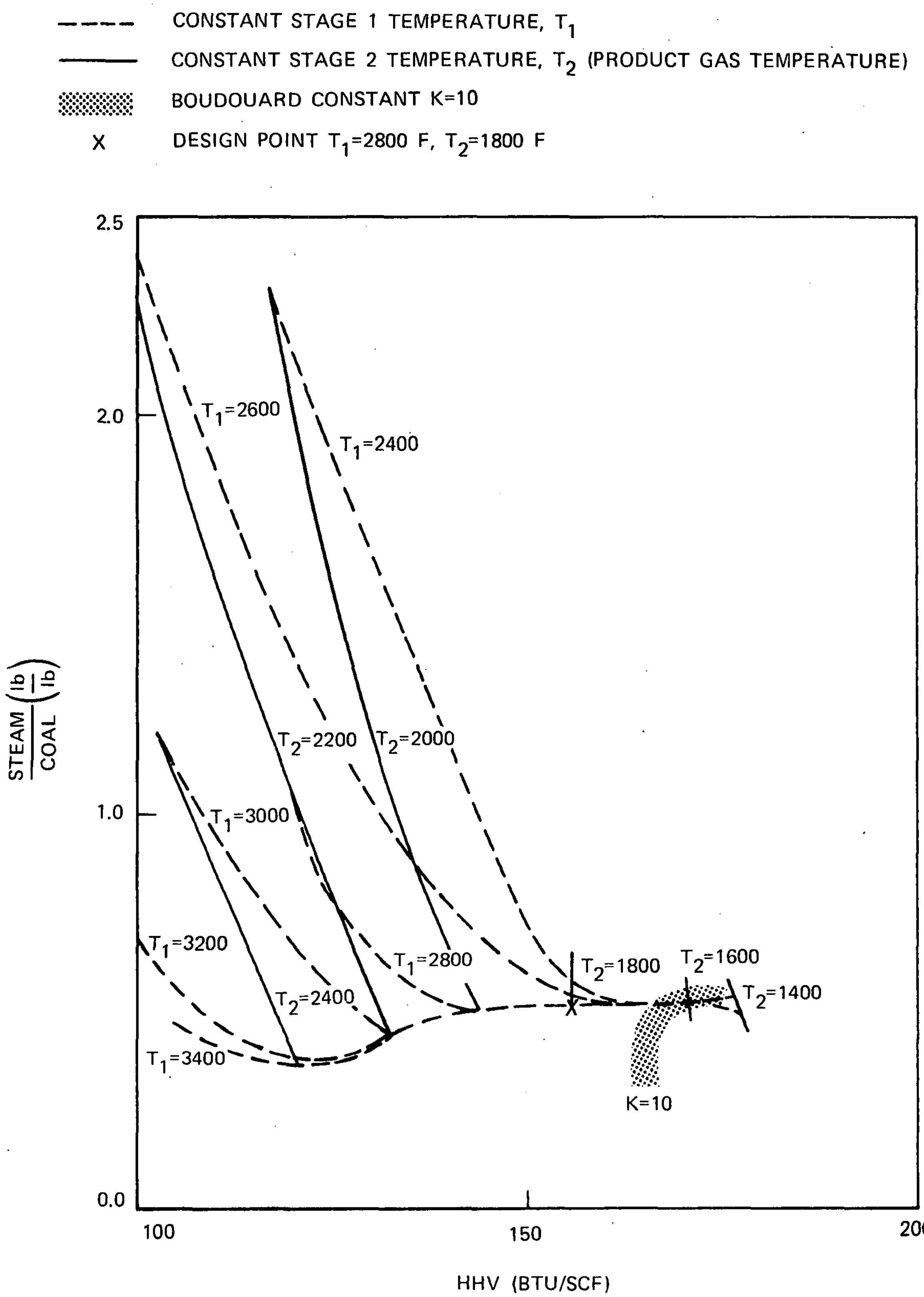

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FIG. 23

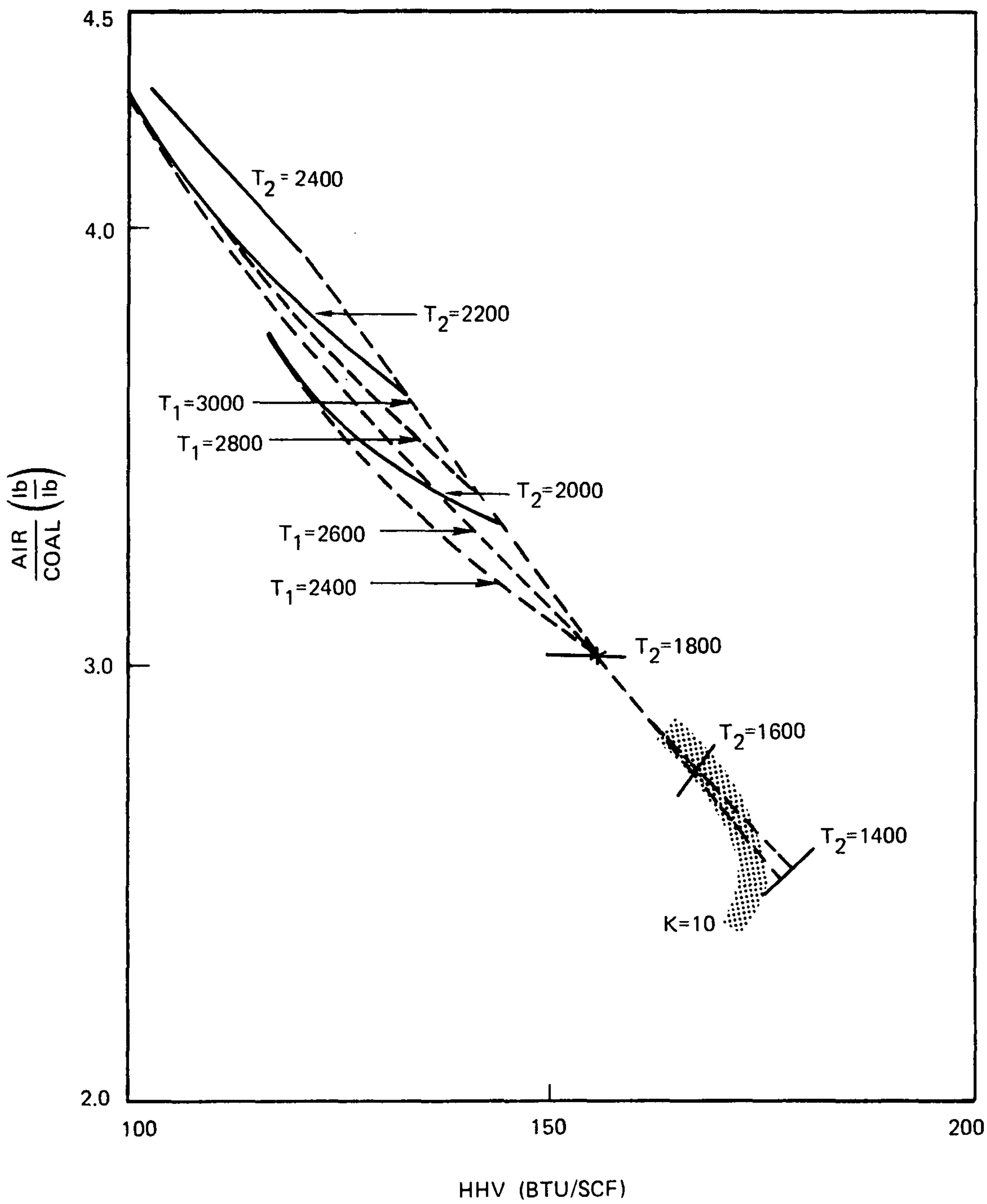
BCR TWO–STAGE AIR BLOWN GASIFIER . AIR/COAL VERSUS PRODUCT GAS HHV FOR DIFFERENT OPERATING CONDITIONS. P=1atm (14.7 PSIA)

---- CONSTANT STAGE 2 TEMPERATURE, T_1

—— CONSTANT STAGE 2 TEMPERATURE, T_2 (PRODUCT GAS TEMPERATURE)

▒▒ BOUDOUARD CONSTANT K=10

X DESIGN POINT T_1=2800, T_2=1800F



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constant K = 10 suggests a very limited operation region from a kinetic viewpoint. (The design point at 500 psia, T_1 = 2800 F, T_2 = 1800 F has K = 5, in fact.)

Figures 24 and 25 show the variation of steam and air requirements against prodict gas chemical energy (HHV) for various operating temperatures, T_1 and T_2, at 68 atm (1000 psia). The general descriptions of these variations is the same as for the 34 atm (500 psia) case. Comparing the 1000 psia case with the 500 psia case shows that the 1000 psia cases has lower steam and air requirements and a higher product gas chemical energy (HHV) for the same operating conditions T_1 and T_2. Without a detailed analysis, it is difficult to determine the net value of higher pressure operation.

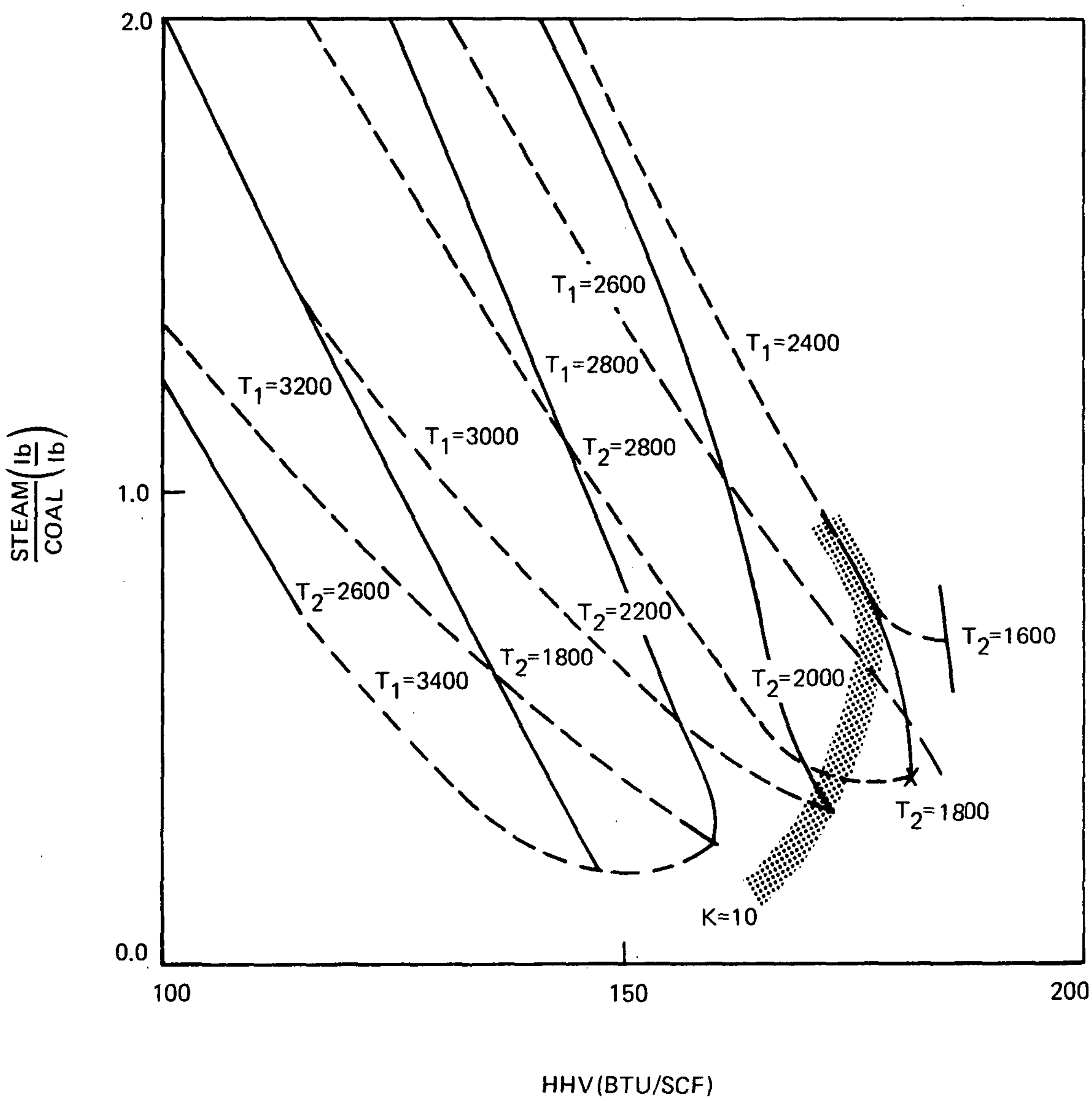
BCR TWO –STAGE AIR BLOWN GASIFIER. STEAM/COAL VERSUS PRODUCT GAS HHV FOR DIFFERENT OPERATING CONDITIONS. P=68 atm (1000 PSIA).

---- CONSTANT STAGE 1 TEMPERATURE, T_1

——— CONSTANT STAGE 2 TEMPERATURE, T_2 (PRODUCT GAS TEMPERATURE)

(shaded) DESIGN POINT T_1=2800 F, T_2=1800 F

X BOUDOUARD CONSTANT K=10



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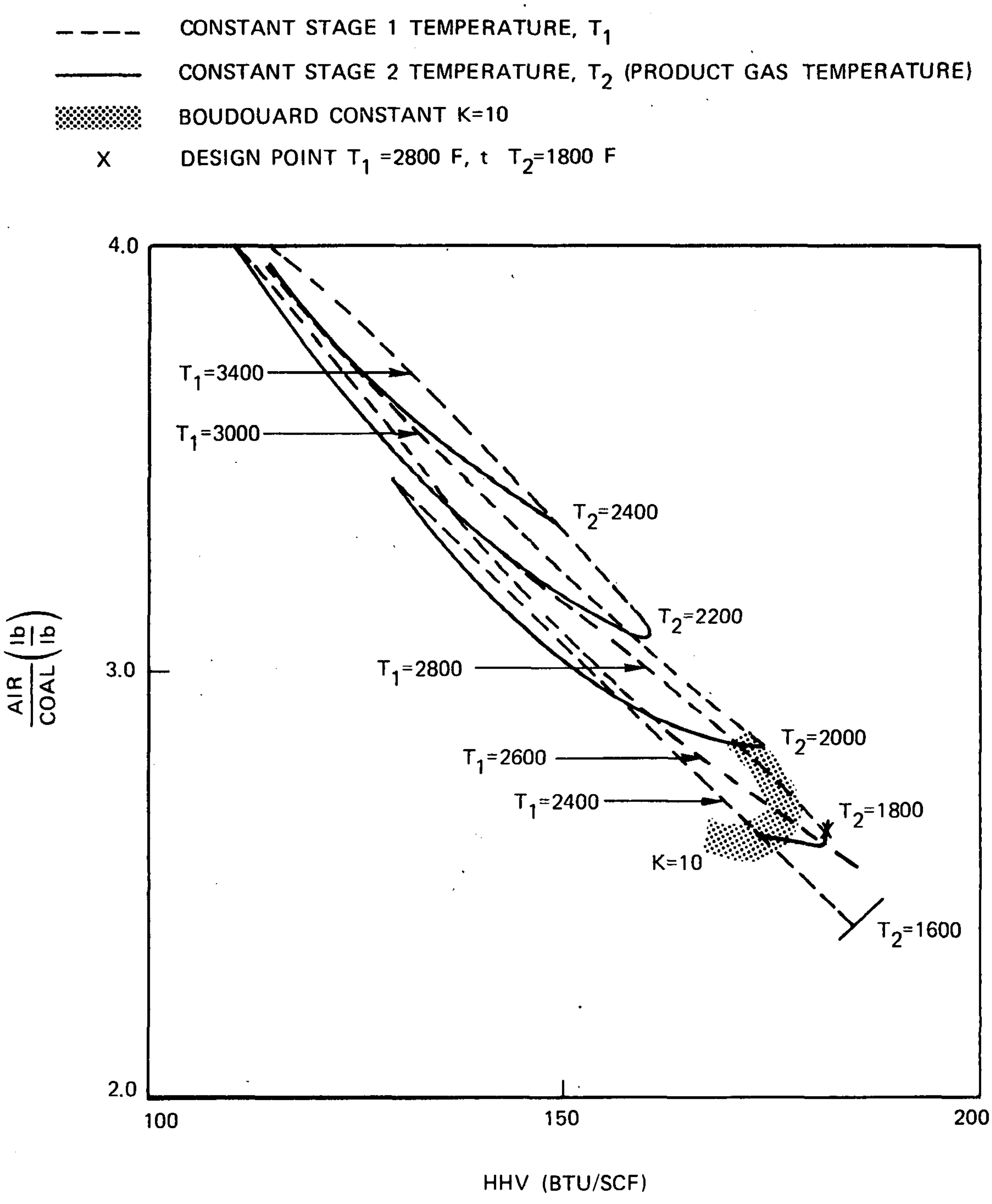
BCR TWO–STAGE AIR BLOWN GASIFIER. AIR/COAL VERSUS PRODUCT GAS HHV FOR DIFFERENT OPERATING CONDITIONS. P=68 atm (1000 PSIA)



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SECTION 4

PERFORMANCE AND COST OF INTEGRATED SYSTEMS

SUMMARY

The performance and cost of eight integrated power systems are presented. These include five variations of the BuMines and BCR systems previously considered as well as two residual oil partial oxidation systems and a Koppers-Totzek gasifier. A summary of the performance of these systems is given in Table 40, and the costs of power for these systems is given in Table 41 and Fig. 26. For comparative purposes, the cost of power for a conventional coal fired steam station with FGD have been developed. All the costs are based upon mid-1975 dollars.

The results show that the high-temperature cleanup systems have discernible performance and cost benefits over those systems using low-temperature cleanup. However, improvements in the low-temperature processes previously considered(1) have narrowed the gap in power costs. These improvements also make these systems a more viable competitor to conventional steam with FGD.

PERFORMANCE

The gasification and cleanup system combinations presented in previous sections have been integrated with either a first generation (16:1 pressure ratio, 2200 F turbine inlet temperature) or second generation (24:1 pressure ratio, 2600 F turbine inlet temperature) combined cycle or COGAS system. In general, the integration consists of utilizing engine bleed air for the gasifier air supply and an interchange of heat usually in the form of steam raised in the gas turbine exhaust heat recovery boiler, the fuel gas streams, or bleed air stream and used elsewhere in the process. A versatile simulation system described in Ref. 1 has been used to represent these systems and to estimate performance.

Table 40

INTEGRATED SYSTEMS PERFORMANCE SUMMARY

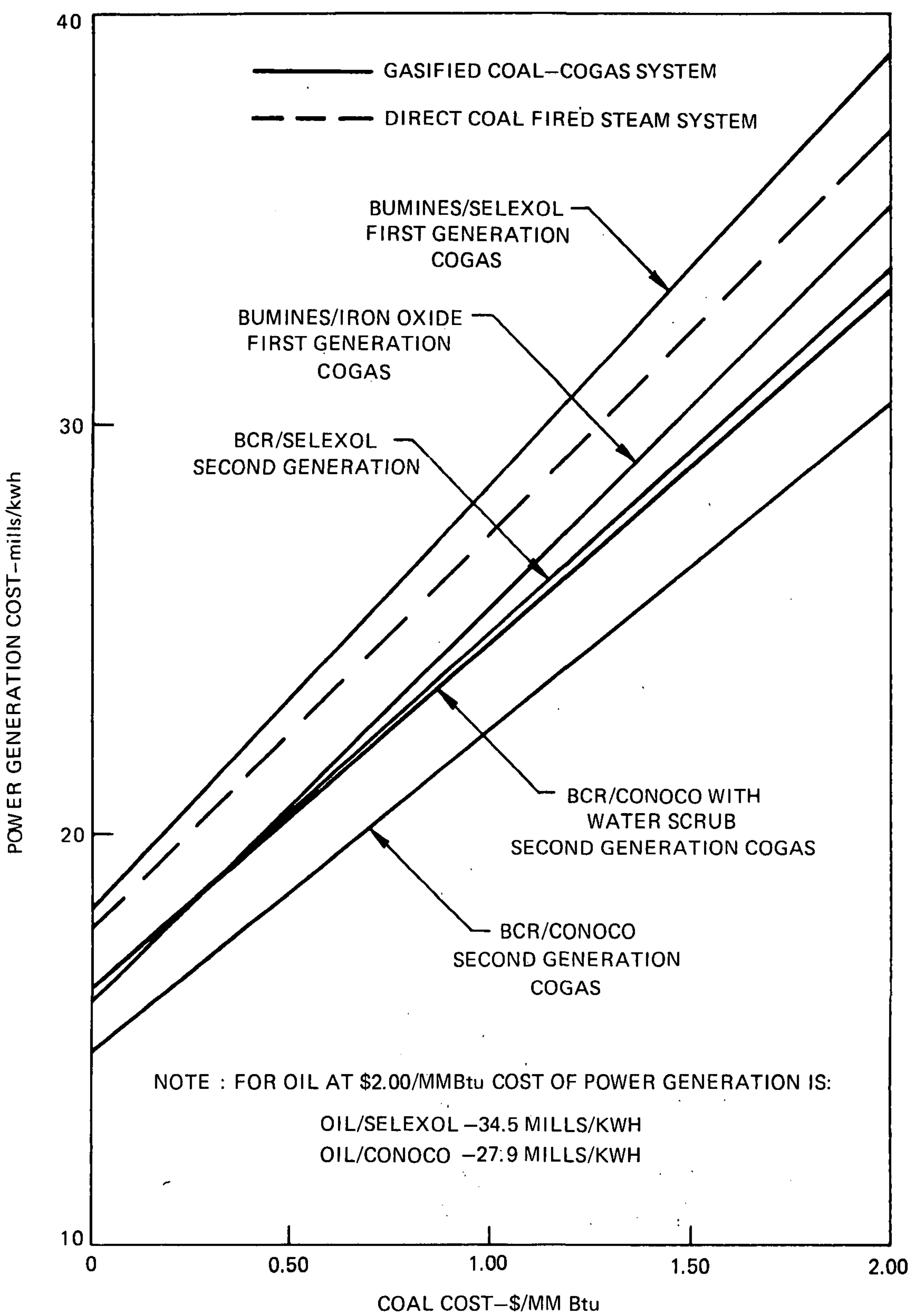
	BuMines/Selexol With Resaturation		BuMines/Iron Oxide		BCR/Selexol Without Cos Converter	BCR/Selexol With Cos Converter	BCR/Conoco No Water Scrub	BCR/Conoco With Water Scrub	Oil/Selexol		Oil/Conoco	K-T/Selexol
Gas Turbine												
Turbine Inlet Temperature - F	2200	2600	2200	2600	2600	2600	2600	2600	2200	2600	2600	2200
Compressor Pressure Ratio	16	24	16	24	24	24	24	24	16	24	24	16
Exhaust Temperature - F	927.	1127.	913	1106	1107	1110.	1115	1115	908.	1101.	1100.	920
Output Power - Mw	610.4	688.9	619.1	701.1	727.3	733.9	857.6	769.6	653.6	737.2	829.2	705.4
Steam Cycle												
Steam Temperature - F	827	1000	813.	1000	1000	1000	1000	1000	808	1000	1000	820
Steam Pressure - psia	1250	1250	1250	1250	1250	1250	1250	1250	1250	1250	1250	1250
Condenser Pressure in. Hg Abs	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Single or Two Pressure System	2	2	2	2	2	2	2	2	2	2	2	2
Net Steam Cycle Output - Mw	226.7	244.3	259.8	279.3	293.3	320.7	296.7	293.0	412.9	430.1	401.9	378.9
Gasifier and Cleanup System												
Fuel Feed Rate - lb/hr	700000	700000	700000	700000	700000	700000	700000	700000	500000	500000	500000	700000
Air/Fuel Ratio	3.013	3.013	2.688	2.688	3.088	3.088	3.088	3.088	6.0	6.0	6.0	.859*
Steam/Fuel Ratio	.405	.405	.349	.349	.567	.567	.567	.567	.567	-0-	-0-	.349
Air Temperature - F	800	800	800	800	800	800	800	800	800	800	800	220
Steam Temperature - F	584	584	584	584	1000	1000	1000	1000	--	--	--	275
Steam Pressure - psia	1250	1250	1250	1250	1250	1250	1250	1250	--	--	--	45
Gasifier Exit Temperature - F	1000	1000	950	950	1800	1800	1800	1800	2425	2425	2425	2200
Cleanup System Exit Temperature - F	252	252	1070	1070	1000	1000	1700	1000	1000	1000	1600	250
Fuel Gas HHV - Btu/scf	141.7	141.7	165.1	165.1	159.3	156.4	135.8	136.3	127.45	127.45	122.09	299.35
Integrated Station												
Gross Power - Mw	837.1	933.1	878.9	980.4	1020.6	1054.6	1154.3	1062.6	1066.5	1167.3	1231.1	1084.3
Boost Compressor Power - Mw	34.0	25.8	26.9	20.3	33.4	33.4	38.2	38.2	49.7	39.0	37.0	99.5
Gasifier & Cleanup Aux. Power	33.6	27.8	18.9	18.8	56.9	36.8	27.2	29.3	30.2	30.2	24.4	132.3
Plant Auxiliaries - Mw	8.4	9.2	8.0	8.9	11.0	11.0	10.4	10.0	13.2	14.1	12.6	11.2
Net Plant Output - Mw	761.1	870.3	825.1	932.4	919.3	973.4	1078.5	985.1	973.4	1084.0	1157.1	841.3
Net Plant Efficiency (HHV Coal)	.324	.370	.351	.397	.364	.386	.427	.390	.363	.404	.431	.301
Net Heat Rate - Btu/kwh	10531	9213	9721	8596.	9366	8845	7984	8740	9401	8439	7908	11345

* Oxygen-blown system

TABLE 41
POWER GENERATION COST SUMMARY

GASIFIER/CLEANUP COMBINATION	BUMINES/SELEXOL WITH RESATURATION	BUMINES/IRONOXIDE	BCR/SELEXOL WITH COS CONVERTER	BCR/CONOCO NO WATER SCRUB	BCR/CONOCO WITH WATER SCRUB	OIL/SELEXOL	OIL/CONOCO	K-T/Selexol
POWER SYSTEM - PR/TEMP	16:1/2200F	16:1/2200F	24:1/2600F	24:1/2600F	24:1/2600F	16:1/2200F	24:1/2600F	16:1/2200 F
Capital Costs - $/kw								
Power System Cost - $/kw	278	267	228	229	230	283	227	323
Gasification & Cleanup Cost - $/kw	214	168	207	170	204	150	109	341
Total Capital Cost - $/kw	492	435	435	399	434	433	336	664
Owning & Operating Costs - Mills/kwh								
Owning Costs (17% of Capital)	13.64	12.06	12.06	11.06	12.03	12.0	9.31	18.41
Operation and Maintenance								
Power System	1.59	1.52	1.30	1.31	1.31	1.62	1.30	1.84
Gasification & Cleanup	2.97	2.33	2.87	2.36	2.83	2.08	1.51	4.73
Fuel Cost at 60¢/MM Btu Coal, $2.00/MM Btu Oil	6.32	5.83	5.31	4.79	5.24	18.8	15.82	6.81
Total Generating Cost	24.52	21.74	21.54	19.52	21.41	34.5	27.94	31.79

POWER GENERATION COST SUMMARY



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For each system an optimization of engine pressure ratio based on cost or performance could, depending on the criteria, result in a different configuration for a particular turbine inlet temperature. However, such an optimization was outside the scope of this study and a representative pressure ratio was selected for each generation of turbine inlet temperature. This selection is discussed more fully in Appendix C. In a like manner, various steam systems could be used, depending on the characteristics of gas turbine exhaust heat and that available from gasifier and cleanup systems. However, a simple, low pressure (1250 psia) nonreheat steam cycle was used as a standard in all cases. The only variation is the addition of a second low pressure section, if needed, to achieve a 300 F stack temperature. In the course of the study, estimates were made to evaluate the performance benefits associated with reheat steam cycles. In general, an improvement of 20 percent or more in steam cycle performance is possible if there is sufficient high temperature heat available to support a 1000/1000 F reheat cycle. At the normal ratio of steam cycle to gas turbine power this translates into an overall system performance increase of 7-8 percent. Power system costs would naturally increase to some extent.

For all systems the effect of a lower fuel control supply pressure has been factored into system performance. A review of the fuel control requirements has shown that the fuel gas supply pressure can be reduced to as low as 3 atmospheres above burner pressure. This has been reflected in the performance of all systems.

Coal-Fired Steam Station

As is usual in making comparisons of advanced power systems, a reference system must be defined against which the various advanced systems are compared. The previous study[1] used as this basis a two unit 1000-MW coal-fired steam station with a lime-limestone FGD process.

It is unfortunate that the cost of FGD processes have yet to be fully defined, even though such excellent estimates are available[25,28]. The problem appears to arise from the confusion as to what should be considered as part of the FGD and what is chargeable to other parts of the power system; i.e., higher cost high-temperature electrostatic precipitators, revised air preheaters, etc. For example, in a study currently being carried out under NASA sponsorship, the TVA and GE have given preliminary estimates[29] of a wet scrubber system which added $261/kW to the estimated $574/kW for a 3500 psi/1000 F/1000 F power station. This system, which uses extraction steam to reheat the stack gas to allow a 250 F stack, as well as an electrostatic precipitator operating at 750 F, has an estimated efficiency of about 32 percent. The net effect of this system is to add over 34 percent to the cost of electricity.

While the foregoing may be an extreme, it does appear to account for all the elements required for effective FGD. In the current study, the wet lime/limestone system was assumed to cost approximately $92/kW using costing procedures consistent with Ref. 25. This is consistent with the previous costs(1) escalated to the mid-1975 period.

A significant change in the station costs shown in Table 42 from those previously estimated arises from an increase in the time of construction. Until recently, a multi-unit coal-fired station could expect a construction time of approximately four years. Within the last several years, however, construction schedules have been extended on this type of station to about five years. This change alone is equivalent to nearly $43/kW assuming a 7 percent escalation and 10 percent interest. In reality, recent escalation rates have been in excess of 10 percent with some items approaching 15 percent. Thus the estimates given in Table 42 may be viewed as being low and therefore conservative in nature when used as a yardstick to identify the potential benefits of future systems.

The performance of this station is estimated to be 35.1 percent giving rise to a cost of electricity of 23.5 mills/kWhr (Table 43) with coal at $.60/MMBtu. Figure 26 shows the relation between fuel cost and cost of power for this station.

K-T Selexol Integrated System Performance

For the configuration shown in Fig. 27 the resultant performance is summarized in Table 40. Clearly the K-T coal gasifier, when integrated with a combined cycle power system shows relatively poor performance when compared to the high-pressure gasification systems. In general, the differences can be ascribed to the relatively high power needed to compress the product gas and the power consumed by the oxygen plant. The cold gas efficiency of the K-T/Selexol system is low (76 percent) compared to the BuMines/Selexol system (83 percent). It is only slightly higher than that of the BCR/Selexol system (75 percent) and since the product gas is clean and the sensible heat can be used to raise steam and/or regenerate fuel gas, the system is quite similar to the BCR/Selexol on a heat in/heat out basis. However, since the power systems used are different, a direct comparison is not possible.

Table 42

COAL-FIRED STEAM STATION CAPITAL COSTS

Two 500-Mw Units

FPC Account No.		Mid-1975 Dollars
310	Land	52,000
311	Structures and Improvements	23,944,900
312	Boiler Plant Equipment	105,216,000
314	Turbogenerator Sets Steam	62,060,000
315	Accessory Electrical Equipment	18,756,800
316	Miscellaneous Power Plant Equipment	878,900
353	Station Equipment	2,616,900
	Subtotal (Excluding Land)	213,473,500
	Other Expenses	4,269,500
Direct Construction Cost		217,743,000
Indirects		
	Contingency	17,419,000
	Engineering and Supervision	32,661,500
Total Station Costs		267,823,900
Escalation (Five Year Construction; Turbogenerator Firm for Three Years)		50,407,600
Investment Subject to Interest		318,231,500
Total Installed Cost		415,373,200
Total Installed Cost with FGD		509,328,200
Cost Per Net KW		532

TABLE 43

COAL-FIRED STEAM STATION POWER GENERATING COST SUMMARY

Capital Cost - $/kw	
Direct Coal Fired Plant	438
Stack Gas Cleanup	94
Total Capital Cost	532
Owning and Operating Costs - Mills/kwh	
Owning Cost (17% of Capital)	14.7
Operation and Maintenance	
Steam System	1.7
Stack Gas Cleanup	1.3
Fuel Cost at 60¢/MMBtu	5.8
Total Cost of Power	23.5

K–T/SELEXOL/ INTERGRATED POWER SYSTEM

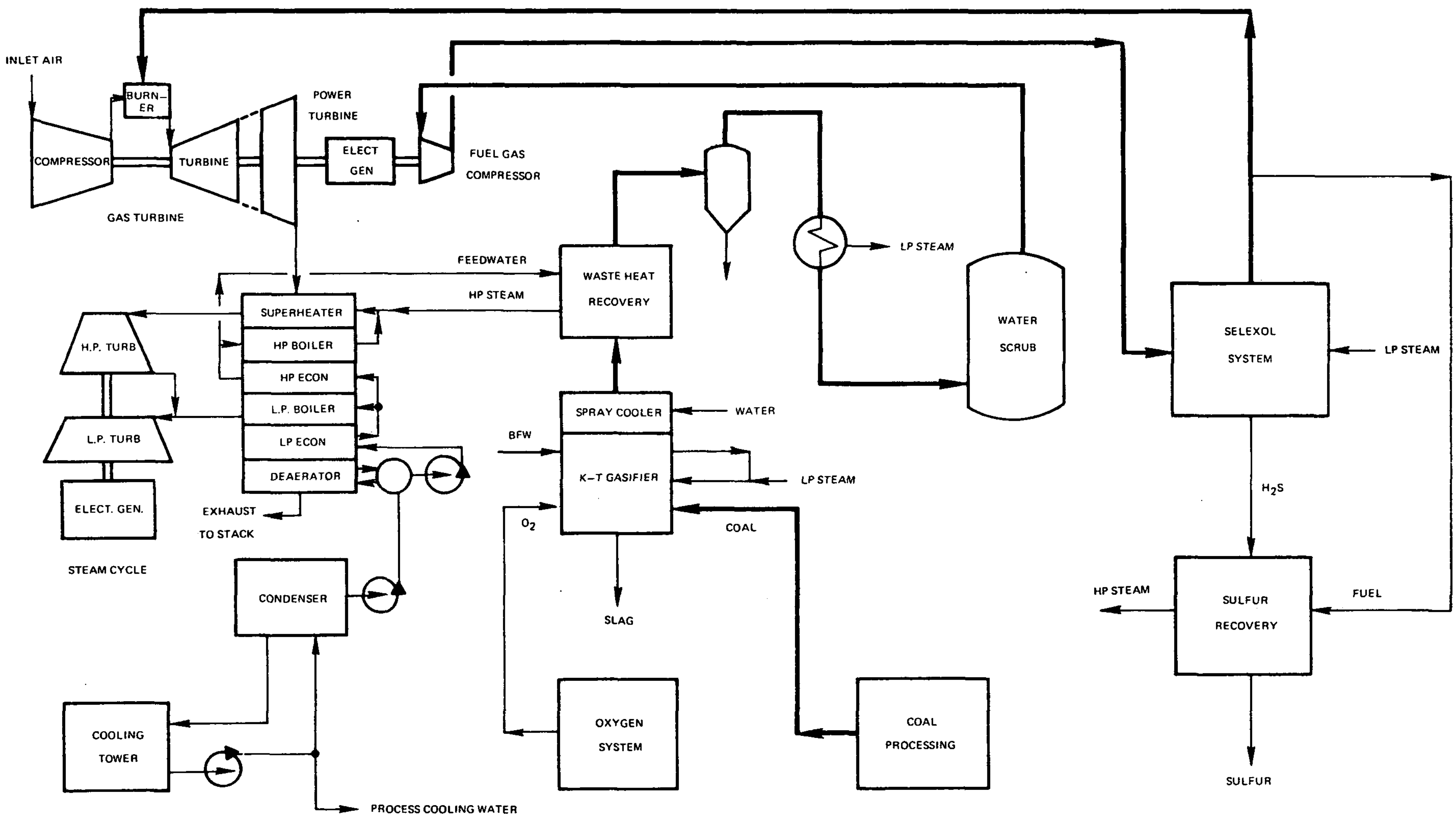

FIG. 27

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In order to identify the factors that are responsible for the poor performance of the integrated system, the K-T/Selexol was compared with the BuMines/Selexol system which has the same pressure ratio and turbine inlet temperature. Also, both have about the same clean fuel temperature. The parameters of interest are shown in Table 44. To facilitate comparison, the K-T/Selexol values have been scaled to a fuel input that is equivalent to the BuMines system. Thus, the comparison is made between the first and third columns of the table.

It can be seen that there is nearly a 10 percent difference between the cold gas efficiencies. However, this is more than made up for by the net heat recovered which is the difference between the high temperature heat recovered from the process and the sensible heat required to raise steam and heat air for the gasifier. Because this sensible heat can be used only at steam cycle efficiency, its value is approximately 60 percent of an equivalent fuel energy. This relationship has been shown in Table 46 of Ref. 1. Thus, if the clean fuel energy for each system is adjusted by adding 60 percent of the net sensible heat recovered, the K-T system shows a total fuel energy available to the power system of 6652 MMBtu/hr as opposed to 6494 MMBtu/hr or 2.5 percent more than the BuMines system for an equivalent coal input.

With a slightly higher energy input to the power system, it would be expected that power system output would be commensurately higher and the differences in system output would be the result of power requirements for fuel gas compression and for the oxygen plant. However, the difference in power requirements is only 30 MW compared to an overall plant output difference of 55 MW. The remainder of the difference lies in the energy that is recovered in the expansion of the fuel gas in the gas turbine. At the fuel delivery temperature, approximately .67 kW/mol of gas can be obtained by expanding through the engine pressure ratio. The differential of 70,000 mol/hr can therefore be equated to more than 40 MW and the combination of low fuel flow rate and higher utility power consumption can be shown to account for the difference in output between the two systems.

In other systems, thermal regeneration of the product gas has been shown to be very desirable. In the case of the K-T gasifier, the low flow rate of product gas minimizes the benefits of regeneration. A comparison was made and showed that regeneration to 1000 F could change efficiency from 0.301 to 0.307. Consider the changes that this would necessitate in the basic K-T design, it was judged not to be desirable.

Table 44

PERFORMANCE COMPARISON K-T/SELEXOL AND BUMINES/SELEXOL

	BuMines/Selexol	K-T/Selexol	K-T Selexol Scaled To BuMines Coal Energy Input
Coal Input-MMBtu/hr (HHV)	8,015	9,544	8,015
Clean Fuel Energy - MMBtu/hr (HHV)	6,662	7,283	6,116
High Temperature Heat Recovered - MMBtu	328	1,342	1,127
Sensible Heat to Gasifier - MMBtu	608	266	233
Net Heat Recovered	-280	1,076	894
Air or Gas to Compressor - Mol/hr	73,091	70,169	58,927
Fuel to Burner -Mol/hr	124,201	64,280	53,982
G.T. Bleed Air Power - Mw	102		
Boost Compressor Power - Mw	34		
Fuel Gas Compressor Power - Mw		99.5	83.6
Oxygen Plant Power - Mw		99.2	83.3
Total Auxiliary Power - Mw	136	198.7	166.9
Net Plant Output - Mw	761.1	841.3	706.5

Based on the foregoing analysis of this system, it is apparent that the K-T gasifier is not well suited for integration with a combined gas and steam turbine type power plant. While the lack of ammonia and other troublesome constituents in the product gas makes the K-T system very desirable from an emissions viewpoint, it appears to be better suited for use with other, low pressure power systems. Consideration of such systems was outside the scope of this study and was not pursued.

Oil Gasifier/Selexol Cleanup System Performance

A schematic of the integrated system is shown in Fig. 28. It is quite similar to the BCR/Selexol except that ammonia removal is not required; however, a means of recovering soot and returning it to the gasifier must be included. Because of the high temperature out of the gasifier, a large amount of high temperature heat is available. By doing all the feedwater heating in the gas turbine exhaust heat recovery boiler and using the gasifier system heat only for evaporation, it is possible to achieve a 300 F stack temperature while having a single pressure steam system. The resultant performance is given in Table 40 for both first and second generation power systems. As previously noted, for all systems considered the steam cycle was simply a nonreheat 1250 psi single pressure cycle or, where necessary to reduce stack temperature, a second low-pressure section was included. For the partial oxidation oil gasifier operating with a second-generation power system it would be possible to use a reheat steam cycle. A performance improvement of 8 percent or 3 points could be expected with such a change.

One of the reasons for investigating the gasification of residual oil is that the process lends itself to modeling. Because of the high operating temperature, equilibrium calculations give results that closely agree with published operating data. The effect of varying air to oil and steam to oil ratios thus can be examined.

The equilibrium model used was developed at UTRC and is described in Ref. 30 and Appendix A. Typical feed ratios for commercial residual fuel oil gasifiers would be between 0.0 and 0.2 for steam/oil and 6.0 to 6.5 for air/oil ratios. The minimum air/oil ratio that would provide 1 atom of oxygen per atom of carbon is approximately 5.0. In practice it is necessary to increase that ratio to increase raction temperature and obtain a reasonable reactor size. As would be expected, volumetric heating value drops sharply with increased air/oil ratios. Since gas turbine and combined-cycle performance are directly related to fuel heating value, air/oil ratio is of particular interest in the system analysis. Because the heating value is on a volumetric basis, it will

OIL/SELEXOL/ INTERGRATED POWER SYSTEM

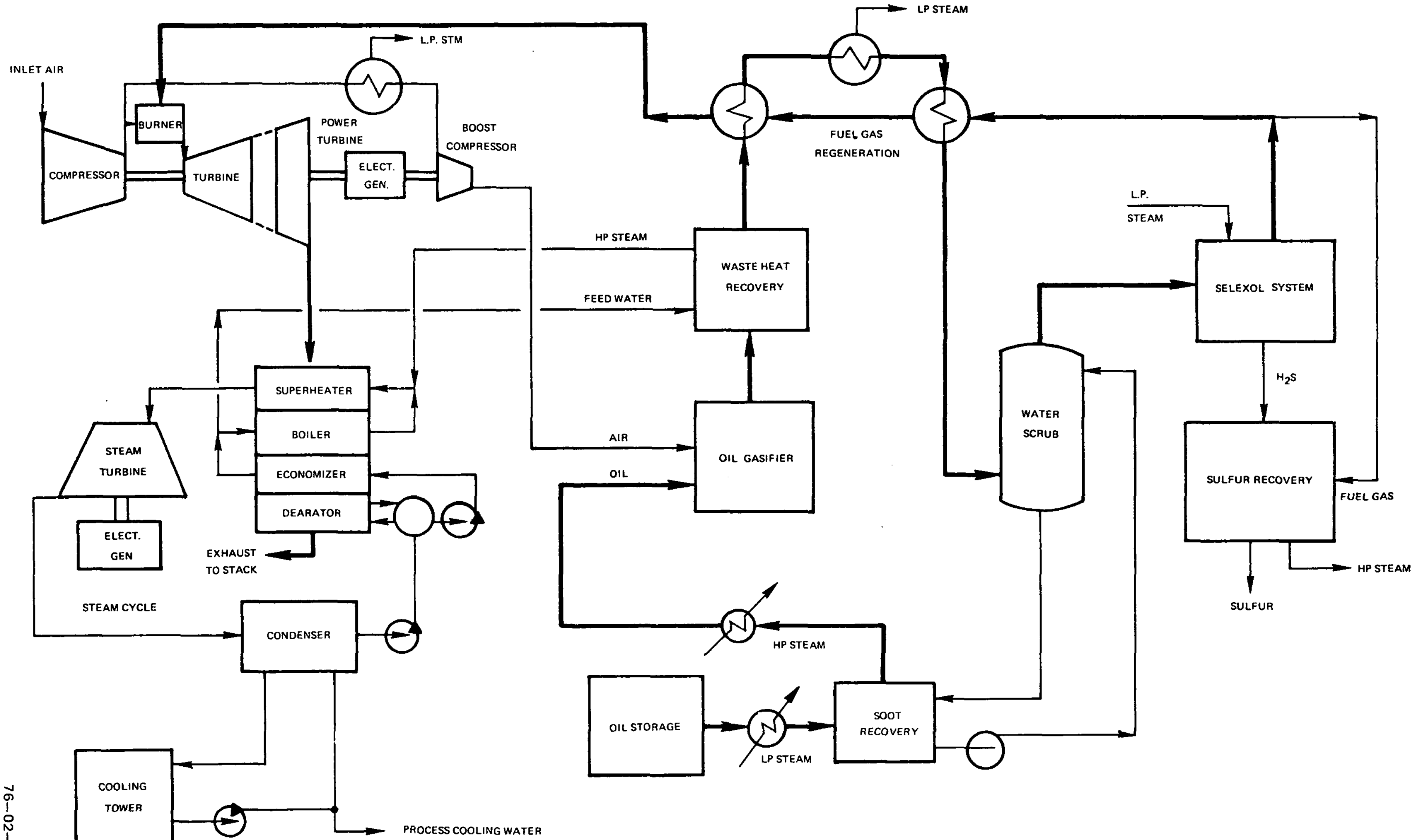

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FIG. 28

increase as water vapor, sulfur compounds and carbon dioxide are removed. The relation between input and output heating value is shown in Fig. 29, which presents the chemical heating value of the product gas in terms of Btu per pound of oil consumed. This amount of energy can be used in both the gas turbine and steam cycle. The remainder of the initial oil heating value leaves the gasifier as sensible heat and when mated with a low temperature cleanup system can only be used in the steam cycle.

The change in volumetric heating value of the fuel gas is very small over the range of operational steam/oil ratios. When viewed in terms of chemical heating value per pound of oil consumed, the output of the gasifier is constant over the range of steam/oil ratios considered and Fig. 29 therefore applies to a gasifier run both with and without steam addition. The effects of steam addition on composition are shown in Table 45 to be an increase in hydrogen and carbon dioxide production coupled with a decrease in CO. Since each additional molecule of hydrogen brings with it an oxygen atom which will react with one CO molecule, there is a one for one correspondence in the increase of hydrogen and decrease of CO. Because the higher heating value of each molecule is almost the same, the above results are to be expected. Further examination of the product gas shows that about 25 percent of the input steam shows up as hydrogen and the remainder leaves as water vapor in the product gas. Thus, the net effect of steam addition on the product gas is minimal and the heat needed to raise the steam is mostly lost since the latent heat cannot practically be recovered from the water vapor in the fuel gas. The primary function of steam in oil gasification is to control reactor temperature and its use will depend on gasifier and heat recovery equipment design. While the presence of steam in the fuel gas does increase gas turbine output power due to its mass, the incremental heat rate is on the order of 15,000 Btu/kWhr making the use of steam undesirable from the power system viewpoint.

The equilibrium gasifier model was used along with a simplified model of the Selexol cleanup system and Claus plant sulfur recovery performance. Using that model, the result of variations in air/oil ratio are shown in Fig. 30. Quite clearly, the power system benefits from lowered air/fuel ratios. In practice, as the air/oil ratio is desreased below 6.0, a number of factors including imperfect mixing, residence time and low temperature (slower reaction rate) combine to cause nonequilibrium conditions at the gasifier outlet. This in turn will have a significant effect which will tend to reduce overall efficiency from the predicted values. However, operation in this area is certainly desirable and the improved performance may be worth pursuing.

RAW FUEL GAS CHEMICAL HEATING VALUE

BTU/LB RESIDUAL OIL CONSUMED

(NO CREDIT FOR SULFUR COMPOUNDS)

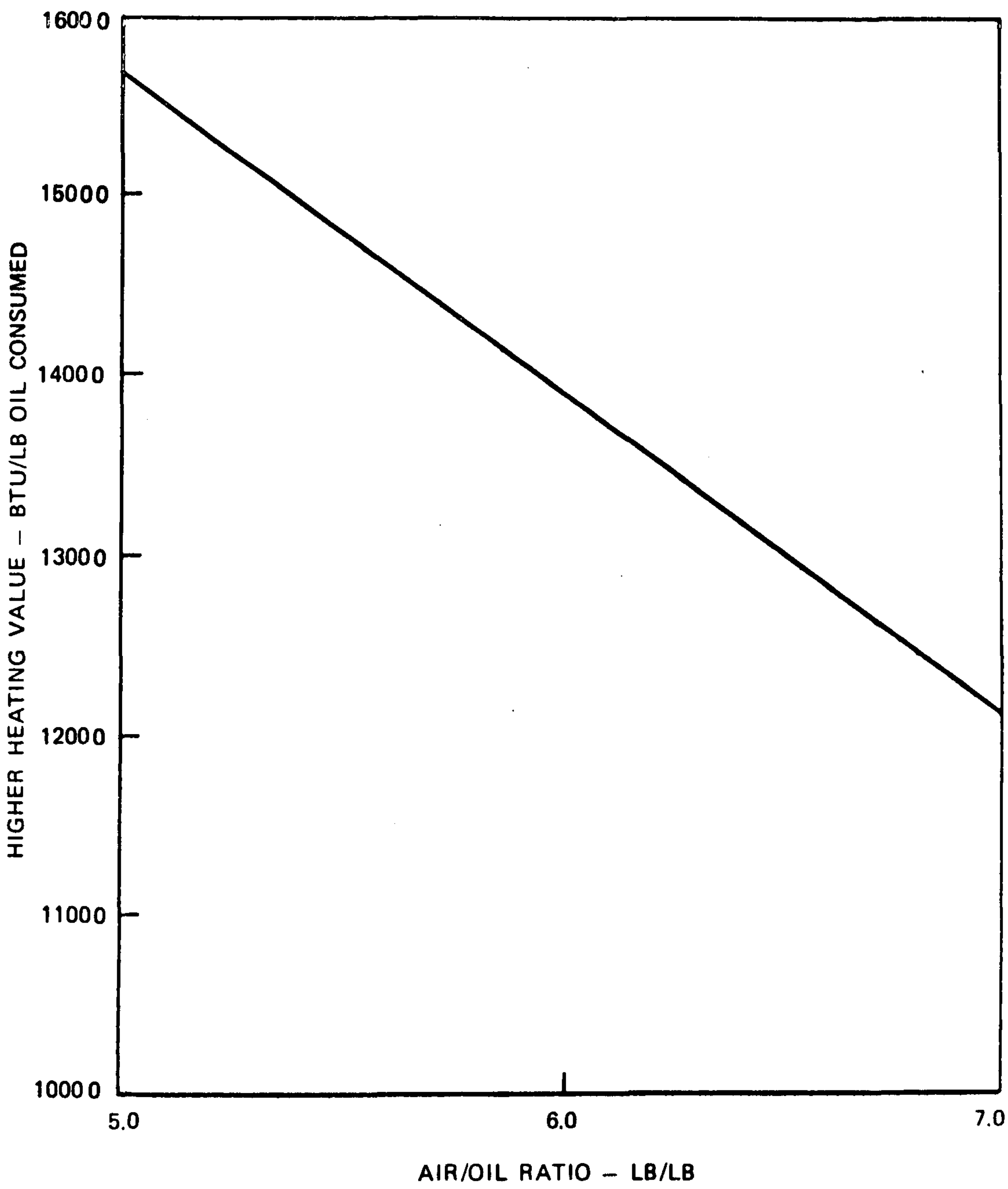

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Table 45

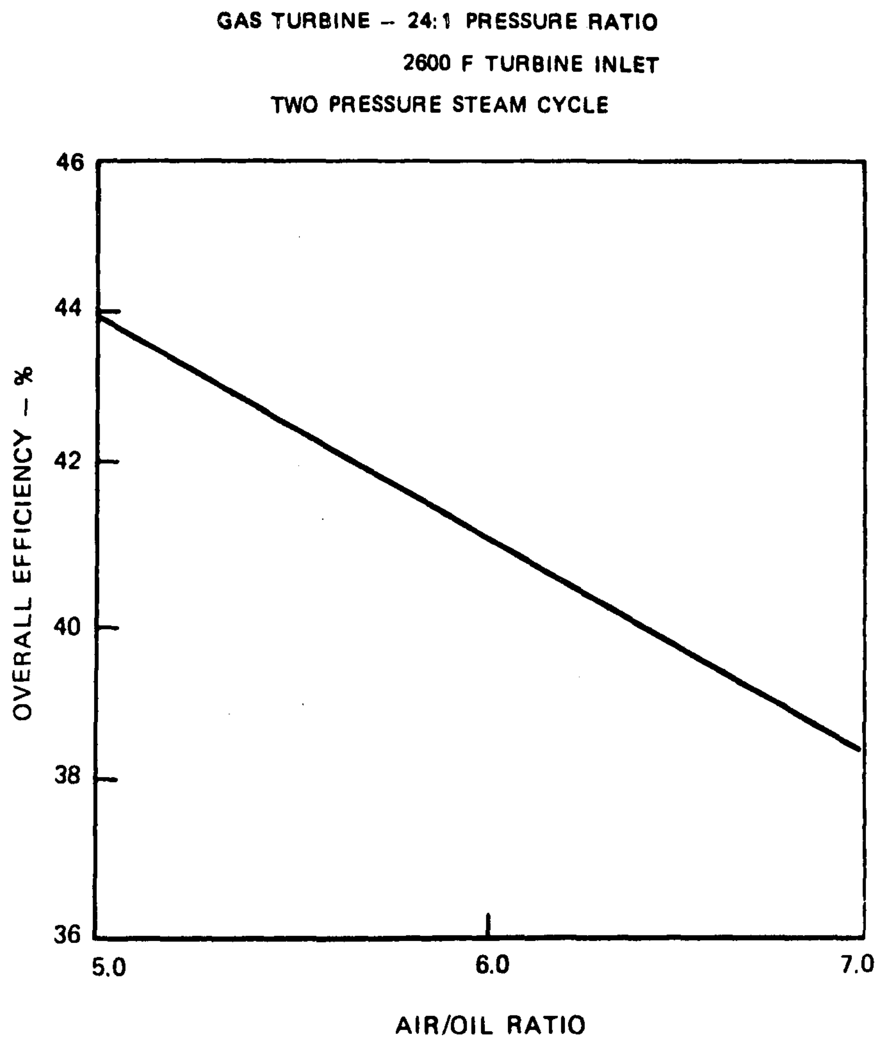
EFFECT OF STEAM ADDITION ON FUEL GAS CHEMICAL HEATING VALUE

Fuel - Venezuelan Residual Oil

Air/Oil Ratio = 6.0

	Steam/Oil Ratio		
Fuel Gas Characteristics	0.	0.2	0.4
Mole Fraction H_2	.1469	.1514	.1548
Mole Fraction H_2O	.0335	.0612	.0858
Mole Fraction CO	.2335	.215	.1985
Mole Fraction CO_2	.0154	.0248	.0328
H_2 SCF/lb Oil	16.66	17.83	18.91
CO SCF/lb Oil	26.49	25.32	24.24
HHV Btu/SCF	122.9	118.4	114.2
Gas Produced SCF/lb Oil	113.43	117.78	122.13
Output Gas HHV - Btu/lb Oil	13940	13945	13947

RESIDUAL OIL GASIFIER /SELEXOL CLEANUP
PERFORMANCE EFFECT OF AIR/OIL RATIO



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The above exercise tends to reinforce the view that for use with combined cycle power generation, gasifier steam input should be minimized since this will generally result in minimum air use as well. From a power system standpoint, minimum steam requirements would be those necessary to produce a hydrogen content sufficient to maintain proper combustion.

Oil Gasifier/CONOCO Cleanup System Performance

This combination of gasifier and cleanup system represents a very good match in that there is little ammonia in the raw fuel gas and the low partial pressure of water vapor and carbon dioxide result in a very favorable equilibrium concentration of H_2S in the cleanup system. A schematic of the integrated system is shown in Fig. 31 and the resultant performance is presented in Table 40. Only the second generation power system was considered and the resultant performance is the best of all systems investigated.

The use of a reheat steam cycle was also investigated for this system. It was found that a 900/900 F system could be used with the 24:1/2600 F gas turbine. The resulting performance estimate showed the efficiency to be 47 percent.

BuMines/Selexol Performance

There are several methods that offer the potential for improving the performance of the BuMines/Selexol system. Some of these, such as a reduction in the steam to coal ratio are beyond the scope of this study. However, some improvement in performance can be made by a slight restructuring of the cleanup system as shown previously in Section 3, Fig. 18. The revised system is shown in Fig. 32 and the performance summarized in Table 40.

Several means of improvement were considered; resaturation of the fuel gas, reduced stack gas temperature and fuel gas regeneration. Each of these is discussed in the following paragraphs but only resaturation was incorporated into the system.

The addition of water vapor to the fuel gas stream increases the mass flow rate of the fuel gas and decreases the amount of excess air needed to produce the desired turbine inlet temperature. Thermodynamically, since the specific heat of water vapor is about twice that of air, one pound of water vapor decreases the necessary air flow by two pounds. This results in lower compressor power while the power extracted in the turbine remains essentially constant. Since the temperature required

OIL/CONOCO/INTERGRATED POWER SYSTEM

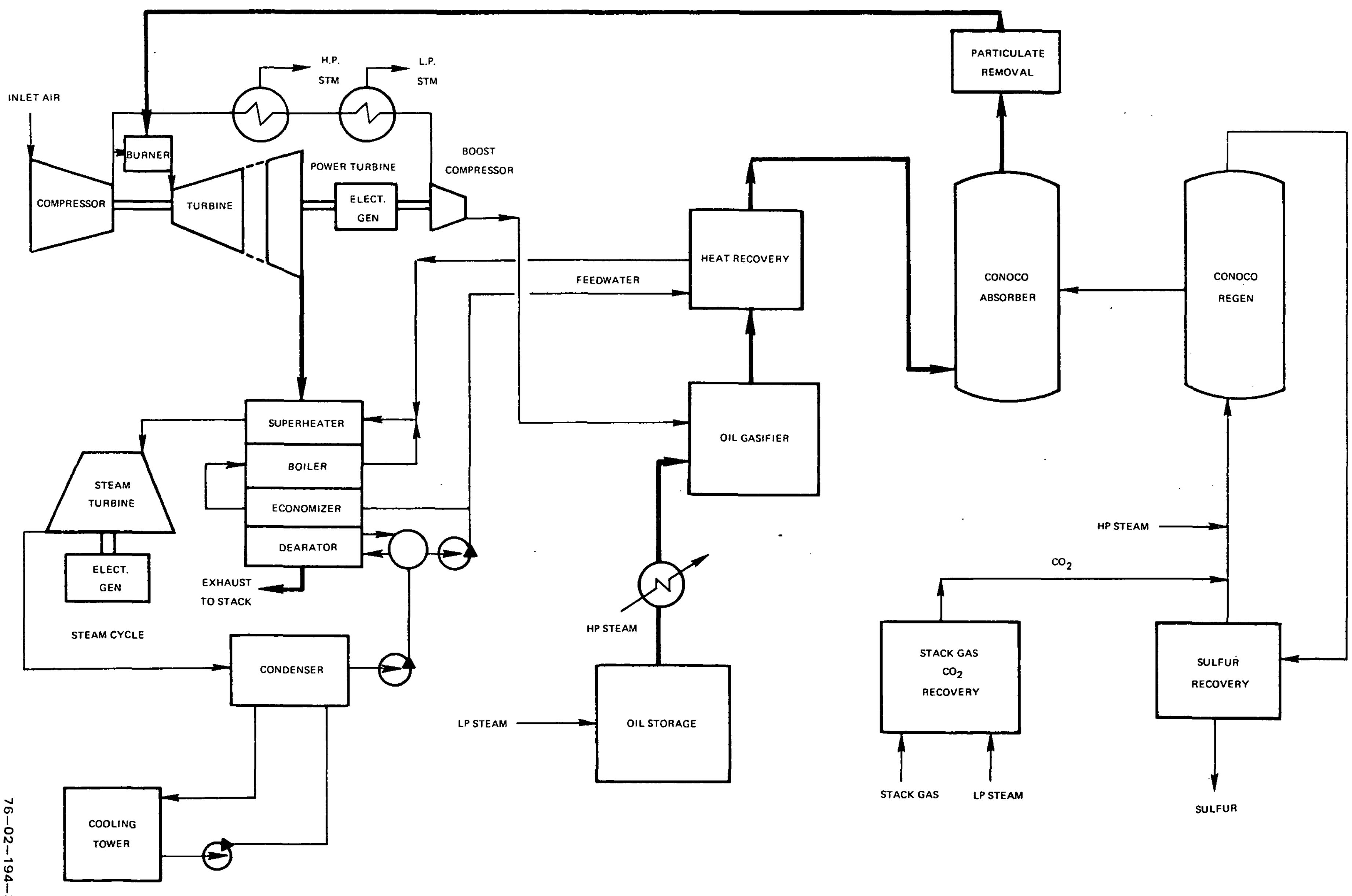

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FIG. 31

REVISED BUMINES/SELEXOL SYSTEM

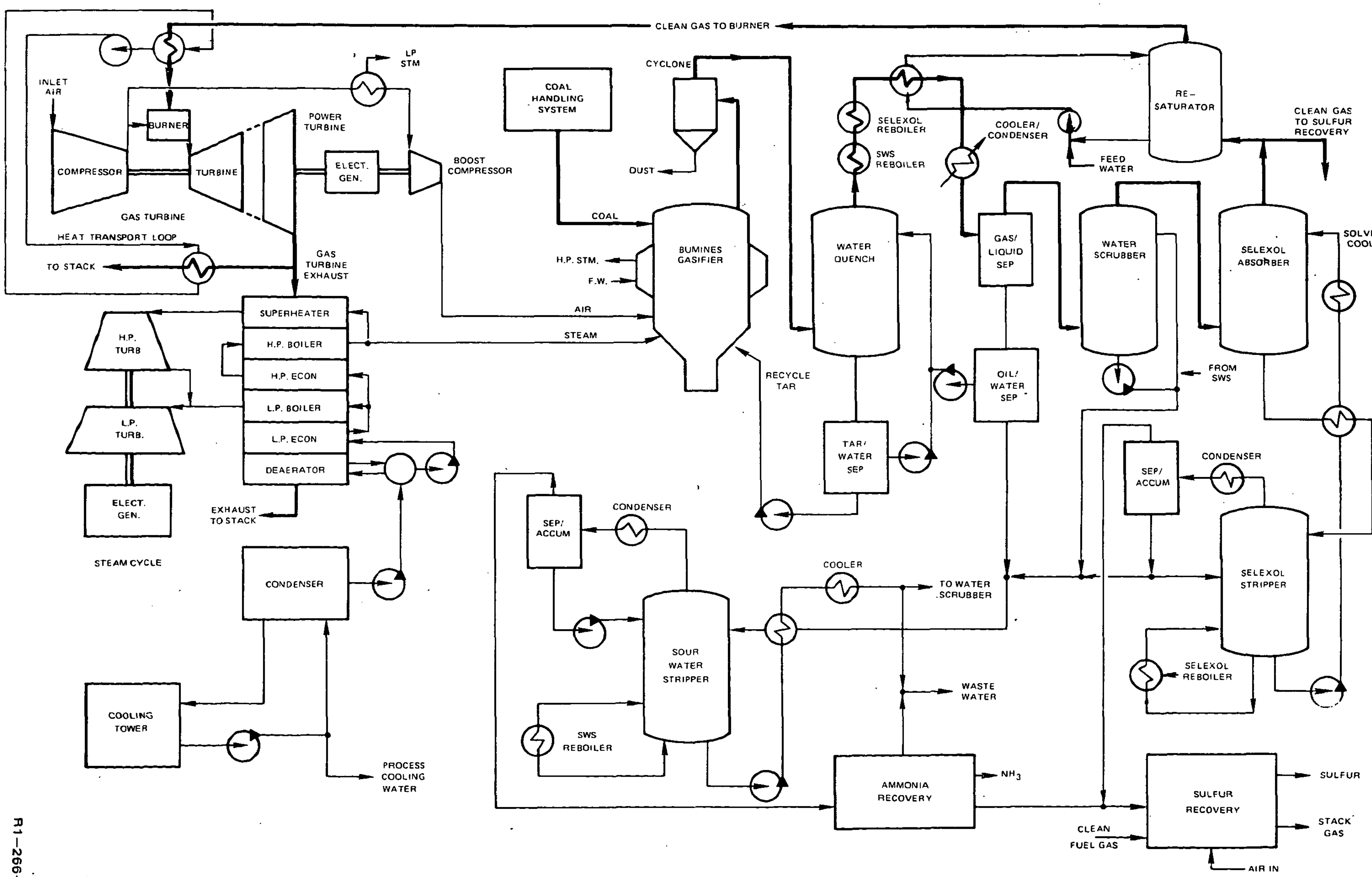

FIG. 32

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for saturation of the gas is generally quite low, it is a good means of utilizing low-temperature heat.

Drawbacks to the use of resaturation are the need for large quantities of makeup water and the reduced fuel gas heating value that could result in burner design problems at higher turbine inlet temperatures. Both the availability of water and the burner design represent potential problems in system application and were not considered further except to identify the rate of water usage associated with each alternative system.

The potential performance improvement to be achieved with the addition of water vapor to the fuel gas was estimated by varying the cleanup system output composition. The results are shown in Fig. 33. In determining performance, no penalty was associated with the addition of the vapor so the trends shown in that curve are the maximum that can be achieved, i.e., the need to provide heat to achieve the humidification will result in less performance improvements. In terms of water used per megawatt of power, the incremental power produced requires about 14,000 lb/hr for each additional megawatt of electrical power. This is nearly constant over the range considered (up to .28 mol fraction of water). Since total pressure just downstream of the cleanup system will be about 270 psia, a 300 F dew point will produce a water vapor mol fraction of .248. It is likely that resaturation to higher mol fractions will produce limited gains since they will require the use of heat at a temperature in excess of 300 F. At that temperature each pound of water needs about 1090 Btu to produce vapor from feedwater at 120 F. The resultant incremental heat rate is therefore about 15,250 Btu/kWhr which is quite undesirable for use with anything other than waste heat. Possible sources of heat are the gasifier outlet stream and the main boiler stack gas. Following the quench and removal of tars from the gasifier outlet stream, the latent heat of water vapor in the saturated gas stream greatly increases its heat capacity. In order to use that heat in resaturating the clean gas, a heat exchanger and saturator connected by a water heat transport loop were added to the basic system schematic. The flow sheet including these components and the revised stream compositions have been presented in Section 3.

The resultant system uses the latent heat in the quenched gas stream to provide the necessary process heat for both the Selexol and sour water strippers. Using the quenched stream to supply that heat results in only an 18 F drop in the stream temperature. Maintaining a 50 F approach, the corresponding saturation temperature that can be achieved in the product gas is 252 F giving a water mol fraction of .114.

EFFECT OF WATER VAPOR IN FUEL GAS BUMINES–SELEXOL SYSTEM

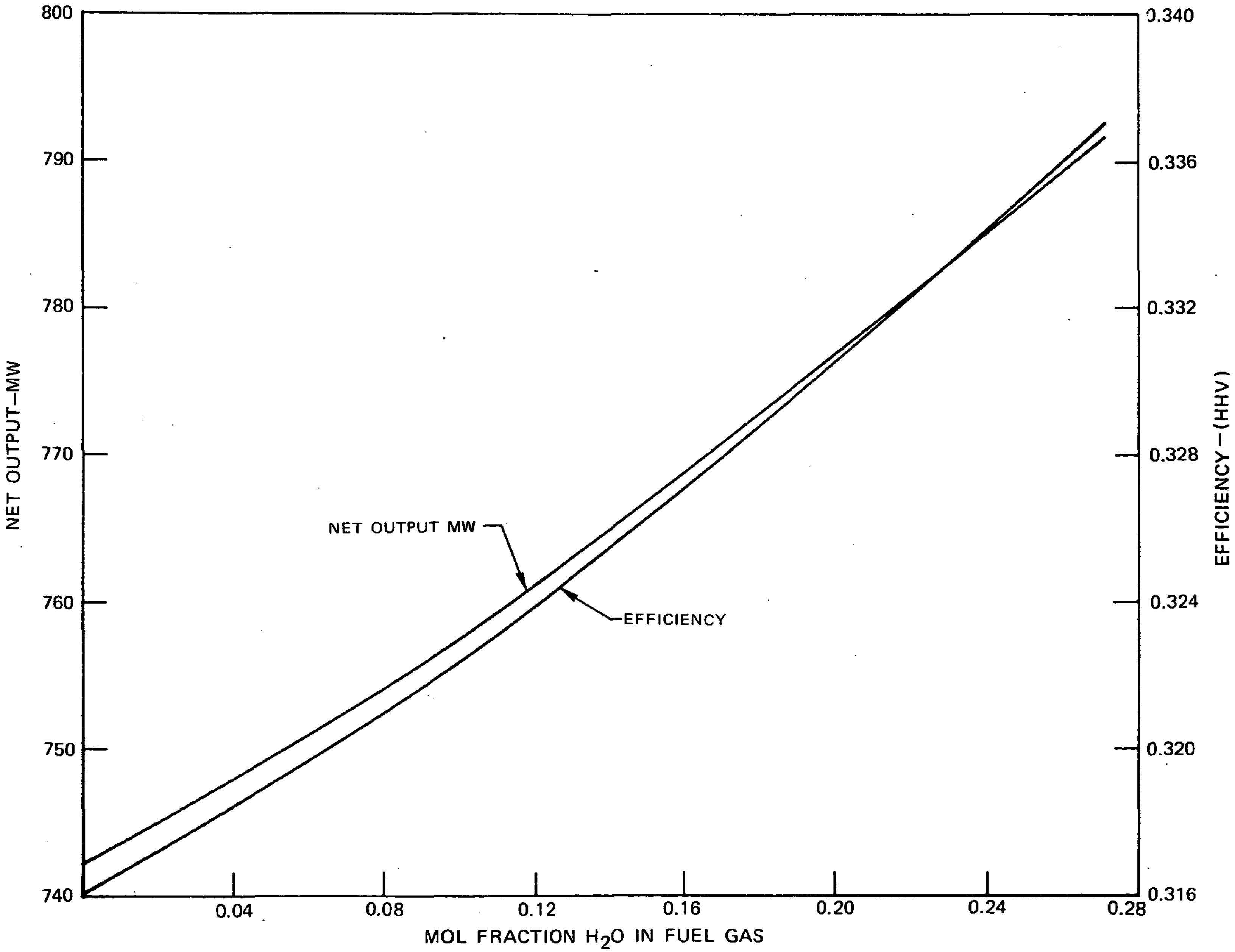

FIG. 33

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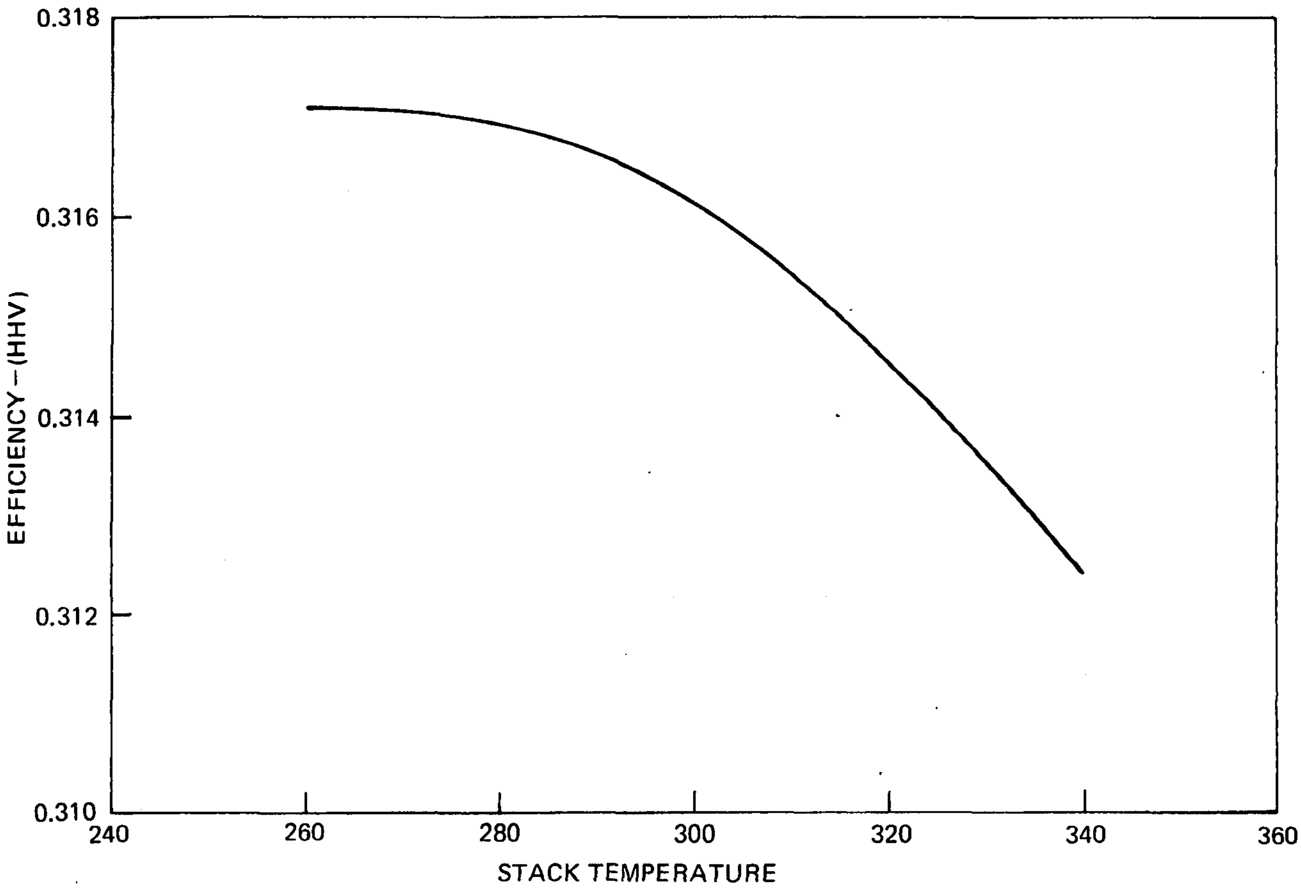
For the basic BuMines/Selexol configuration, the sensitivity of the system to stack gas temperature was evaluated. This is shown in Fig. 34 which gives overall efficiency as a function of stack temperature. The flattening effect at temperatures below 300 F is a characteristic of the combined-cycle system where there is no air preheater. The important part of the curve is the slope above 300 F which shows a decrease in efficiency of about 0.1 percent for each 10 F increase in stack temperature. At the conditions of interest, the 10 F increment in stack temperature is equivalent to about 44.5 MMBtu/hr. Comparing this to the benefits due to rehumidication shows that an additional megawatt output requires about 15.5 MMBtu/hr and produces an increment in efficiency of 0.04 percent. If the heat must be extracted from the stack gas this increment is reduced by about 75 percent making rehumidification under such conditions marginal at best. Again, for the basic BuMines/Selexol configuration the effect of fuel gas temperature was evaluated. This is shown in Fig. 35. It should be noted that this represents only the benefits from heating the fuel gas and does not account for the source of the heat. However, if the heat were taken from either the steam cycle or stack gas it would be returned for use there with only the turbine work extracted.

In order to derive a significant performance improvement from regeneration of the fuel gas against the turbine exhaust, it is necessary to use only a fraction of the exhaust stream for regeneration. The remainder of the exhaust stream is then used to raise steam at the highest possible temperature. If the heat for regeneration were taken from the full exhaust stream, not only would that amount of heat be removed from the steam cycle, but the remainder would be available at a lower temperature. Both approaches were evaluated and the resulting performance improvement was approximately 1 percent with regeneration against the full exhaust stream, while against a bleed stream it was 3 percent or just over one point. However, the heat transport equipment necessary to isolate the exhaust gas from the fuel stream was judged to be an excessive price to pay for the performance improvement.

BuMines/Iron Oxide System Performance

The excessive utilities required by the combination of iron oxide absorbent and Claus plant for the production of elemental sulfur from SO_2 produced during regeneration of the iron oxide are the focal point in an attempt to improve performance of this system. Previous performance estimates had shown a significant amount of oxygen in the off gas during regeneration, and a low (about 5 percent) concentration of SO_2. More recent data[24] show the concentration of SO_2 in the off gas to be

EFFECT OF STACK TEMPERATURE ON BUMINES/SELEXOL PERFORMANCE



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EFFECT OF DRY FUEL GAS TEMPERATURE BUMINES / SELEXOLSYSTEM

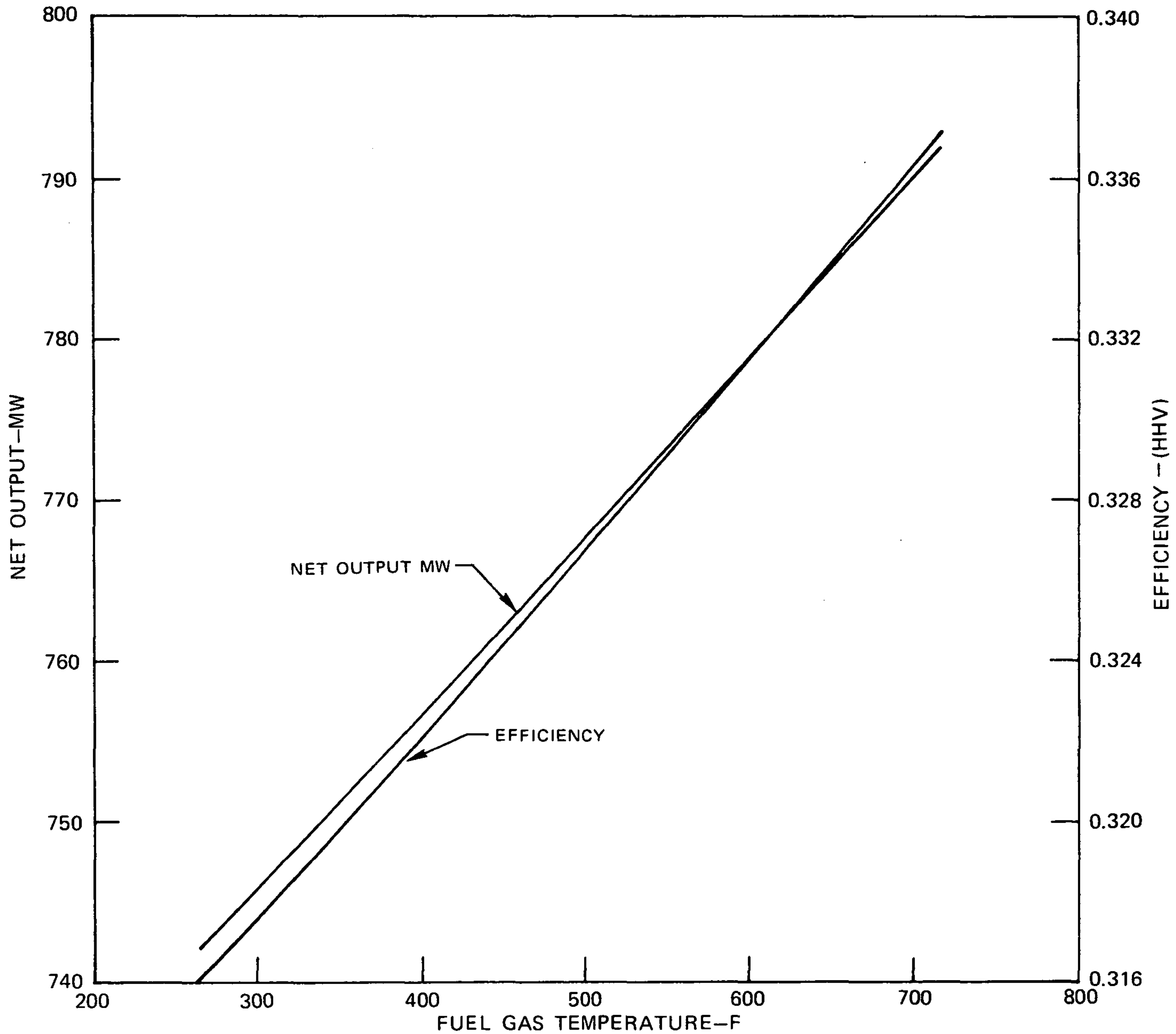

FIG.35

R05—122—4

about 12 percent and to rise sharply to that value on initiation of regeneration and to fall sharply when regeneration is completed.

Based on the air flow to the bed during regeneration, an SO_2 concentration of 15 percent would be expected in the off gas. The difference has been attributed to oxidation of carbon carried into the bed during absorption. System performance was revised using the following assumptions.

1. SO_2 concentration is 12 percent
2. No elemental sulfur out of bed
3. Initial composition is $FeS_{1.5}$
4. Regeneration produces all Fe_2O_3
5. All oxygen is consumed by the sorbent or by oxidation of carbon
6. Regeneration is stopped prior to breakthrough of the reaction front

The higher SO_2 concentration makes possible the use of various alternatives to the SO_2 concentrator and Claus system previously used. Those regenerator off-gas process modifications have already been discussed and the performance results presented in Section 3. With the choice of the revised Claus system without the SO_2 concentrator (Fig. 17 in Section 3) the integrated system using the modified process as shown in Fig. 36 has an overall efficiency of 35.1 percent, an increase of 10 percent from the base case.(1)

BCR/Selexol/Catalysis Performance

In an effort to improve the performance of the Selexol plant integrated with the BCR gasifier, catalytic conversion of COS to H_2S upstream of the Selexol unit was used (See Fig. 18 Section 3). It was found that a commercial cobalt molybdenum catalyst can potentially reduce COS in the fuel gas to H_2S at 650 F, with an efficiency of 90 percent or greater. Once the COS is converted to H_2S the Selexol solvent circulation rate and utilities load decreases significantly. The fuel requirement in the Claus plant is also significantly reduced. The reduction in major utilities are:

Selexol Plant:	Steam	64%
	Power	59%
Claus Plant:	Fuel	36%

BUMINES/SINTERED IRON OXIDE SYSTEM

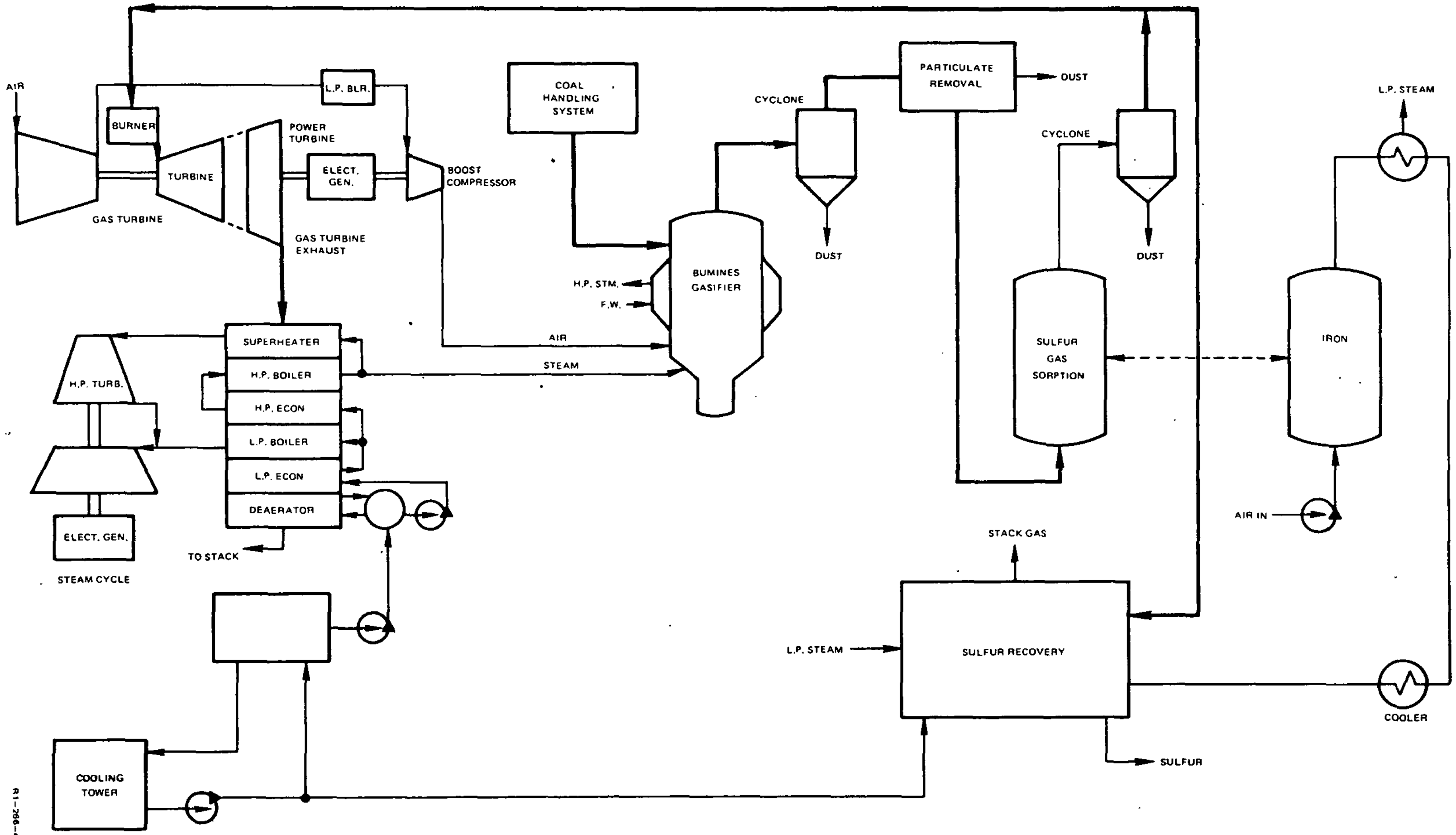

FIG.36

The reduction in auxiliary power is approximately 20 MW. The net effect of the other changes increase both gas turbine output (up by 3 MW) and steam cycle output (up by 27 MW). The improvement in steam cycle output results from both an increase in heat available to raise steam and a slight improvement in steam cycle performance made possible by an increase in the ratio of high to low pressure steam raised in the two-pressure boiler. This, along with the reduced auxiliary power, produces an increase in net plant output of 54.1 MW and a resultant efficiency of 38.6 percent. This is an increase of better than 6 percent over the previous BCR/Selexol system. Figure 37 shows the revised power system.

BCR/CONOCO/Water Scrub Performance

A revised configuration incorporating a water scrub for ammonia and particulate removal was prepared for the BCR/CONOCO coal gasification system. (The flow sheet has been presented previously as Fig. 19 in Section 3.) The overall system configuration is shown in Fig. 38. Gas from the dolomite absorber is passed through a boiler to drop its temperature to the level desired at the inlet of a regenerative heat exchanger. An aftercooler is required to further reduce temperature to 120 F for the water scrub and particulate removal process. Resaturation of the fuel gas is also incorporated into that block. The gas is then reheated in the cold side of the regenerator prior to being sent to the burner.

Inherent in the addition of the water scrub is the need for process steam in both the sour water stripper and ammonia recovery unit. Also, the regenerator temperature and effectiveness will have an effect on system performance. The resultant reduction in fuel gas mass flow rate due to removal of both ammonia and water vapor also affects performance. Table 46 presents the performance effects of increased process steam requirements and reduction in fuel mass flow rate due to absorption of ammonia and other constituents and condensation of water vapor. Clearly, the loss of water vapor has the most significant effect. Because of the relatively inexpensive equipment involved and the availability of low temperature waste heat, it was concluded that resaturation would be desirable. For a system with full resaturation, the effect of regenerator effectiveness and operating temperature are shown in Figs. 39 and 40, respectively. To limit the reduction in performance due to regenerator effectiveness, a value of 0.8 was selected for the design. This produces an approach or minimum temperature difference consistent with the values used in the study of the economics of regeneration.[1] Regenerator temperature also has a large effect on performance and while materials are available to withstand temperatures in excess of 1600 F, the practical

BCR/SELEXOL POWER SYSTEM

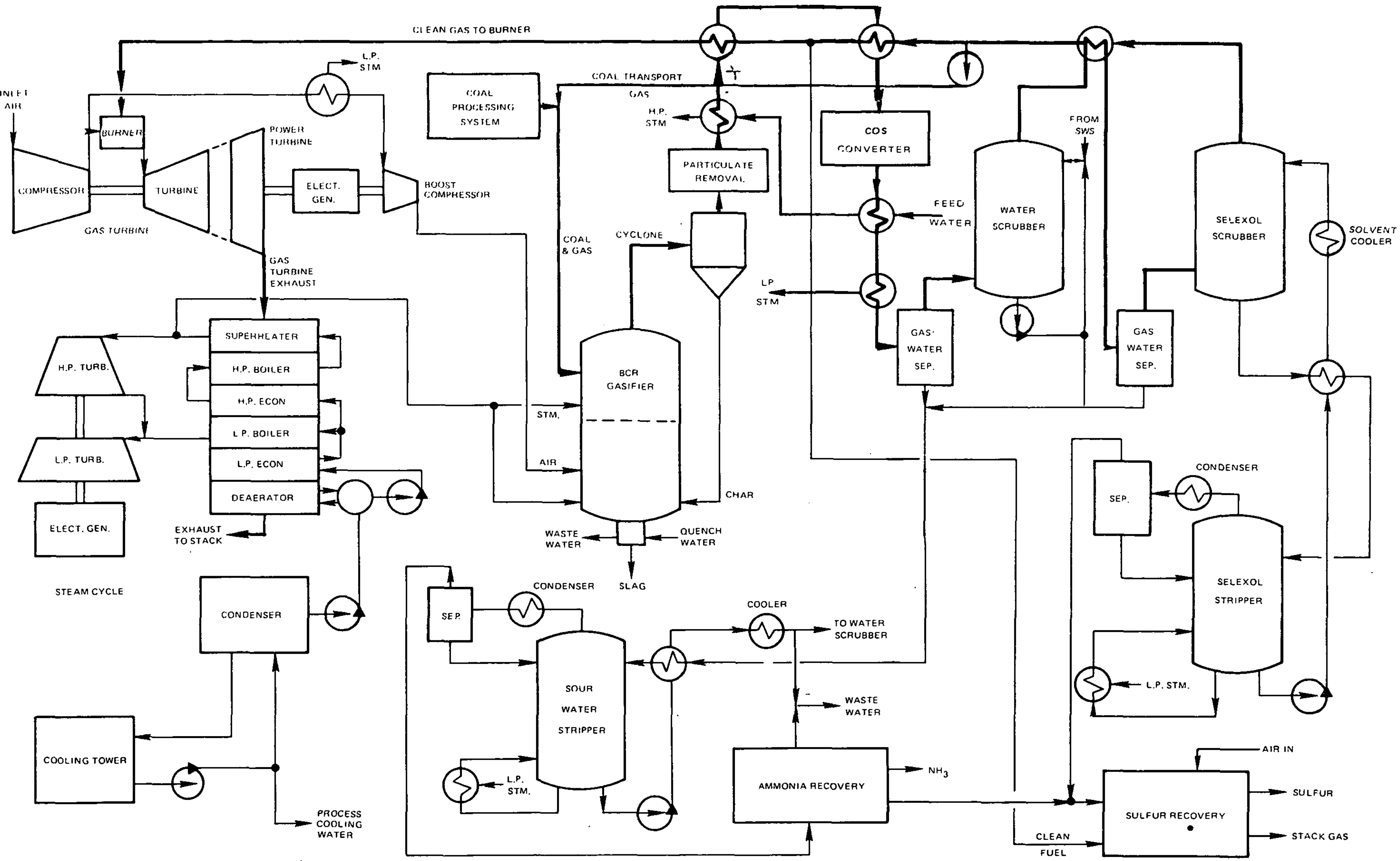

FIG. 37

REVISED BCR/CONOCO SYSTEM

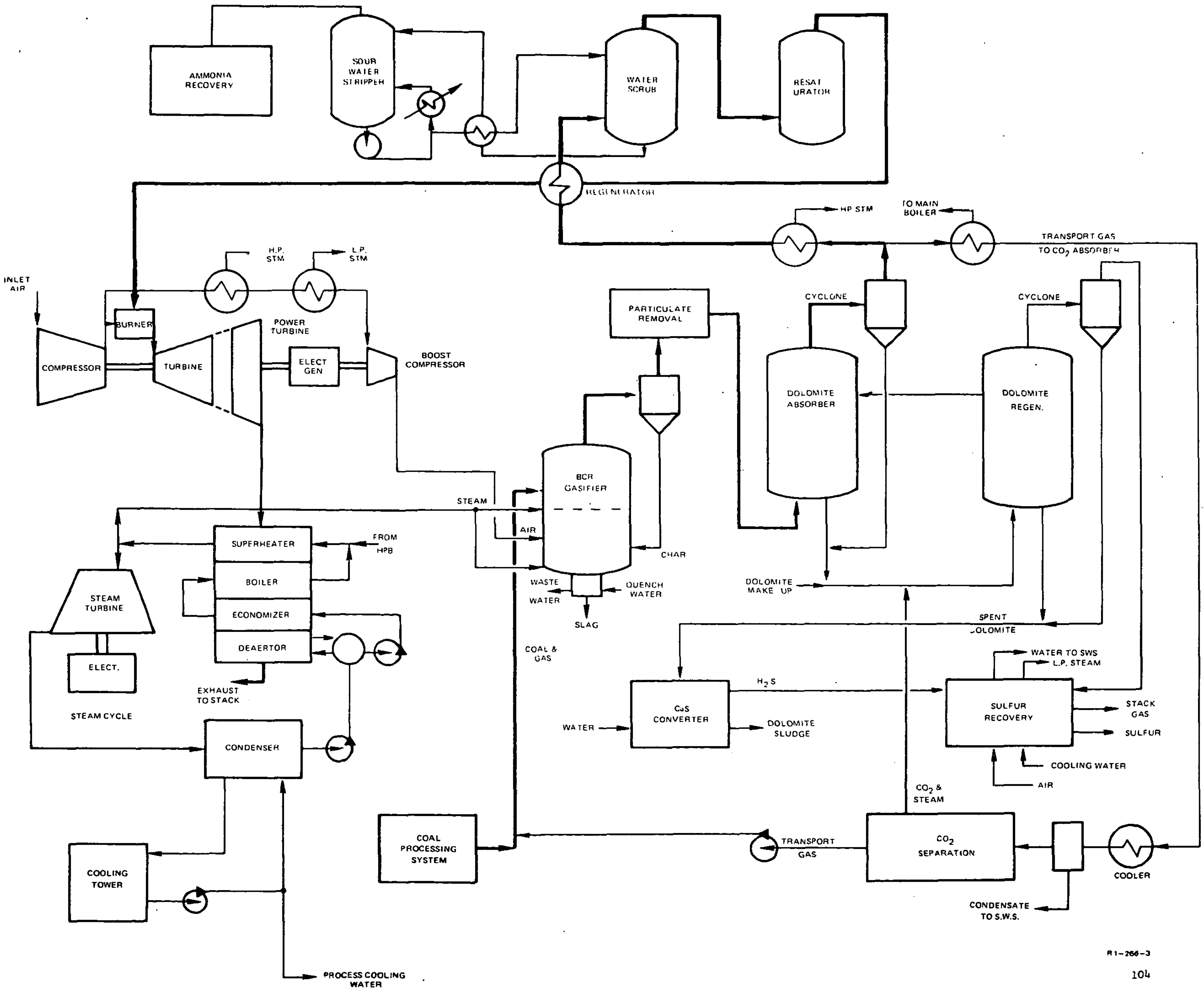

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FIG. 38

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Table 46

BCR/CONOCO—PERFORMANCE EFFECTS OF WATER SCRUB

	Overall System Efficiency - %
Performance Without Water Scrub -	43.1
Effect of Increased Process Steam for Sour Water Stripping and Ammonia Recovery (No Mass Removal) -	42.4
Ideal Regeneration (1700 F Inlet with Effectiveness = 1.0) with Full Resaturation of Fuel Gas (T_{sat} = 281 F) (Absorbed Gas Removal Only) -	42.3
Ideal Regeneration with Resaturation of Fuel Gas to T_{sat} = 250 F -	41.6
Ideal Regeneration with No Resaturation of Fuel Gas -	40.7

NOTE: Base performance is slightly higher than shown in Table 39 due to accounting process. Numbers are mutually consistent in all other respects.

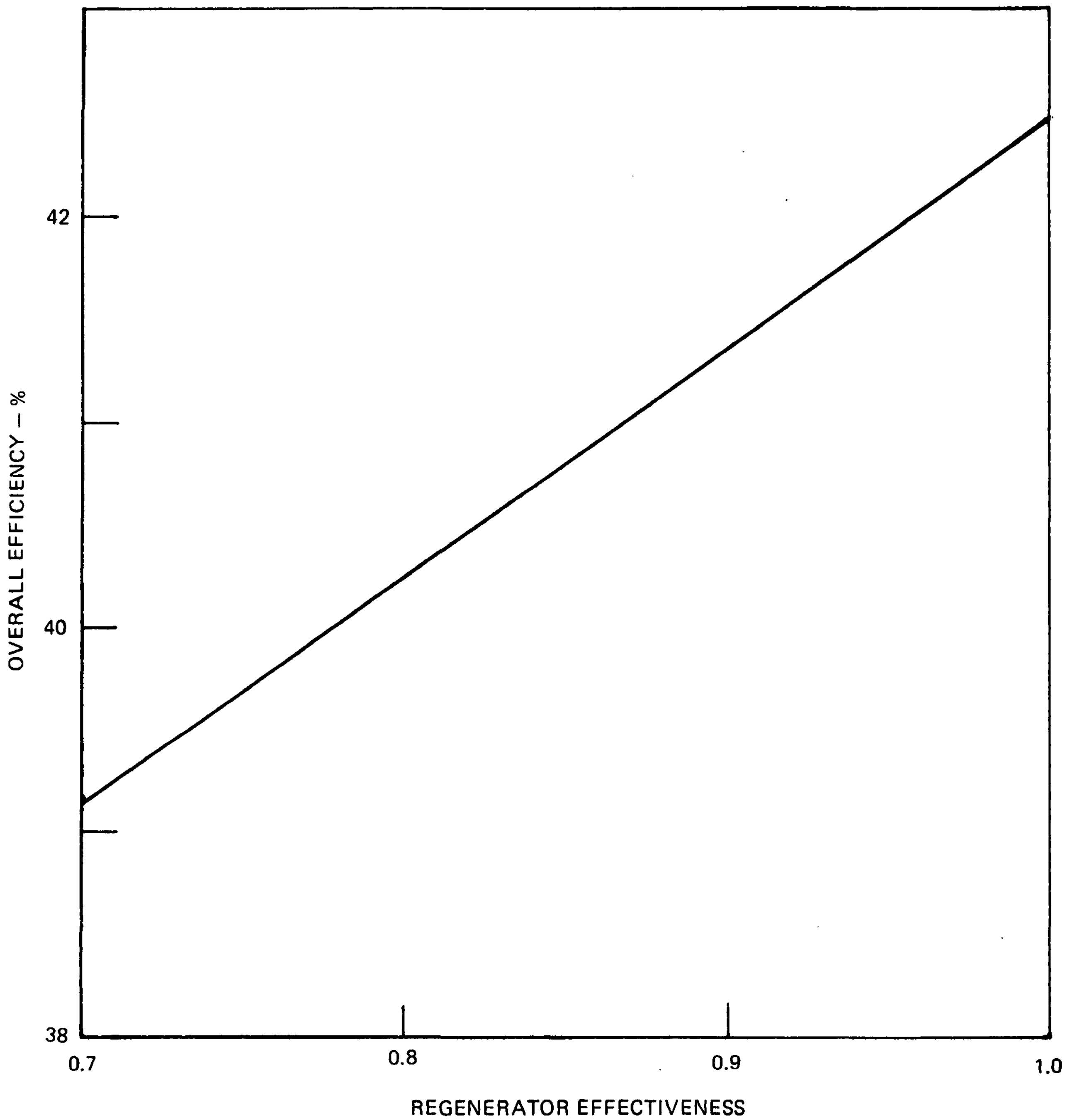
FIG. 39

BCR/CONOCO WITH WATER SCRUB

EFFECT OF REGENERATOR EFFECTIVENESS

(FULL RESATURATION OF FUEL GAS)

(1700F REGENERATOR INLET TEMP.)



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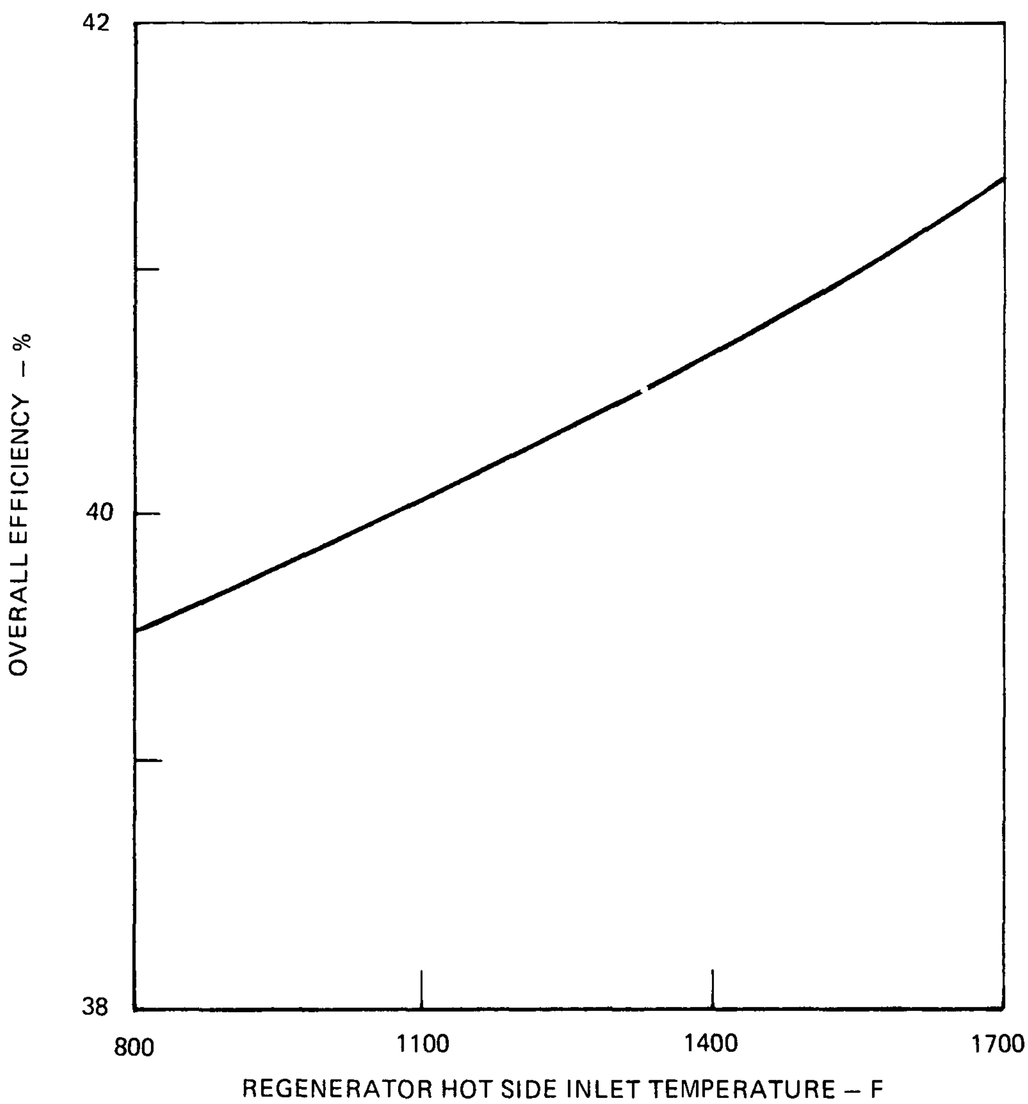
BCR/CONOCO WITH WATER SCRUB

EFFECT OF REGENERATOR INLET TEMPERATURE

(REGENERATOR EFFECTIVENESS = 0.9)

(FULL RESATURATION OF FUEL GAS)



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design and operational problems associated with thermal stress, operational life and cost make their use questionable. Therefore, alternate solutions to achieve better performance at more conventional temperatures were considered (1200 F hot side inlet with regeneration to 1000 F).

The high temperature heat available from the fuel gas as it is cooled from 1700 to 1200 F also could be used to improve steam cycle characteristics. In essence, it could provide almost all the heat used in vaporizing the steam while the exhaust gas is used for superheating and feedwater heating. As a result, a 300 F stack temperature could be achieved at increased feedwater supply temperatures. If regenerative (steam) feedwater heating to 250 F is used, steam cycle efficiency will improve by about 6 percent thereby increasing the utilization of the heat available to the steam cycle and increasing output by 6 percent. This would produce an increase of 0.8 points in overall cycle efficiency. Another, more costly alternative would be to use a reheat steam cycle to achieve even greater performance improvement. However, to allow a better comparison of the effects of the cleanup system revision and to be consistent with the other systems, the basic steam cycle operating parameters were not changed from those of the BCR/CONOCO system without water scrub.

SYSTEM COSTS

The following paragraphs discuss the costs of the various integrated systems considered to date. All costs are in mid-1975 dollars for a North Central location. Costs previously presented[1] have been escalated using recognized escalation procedures.[31,32,33] Capital charges of 17 percent/yr and a 0.7 load factor were assumed.

The costs of equipment are based upon values found in the literature, upon vendor quotes and upon Contractor-developed costing procedures. Of particular use in developing the costs for steam stations and for trends in equipment costs was the work done by United Engineers for the AEC.[34]

The cost of coal was assumed to be $.60/MMBtu at the mine mouth. While coal costs have risen dramatically in the past several years, it would appear that power plants in the North Central Region could obtain coal at or near this cost.[35] The cost of residual oil was assumed to be $2.00/MMBtu, a cost typical of high-sulfur residual in barge quantities.[36]

A summary of the gasifier and cleanup system capital costs is given in Table 47 and a summary of the power system costs is given in Table 48. In addition, the discussion of the various systems contains comparative cost summaries.

Cost of Hot Particulate Removal Systems

In the previous study, the cost of particulate removal from the gas stream was assumed to be relatively low, in the order of <$2/kW, based upon the cost of materials for high-temperature cyclones. Because of the immature state-of-the-art in this area, definitive costs are difficult. However, consideration of the need for coarse separation followed by several stages of fine filtration indicate that the cost of hot particulate removal could be quite high.

As part of a study of fluid-bed combustors carried on under Corporate sponsorship, a particulate removal system operating at conditions similar to those of interest, i.e., 1650 F, 250 psi was considered. This system contained cyclone, multiclone and granular filters and had installed costs in the range of $75 to $100/ACFM (actual cubic foot per minute) including high-temperature piping. Thus, for the system considered herein, total system costs were of the order of $20/kW rather than $2/kW. As will be seen in the following paragraphs, this has a significant effect on system costs.

Table 47

GASIFIER & CLEANUP SYSTEM CAPITAL COST BREAKDOWN

Millions of Mid-1975 Dollars

	BuMines/ Selexol	BuMines/ Iron Oxide	BCR/ Selexol	BCR/ Conoco	BCR/ CONOCO Water Scrub	P.O./ Selexol	P.O./ Conoco	K-T/ Selexol
Gasification	68.98	68.98	91.97	91.97	91.97	34.47	32.43	207.12 (1)
Gas Cooling	16.42	---	26.28	---	26.28	29.74	3.52	(2)
Hot Particulate Removal	---	16.80	---	24.1	---	---	26.00	----
Desulfurization	26.28	23.0	26.77	23.00	23.00	46.77	24.80	23.55
Sour Water Stripping	6.56	---	6.56	1.65	6.56	2.35	1.78	------
Ammonia Recovery	11.49	---	9.86	---	9.86	---	---	------
Sulfur Recovery	3.28	4.63	3.28	9.86	9.86	3.24	10.63	3.28
Waste Water Treatment	5.33	4.14	6.83	5.06	5.06	6.55	5.46	5.33
Boost Compressor & Boiler	11.98	11.90	12.21	13.02	13.02	16.40	17.98	33.90
Feedwater Treatment	7.85	6.76	10.99	10.99	10.99	---	---	6.76
Cooling Tower	1.22	---	2.01	.48	.48	3.68	1.15	1.07
Condensate Polishing	.07	.24	.28	.03	.03	---	---	.04
Other Expenses	3.19	2.53	4.06	3.12	3.94	2.86	2.47	5.62
Total Captial Cost (Includes Escalation & Interest)	162.65	138.98	201.10	183.28	201.05	146.06	126.23	286.67

NOTES:

(1) Includes $\$100.7 \times 10^6$ for oxygen plant.
(2) Included in gasification cost.

POWER SYSTEM CAPITAL COST SUMMARY

COSTS - $1,000

Gasifier/ Cleanup Combination	BuMines/ Selexol With Resat.	BuMines/ Iron Oxide	BCR/Selexol With COS Conv.	BCR/CONOCO No Water Scrub	BCR/CONOCO With Water Scrub	Oil/ Selexol	Oil/ CONOCO	K-T/ Selexol
Gas Turbine-PR/Temp	16:1/2200F	16:1/2200F	24:1/2600F	24:1/2600F	24:1/2600F	16:1/2200F	24:1/2600F	16:1/2200F
FPC Account								
341 - Structures and Improvements	8,558	9,078	12,997	12,648	11,579	10,972	13,609	9,481
343 - Prime Movers (Gas Turbine)	34,027	34,405	30,730	34,942	31,353	36,435	33,786	39,322
344 - Electric Generators (Gas Turbine)	11,018	10.768	10,138	10,640	9.547	11,798	10,288	10,937
312 - Boiler Plant Equipment	31,570	30,200	34,637	37,753	33,875	40,755	36,443	43,303
314 - Steam Turbine Generator Units	21,518	26,003	29,204	26,264	25,958	39,082	35,546	35,845
345 & 353 - Accessory Electrical Equipment	10,267	11,101	12,900	14,045	12,857	13,163	15,112	11,374
346 - Miscellaneous Power Plant Equipment	399	426	455	461	422	511	496	442
Other Expenses	2,347	2,440	2,621	2,735	2,511	3,054	2,096	3,014
Direct Construction Costs	119,704	124,421	133,682	139,488	128,103	155,770	148,186	153,718
Contingency Engineering & Supervision	27,532	28,617	30,747	32,082	29,464	35,827	34,083	35,355
Total Construction Costs	147,236	153,038	164,429	171,570	157,567	191,597	182,269	189,073
Interest & Escalation	64,592	67,138	67,748	75,268	69,124	84,053	79,961	82,946
Total Capital Cost (Power System Only)	211,828	220,176	232,177	246,838	226,691	275,650	262,230	272,019

K-T/Selexol System Costs

As discussed in the performance section, the K-T gasifier does not mate well with a high-pressure combined cycle power system. The increased proportion of steam power generation, fuel gas compression and oxygen plant requirements not only affect performance but result in increased capital costs as shown in the summary Table 40. Costs for the K-T gasifier and heat recovery system were taken from the literature.[7] The remainder of the plant costs were assembled using contractor-developed costing procedures and data obtained during the previous contract phase from sources such as Allied Chemical for their Selexol process.

As can be seen from the tabulated power system costs (Table 48) and performance summary (Table 40), the primary reason for the relatively high cost per unit of installed power is the large proportion of steam power generation. On the fuel gas production side, Table 47 shows the capital cost breakdown. Gasifier and heat recovery costs by themselves are considerably lower than those of the other high temperature coal fired gasifier. However, the oxygen plant costs almost double the capital investment. Once the fuel gas has been compressed, acid gas removal costs are comparable to the other systems. However, the high power required by the fuel compressor (approximately three times that of the bleed air boost compressor in pressurized systems) shows up as a large cost increase.

The resultant power costs are sufficiently higher than for the other systems to conclude that this particular combination of gasifier and power system is not economically practical. A low pressure power system could undoubtedly show a real improvement but the investigation of such a system was outside the scope of this study.

Oil Gasifier/Selexol System Costs

For this system, fuel cost is clearly the dominant problem area. From Table 41 it can be seen that capital cost per unit power output is significantly less than comparable coal fired systems.

Costs for the gasification system were developed from data made available by the TPM Division of United Technologies Corporation[37] and reports from equipment manufacturers.[38] The basis for the remaining costs had been previously assembled for evaluation of other systems and was used here. The cost breakdown for power and fuel systems is given in Tables 47 and 48.

Oil Gasifier/CONOCO System Costs

As with the partial oxidation/Selexol system the cost of fuel represents over 50 percent of the power generating cost. As a result the desirable performance, capital cost, and emissions characteristics of this system are of little benefit.

Cost data were assembled in a manner similar to that for the previous system. There is little doubt that the resultant comparison is consistent even though we are dealing with a different fuel.

BuMines/Selexol Costs

The major changes in the BuMines/Selexol system costs are the result of escalation and improved performance. The improved performance results from the addition of a fuel gas resaturator which adds water vapor and heats the clean gas to the saturation temperature, eliminating the need for a regenerative heat exchanger. Estimates costs show little difference when the heat exchanger is replaced by resaturation equipment. This is due to the reduction in heat exchanger size when the cold side fluid is changed from gas to water.

The costs for the BuMines/Selexol with and without resaturation are shown in Table 49. As can be seen, the increased power out (6 percent +) and efficiency results in a reduced cost of power compared to the original system.

BuMines/Iron Oxide Costs

The revised BuMines/Iron Oxide system has an estimated cost of $138.98 million (Table 45) which is an increase of nearly 8 percent over the base system[1] with both escalated to a common mid-1975 dollar basis. This increase is due entirely to the additional cost of the hot particulate cleanup system, which is only partially offset by other system component cost reductions.

The increase in SO_2 concentration to 12 percent allows the elimination of the hot potassium carbonate scrubber which was used previously to concentrate the stream (remove CO_2) prior to the Claus system. While this requires a slight addition to the fuel used by the Claus plant, the reductions in overall utilities requirements more than offset this increase in fuel. The Claus plant is also increased in size, but the revised estimates indicate a reduction in costs by 60 percent in the overall sulfur recovery step.

Table 49

BUMINES/SELEXOL COST SUMMARY

Capital Costs - $/kW	Without Resaturation	With Resaturation
Power System	280	278
Gasification System	124	119
Cleanup System	101	95
Total Plant Cost	505	492

Owning and Operating Costs - Mills/kWhr	Without Resaturation	With Resaturation
Owning Costs (17% of Capital)	14.00	13.64
Operation & Maintenance		
Power System	1.60	1.59
Gasifier and Cleanup	3.12	2.97
Fuel Cost at 60¢/MMBtu	6.52	6.32
Total Cost of Power	25.24	24.52

The net result of the performance improvement and the cost increase is a small reduction in the cost of power. This is shown in Table 50 where the costs of the revised and base systems are compared. It should be noted that this table differs from Table 28, which was for comparative purposes and used as a basis the costs presented in the Phase Report.[1] The data contained in Table 50 reflects mid-1975 dollars and shows the effect of updated particulate removal system costs.

BCR/Selexol-Cost

The major cost reduction in the BCR/Selexol system is due to the inclusion of a COS to H_2S catalytic converter which results in a reduction of the solvent flow rate of the Selexol system. The cost reductions have been discussed in Section 3 and will not be repeated here.

The reduced steam requirement in the cleanup can be used to increase the power out; thus, there is a second benefit. The two systems are compared in Table 51 and the cost of power for the revised system is shown as a function of fuel cost in Fig. 26.

BCR/CONOCO/Wet Scrub-Costs

The BCR/CONOCO system with the wet scrubber requires a good deal of additional components. At the exit of the CONOCO system, a high-pressure boiler and economizer would be used to drop the gas temperature prior to entering the fuel gas to fuel gas regenerator. At the exit of the regenerator, the fuel gas is further cooled before passing into the wet scrubber for particulate and ammonia removal. The gas is then resaturated and sent through the cold side of the regenerator.

Those changes result in an estimated $9 million increase in cost over the high-temperature BCR/CONOCO and introduce a performance penalty. However, this system has the capability of meeting the most stringent forseeable emissions standards with the use of a premixed combustor. The implications of this are discussed below.

Comparison of Three BCR-Based Systems

Three BCR-based integrated power systems have been investigated:

(1) BCR/Selexol/COS Converter - low-temperature
(2) CBR/CONOCO - high-temperature
(3) BCR/CONOCO/Wet Scrub - high and low temperature

Table 50

BUMINES/IRON OXIDE COST SUMMARY

Capital Cost - $/kW	With SO_2 Concentrator	Without SO_2 Concentrator
Power System	278	267
Gasification System	117	106
Cleanup System	55*	62
Total Plant Cost	450	435
Owning and Operating Costs - Mills/kWhr		
Owning Costs (17% of Capital)		
Operation and Maintenance	12.47	12.06
Power System	1.59	1.52
Gasifier and Cleanup	2.38	2.33
Fuel Cost at 60¢/MMBtu	6.40	5.83
Total Cost of Power	22.84	21.74

*Does not include high-temperature particulate removal

Table 51

BCR/SELEXOL COST SUMMARY

Capital Costs - $/kW	Without COS Converter	With COS Converter
Power System	251	228
Gasification System	130	121
Cleanup System	98	85
Total Plant Cost	479	434

Owning and Operating Costs - Mills/kWhr		
Owning Costs (17% of Capital)	13.27	12.03
Operation of Maintenance		
Power System	1.43	1.30
Gasifier and Cleanup	3.16	2.86
Fuel Cost at 60¢/MMBtu	5.69	5.31
Total Cost of Power	23.56	21.5

The costs, performance and emissions of these systems are summarized in Table 52. It is apparent that the gap in power costs between the BCR/Selexol and the BCR/CONOCO has narrowed from the previous study, e.g., 2.0 mills/kWhr versus the previous 4.5 mills/kWhr. This change is attributable to several factors: (1) the additional cost for high-temperature particulate removal, (2) the reduced cost of Selexol/Catalytic system, and (3) the increased BCR/Selexol system efficiency.

Both the BCR/Selexol and the BCR/CONOCO/water scrub have essentially the same power cost. As fuel costs increase, the BCR/CONOCO high-temperature system does show a slight advantage.

There are definite differences in emissions. As will be discussed in the subsequent section, the use of a premix combustor, one in which the fuel and air are mixed prior to introduction into the combustion, can reduce thermal NO_x by about 80 percent. This type of combustor has yet to be domonstrated at the operating conditions of interest to this study. Currently, it does not appear to be possible to premix 1600 F fuel gas with 800 F air, thus only fuel gas at 1000 F or lower can be considered. Assuming the use of this type combustor, both the BCR/Selexol and BCR/CONOCO/wet scrub systems would meet all forseeable emission standards. The BCR/CONOCO has NO_x emissions potentially eight times the present limit. This emission is about equally divided between thermal and fuel NO_x, thus combustor changes beyond the premix concept must be considered.

It must again be stated that use of a gasifier having higher operating temperatures will solve the major portion of the fuel-bound NO_x problem, since most nitrogen compounds will be cracked in such a gasifier. (See Section 5 for emissions from the partial oxidation gasifier.)

Table 52

COMPARISON OF BCR-BASED INTEGRATED SYSTEMS

Cost-$ Millions	BCR/Selexol	BCR/CONOCO	BCR/CONOCO/Water Wash
Gasification	91.97	91.97	91.97
Desulfurization	26.77	23.00	23.00
Particulate Removal	*	26.63	*
Heat Recovery	26.28	-----	26.28
Ammonia Recovery	9.86	-----	9.86
Other Process Costs	46.22	44.21	46.85
Power System	222.18	246.84	226.69
Total	423.28	432.65	424.64
Efficiency - %	38.6	42.7	39.0
Electricity Cost - Mills/kwhr	21.5	19.5	21.24
Emissions - lb/MMBtu			
SO_2	0.388	0.553	0.553
NO_x (as NO_2)	0.292*	5.50	0.584*
Particulates	<0.01	<0.04	<0.01

*With Premix Combustor

SECTION 5

ANALYSES OF ENVIRONMENTAL INTRUSION

SUMMARY

For each of the integrated systems examined in this study, the air, water and solid residuals have been identified and quantified to the fullest possible extent. A summary tabulation of all air, and solid residuals is made in Table 53. Total recycle of water was assumed and, therefore, none of the water is discharged. All contaminated water is treated and reused except for water used for ash wetting which evaporates. There are water losses from evaporation, drift, etc., but these are not included in the tabulation under the category of water effluents.

The air emissions have been detailed previously[1], thus emphases have been placed on defining the water and solid emissions of these integrated systems.

Existing EPA Standards and Their Implication Relative to This New Point Source

EPA Standards exist for residuals from conventional coal-fired power plants. No such standards have yet been promulgated for the integrated combined-cycle power plants examined in this study. Therefore, a comparison between the quantities of residuals determined in this study and existing EPA Standards for conventional coal-fired power plants is in order. The EPA New Source Stack Emission Standards for power plants are:

	COAL-FIRED	OIL-FIRED
SO_2	1.2 lb/MM Btu.	0.8 lb/MM Btu.
NO_x (as NO_2)	0.7 lb/MM Btu.	0.3 lb/MM Btu.
Particulates	0.1 lb/MM Btu.	0.1 lb/MM Btu.

Table 53

SUMMARY OF RESIDUALS FROM INTEGRATED SYSTEMS

Residual		Air			Solid						
Integrated System	Source	SO_2 lb/MM Btu	NO_x + lb/MM Btu	Particu-lates lb/MM Btu	Ash lb/hr	Slag lb/hr	Sulfur lb/hr	Fly Ash lb/hr	Misc. Wastewater Residuals lb/hr	Spent Dolomite lb/hr	Purge lb/hr
1) BuMines/Selexol	Turbine	0.088	0.218	0.016	114132	-	24183	13019	100 to 500	-	-
	Stack	0.320	0.356								
2) BuMines/Iron-Oxide	Turbine		5.06	0.032	114132		20518	13619	*	-	7185
	Stack	0.575									
3) BCR/Selexol	Turbine	0.080	1.43	-	-	60900	24086	-	*	-	-
	Stack	0.306	0.201								
4) BCR/Conoco	Turbine	0.520	2.939	-	-	60900	23952	-	*	15244	-
	Stack	0.033									
5) K-T/Selexol	Turbine	0.057	3.41	0.029	-	36540	24228	24115	*	-	-
	Stack	0.490									
6) K-T/B-W	Turbine	0.168	NA	0.057	-	36540	23160	23873	*	-	-
	Stack	0.468									
7) Oil/Selexol	Turbine	0.108	0.320	0.0007	-	350	12317	544	*	-	-
	Stack	0.142									
8) Oil/Selexol	Turbine	0.060	0.631	0.0014	-	350	12249	537	*	5952	-
	Stack	0.017									

* Wastewater solid residuals were calculated only for the worst case, the BuMines/Selexol system.

\+ Weight considering all oxides as NO_2

Sulfur Dioxide Emission - From the emissions listed in Table 53, it is evident that all the cleanup systems evaluated for first- and second-generation application will comply with the current EPA standard for SO_2 (conventional coal-fired plants). With the exception of the systems using the half-calcined dolomite (Conoco) process, the sulfur plant stack gas accounts for 60-90 percent of the total SO_2 emission. Commercially available tailgas treating processes may be used to further reduce sulfur emissions in these cases. Tailgas treatment in the BCR/Conoco and oil Gasifier /Conoco cases will not significantly reduce the sulfur emission, since at least 91 percent of the SO_2 results from fuel gas combustion.

Nitrogen Oxide Emission - The NO_x emission from an integrated system depends on the type of gasifier and the type of cleanup system used. It is known that a substantial part of the nitrogen contained in the coal is converted to ammonia during gasification. The low-temperature Selexol system removes traces of ammonia that get past the water scrubbing operation. The high-temperature iron oxide and Conoco processes do not significantly affect ammonia at all. Therefore, assuming essentially conventional gas turbine combustors, even if only 50 percent of the ammonia were converted to NO_x during combustion, these systems would not meet the current EPA standard. Thus, high-temperature desulfurization systems used in conjunction with gasifiers operating below the cracking temperature of ammonia are inadequate from a NO_x control viewpoint, although they yield higher thermal efficiencies for the integrated systems.

Particulates - The current EPA Standard for particulates is 0.1 lb/MM Btu, which is equivalent to approximately 0.1 gr/SCF for a typical low-Btu gas. This level of particulate loading is easily achieved by all the low-temperature cleanup systems considered here. Although definitive operating data are lacking for high-temperature particulate removal systems and for the particulate loading/size distribution in the fuel gas produced by various gasifiers, it is expected that these systems will be capable of meeting the existing EPA Power Plant New Source Standard.

However, the concern for particulate removal is dictated by gas turbine operating requirements, rather than emission standards. With the potential for turbine blade erosion in mind, the allowable particulate loading for the clean fuel gas was established to be 0.01 gr/SCF. Even this stringent goal can easily be met by low-temperature cleanup systems with their inherent water scrubbing operations. However, it is not certain at present whether high-temperature particulate removal systems will be able to meet this stringent operating requirement. A number of systems such as high temperature electrostatic precipitators, metallic mesh filters, and granular bed filters claim a high degree of particulate removal (95 percent) but have yet to be proven on a commercial scale.

Water - With total water treatment and reuse, liquid effluents can be completely eliminated, and most impurities that were transferred from the raw fuel gas to the process water can be removed after treatment, and disposed of in solid form. Though theoretically possible for this type power plant facility, this has to be demonstrated and zero liquid effluents have to be proven.

Solids - Considerable quantities of solids including ash, slag, sulfur, etc. are generated from the integrated systems. Most of these solids are stable at ambient conditions and can be utilized or disposed of. Those that are unstable are first treated to render them stable before disposal. From an environmental consideration however, it seems that the quantities of these solid residuals rather than their nature might present the greater problem.

OVERVIEW

To this point, this report has described the nature of the unit operations and systems associated with low- and intermediate-Btu gasification of coal and the subsequent cleanup of the fuel gas produced by the gasification process. This section presents results extracted from the material balances and other appropriate data information concerning the effluents, emissions, and solid wastes produced by low- and intermediate-Btu gas-fired combined-cycle power plants. Further, this section will describe possible options associated with the ultimate disposition of the residuals produced by these plants.

From the standpoint of overall environmental considerations, it appears that advanced low- and intermediate-Btu gas-fired combined-cycle power plants can potentially produce fewer insults to the environment than the conventional coal-fired power plant with flue gas desulfurization (FGD). This advantage stems from two major features of the combined-cycle power plant. First, because a major portion of the electricity being produced by this power plant is produced by the gas turbine portion of the combined cycle, the amount of heat rejected to water and hence, the amount of cooling water required for the combined-cycle power plant is about half that required for the conventional coal-fired plant using some form of water cooling. Second, with the integrated combined-cycle power plant, the sulfur that originates in the coal and ends up in the fuel gas can be removed without producing any solid waste other than the elemental sulfur itself. With the conventional coal-fired plant, either the not-easily-disposed-of scrubber sludge is produced, or a regenerative scrubbing process is used with a significant reduction in plant efficiency. While the scrubber sludge can be disposed of by a number of proven processes, it is a costly undertaking which the power companies would rather avoid. Unfortunately, if a regenerable FGD process is employed, the plant is derated, requiring more coal to be burned to produce the same amount of power. This results in greater air emissions, water effluents and solid residuals.

From the previous discussions and analyses it is apparent that there are numerous low-temperature and several high-temperature fuel gas cleanup systems that are efficient in removing H_2S from the fuel gas, just as there are scrubbers that are efficient in removing SO_2 from flue gas. The resulting sulfur oxide emissions from the integrated combined-cycle power plant, therefore, could be controlled to a level comparable to conventional coal-fired plants with stack gas scrubbing. Since there is less fuel gas than flue gas volume (there is both less fuel gas mass and its pressure is higher) for an equivalent size power plant, the fuel gas cleanup process would probably be more easily controlled and more reliable. The magnitude of these advantages though, would have to be assessed by comparing specific systems. Also, the benefits of sulfur and ammonia recovery units must be weighed against added complexity and additional emission streams.

In actual practice, the particulate emissions from a conventional coal-fired plant would be higher than those from the integrated combined-cycle power plant. This is not through any inherent advantage of the integrated combined-cycle power plant, but rather because of the limited particulate loading that can be tolerated by the gas turbine. Stated another way, because of the potential for erosion damage to turbine blades, the particulates entering the turbine, and hence the particulates in the exhaust of the combined-cycle power plant must be controlled to levels lower than the particulate emission levels of the conventional coal-fired power plant. On the other hand, it may be necessary to reduce allowable emissions since the particulates from the combined cycle tend to be smaller and more harmful.

While it appears(1) that the NO_x emissions from the low-Btu gas-fired combined cycle power plant utilizing a low-temperature fuel gas cleanup system can be controlled to levels comparable to or less than the conventional coal-fired power plant, it is not clear as to whether this would also be true in the case of high-temperature fuel gas cleanup systems used in conjunction with gasification processes that operate below the cracking temperature of ammonia. This is because the ammonia produced by these gasifiers cannot be removed at elevated temperatures with existing technology. As has been discussed earlier in this report, it appears as though this problem could be remedied if a suitable catalyst for promoting the decomposition of ammonia could be developed. With higher temperature gasification processes, like the Koppers-Totzek process and oil-based partial oxidation process, ammonia formation is negligible, thereby eliminating the necessity of its removal.

Thermal NO_x, i.e., NO_x formed from atmospheric nitrogen during the combustion process may also be increased becuase the use of high-temperature fuel gas raises the stoichiometric flame temperature. However, thermal NO_x production is subject to reduction by careful combustor modifications and will not be discussed here other than to be evaluated as part of the total NO_x emissions.

As will be described later in this chapter, all of the water emissions from this integrated power plant facility can be treated so that there will be no release of water borne pollutants to a natural body of water. It will be shown that the integrated power plant could be operated in full compliance with the effluent controls currently mandated for 1983 with respect to the Best Available Technology Economically Achievable.

While at this time it appears as though there are no national shortages of the materials that might be produced by the combined-cycle power plant as solid wastes, there are constructive ways in which these residuals can be utilized. Further, research is being conducted that strives to broaden the range of applications for these residuals. Ash and slag utilization have been the subjects of study for quite a few years and recent environmental regulations limiting sulfur emissions have prompted considerable study in the area of constructive uses for sulfur. A number of these existing and proposed applications for ash, slag, and sulfur are identified and discussed in this section.

AIR EMISSIONS

The air emissions to the surroundings can be divided into two groups, those from the fuel processing system and those from the power system. However, it must be remembered that the power system emissions are very much a function of the fuel processing and therefore, prior to the discussion of power system emissions, it would be worthwhile to briefly review the overall fuel processing system to identify potential pollutent sources.

Review of Fuel Processing System

Gasifiers - As has been noted earlier, there are two generations of gasifiers. The first generation (e.g., BuMines, Lurgi) has off-gases condensible tars, phenols, and other organics. The second-generation gasifiers (e.g., BCR-two-stage, Koppers-Totzek and Texaco/Shell partial oxidation) have off-gases without condensibles. The principal differerences in the performance of these gasifiers is directly related to the operating temperatures within the gasifier. The operating temperature in a fixed-bed gasifier is lower (< 1200 F) than in an entrained-flow or in a fluidized-bed gasifier (2500 F) and therefore the carbon conversion is realtively low. The temperature is low enough to allow the formation and preservation of tar, phenols, and other organics. Organics produced during gasification do not undergo thermal cracking and therefore emerge with the product gas. The lower temperature also favors the formation of ammonia.

In the entrained-flow and fluidized bed gasifiers, not only are the temperatures higher, but the residence times are shorter. As a result, the formation of organics and tars is not favored and therefore, these are not present in the raw gas.

The conditions in the three types of gasifiers viz, fixed-bed, fluidized-bed and entrained-flow are different and the quantities and size distributions of the particulates off each gasifier type are correspondingly different. The conditions differ in:

- The manner in which the coal feed is supported
- The rate of gas flow (superficial velocity)
- Temperature
- Feed size

Based on the above differences, a qualitative estimate of particulate size and quantity can be made. The particulate loading of a fixed-bed is estimated to be fairly high and comprised of fine particules of ash and unburned carbon. Particulate loading in the gas from a fluidized bed is lower and consists of comparatively larger particles than off a fixed-bed gasifier. The particulate loading off an entrained-flow gasifier is very high with its size distribution proportional to the feed size.

Cleanup Processes - This study has addressed the following gasifiers:

- Bureau of Mines (stirred, fixed-bed) gasifier
- BCR (pressurized entrained-flow) gasifier
- Koppers-Totzek (atmospheric entrained-flow) gasifier
- Partial Oxidation (Texaco/Shell entrained-flow) gasifier

Of these, only the BuMines gasifier is a low-temperature gasifier and has condensible tars, phenols, ammonia and organics besides particulates in the off-gases. The simplest scheme of removal of these condensibles involves a water quench followed by the separation and recycle of the condensed tar to the gasifier in order to improve thermal efficiency. The quench also removes phenols, organics and some ammonia from the gas. Further scrubbing with water removes remaining traces of ammonia and some hydrogen sulfide from the gas. Thus, a low-temperature cleanup system is a logical choice for the BuMines gasifier. If however, a high-temperature cleanup system is used to improve overall thermal efficiency, the product gas will contain tar and ammonia which upon combustion will give SO_2 and NO_x.

All of the other gasifiers studied belong to the second generation (high temperature) so that their product gases contain no condensible tars or organics. Therefore, high-temperature cleanup systems can be used in conjunction with them and higher thermal efficiencies can be attained than with low-temperature cleanup systems. Ammonia is present in smaller quantities, but none the less presents a removal problem at elevated temperatures. With current state-of-the-art cleanup systems, ammonia can be removed only at lower temperatures by scrubbing with water.

From some gasifier types, a significant amount of sulfur is present in the form of COS which could constitute a removal problem at lower temperatures. Specifically, the Selexol solvent is not selective to COS and therefore the addition of a catalytic conversion process changing the COS to H_2S prior to desulfurization was considered. The COS is fairly efficiently removed by high-temperature desulfurization processes such as dolomite absorption.

Although there are currently no commercially available particulate removal processes which could operate at the temperatures and pressures required for high-temperature cleanup and meet the projected removal requirements for particulates < 10 μ, there are several processes in the early development stages which show great promise. Therefore, it is not unrealistic to assume that either high- or low-temperature particulate removal systems may be used with equal success depending on the operating temperature of the cleanup system downstream.

Emissions Associated with the Fuel Processing Systems

Claus Plant Tail Gas - The efficiency of a Claus plant is generally less than 95 percent, therefore, some of the H_2S or SO_2 fed to it remains unconverted and has to be vented to the atmosphere as SO_2. Unconverted H_2S is incinerated to SO_2. Much of the fuel for incineration is needed to raise the temperature of the noncombustiles in the Claus plant feed gas. Thus, fuel requirements are largely a function of the cleanup system and increase as the H_2S concentration in the feed decreases. For a typical system (BCR/Selexol with Catalytic Reduction of COS) having a 23 percent concentration of H_2S in the Claus plant feed, fuel requirements are approximately 1 percent of the total gas produced. Other components of a Claus plant tail gas are NO_x, CO_2 and H_2O. The extent of NO_x emission depends primarily on the quantity of ammonia in the Claus plant feed which in turn is a function of the quantity of ammonia removed from the fuel gas. The quantities of CO_2 and H_2O are a function of the quantity of fuel used in the Claus plant. This requirement is higher for a SO_2 Claus feed as compared to an H_2S feed. The Claus plant emissions are shown in Table 54 for the different systems.

Commercially available tail gas cleanup process such as the SCOTT process or the Strethford process could reduce the Claus plant emissions but at additional capital and operating costs. Since the overall plant is below the 1.2 lb/million Btu limit for coal-fired plants, these processes were not included although estimates of the reduced emissions are included in Table 54.

It should be noted that the process changes in the BuMines/iron oxide and the BCR/Selexol have resulted in somewhat different emissions for the Claus plants associated with those cleanup processes than have been reported previously.[1] These changes are noted in Table 54.

Table 54

AIR EMISSIONS FROM INTEGRATED SYSTEMS
(lb/MMBtu)

Pollutent/Source	SYSTEM: BuMines/ Selexol	BuMines/ Iron Oxide	BCR/ Selexol	BCR/ Conoco	K-T/ Selexol	K-T/ BEW	Oil / Selexol[1]	Oil / Conoco[1]
SO_2								
Fuel Processing	0.320	0.575 (0.535)[2]	0.306 (0.487)[2]	0.033	0.490	0.468	0.142	0.017
Power System	0.088	0.334 ---	0.080	0.520	0.057	0.168	0.108	0.060
Total SO_2	0.408	0.909	0.388	0.553	0.547	0.636	0.250	0.077
Total With Claus SO_2 FGD	0.137	0.372	0.103	---	0.094	0.203	0.140	----
NO_x								
Fuel Processing	0.356	0.310	0.201	----	----	NA	----	----
Power System								
Thermal	0.044	1.27[3]	1.42[3]	2.56[3] (1.41)[4]	3.41[3]	----	0.307[3]	0.592[3]
Fuel Bound	0.174	3.79	0.012	2.74 (.296)[4]	----	----	0.013	0.039
Total NO_x	0.574	5.17	1.633	5.50	3.41	----	0.320	0.631
Total Particulates	<0.016	<0.032	<0.01	<0.04	<0.029	<0.057	<0.01	<0.01

1. The standards for oil-fired station are SO_2 = 0.8 lb/MMBtu
   NO_x = 0.3 lb/MMBtu
   Part = 0.1 lb/MMBtu
2. From Ref. 1
3. Thermal NO_x has potential of 80% reduction by combustor design modifications
4. With water wash

SO_2 Scrubber Flue Gas - In the BuMines/iron oxide system, the regeneration of the iron oxide absorbent yields SO_2 in the off-gas. The concentration of SO_2 in the off-gas can be low (5 percent) depending on the amount of excess air used to regenerate the sulfided bed. If the SO_2 concentration is very low, the Claus plant efficiency drops greatly. To circumvent this, the SO_2 must first be concentrated and fed to the Claus plant. This represents an additional step in the process. One alternative to using a Claus plant and an additional unit for concentrating the flue gas is to use a flue gas scrubbing system. A flue gas scrubber may also be used to scrub the Claus plant tail gas to further reduce SO_2 emissions. Such systems are generally limited in their efficiency to about 90 percent SO_2 removal. The remaining SO_2 along with CO_2, H_2O, and NO_x are discharged to the atmosphere.

Coal Feed System (Lock Hopper) Releases - The coal feed system to a pressurized gasifier typically consists of a weigh hopper, a pair of lock hoppers and a pressurized feed hopper. Pulverized coal from the storage bin is fed to the weigh hopper which discharges a measured quantity alternately into two lock hoppers. When one of the lock hoppers is filled to capacity it is pressurized with a coal transport gas (this may be a portion of the product fuel gas). The coal is then conveyed to the feed hopper from which it is fed to the gasifier. The emptied lock hopper is then vented and refilled while the second hopper is pressurized. This sequence of operations allows a continuous flow of coal into the gasifier. The feeding operation results in emissions to the air from the lock hoppers when they are vented. These emissions consist of coal fines, as well as some small amount of the transport gas (which may contain pollutants).

Gas Released by Fuel Gas Quench Water Sent to Water Treatment Facilities - When pressurized fuel gas is quenched, some amount of gas dissolves in the quench water. The quench water also picks up particulates and soluble organic and inorganic compounds such as phenols, ammonia, etc. that may be present in the fuel gas. The contaminated quench water is then sent to water treatment facilities which operate at atmospheric pressure, so that some of the gases that had dissolved under pressure are now released. Therefore, this constitutes a potential source of air emissions including H_2S, NH_3, CO_2, etc.

Gases Released from/with Gasifier Bottom Ash and Slag - The ash (from the BuMines gasifier) is removed from the gasifier through a pressurized lock hopper system. When the lock hopper is filled to capacity it is depressurized and the ash is removed for cooling and disposal. The ash is accompanied into the lock hopper by some raw gas containing pollutants which upon venting the lock hopper, is emitted to the atmosphere.

The second-generation gasifiers produce slag which is collected in a slag pot and is water quenched. The quenched slag is then removed from the gasifier via two slag hoppers. Once again, some raw gas escapes with the slag and is vented to the atmosphere. Some raw gas is also dissolved in the slag which is evolved once the slag is removed from the gasifier.

Emissions Associated with the Power System

Sulfur Dioxide - As in the integrated systems previously discussed(1), the SO_2 emissions from the K-T and the partial oxidation residual oil-fired systems now being considered are within the regulation for SO_2 from coal- and oil-fired steam stations. The emissions from those integrated systems using low-temperature cleanup are lower, especially in the case of the fixed-bed gasifier (BuMines) since, when using the high-temperature cleanup, the tars containing significant amounts of sulfur are passed through the cleanup to the combustor. Values of SO_2 emissions are given in Table 54.

Nitrogen Oxides - The production of NO_x is through two independent mechanisms, thermal NO_x which is a function of local temperature and time, and fuel NO_x which is a function of fuel-bound nitrogen.

Since thermal NO_x is directly proportional to combustion temperature, anything that increases combustion temperatures would increase the NO_x production; a decrease in temperature would decrease the NO_x production. It has been assumed that the gas turbine combustors used in the integrated systems are of the conventional type, i.e., a local stoichiometric flame zone in the front of the can followed by rapid quenching with dilution air. The thermal NO_x for this type system is thus a function of the stoichiometric flame temperature. The factors affecting this parameter are 1) fuel heating values, 2) fuel sensible heat (fuel temperature), and 3) combustion air temperature. Previous work at UTRC(1, 30, and 39) has resulted in the preparation of working charts for the determination of thermal NO_x as a function of combustion temperature and gas turbine firing temperature. In Fig. 41, for example, the effects of both chemical and sensible heat on combustion temperatures are given. Thermal NO_x emissions as a function of combustion temperature can then be estimated by using Fig. 42. Unfortunately, the values of rate constants used to develop Fig. 42 are not well defined and it is estimated that the values shown are probably only within a factor of ± 2 of actual values. As examples of the use of these tools, Table 55 has been constructed.

Without regeneration, the fuel gas from the BCR/Selexol system would have a temperature of about 250 F giving a final combustion temperature of about 3680 F. This would result in a NO_x emission of approximately

EFFECT OF FUEL GAS CHEMICAL AND SENSIBLE HEAT ON COMBUSTION TEMPERATURE

REFERENCE FUEL HHV = 120 BTU/SCF

REFERENCE FUEL TEMPERATURE = 80F

STOICHIOMETRIC FUEL – AIR RATIO

INITIAL AIR TEMPERATURE = 825F

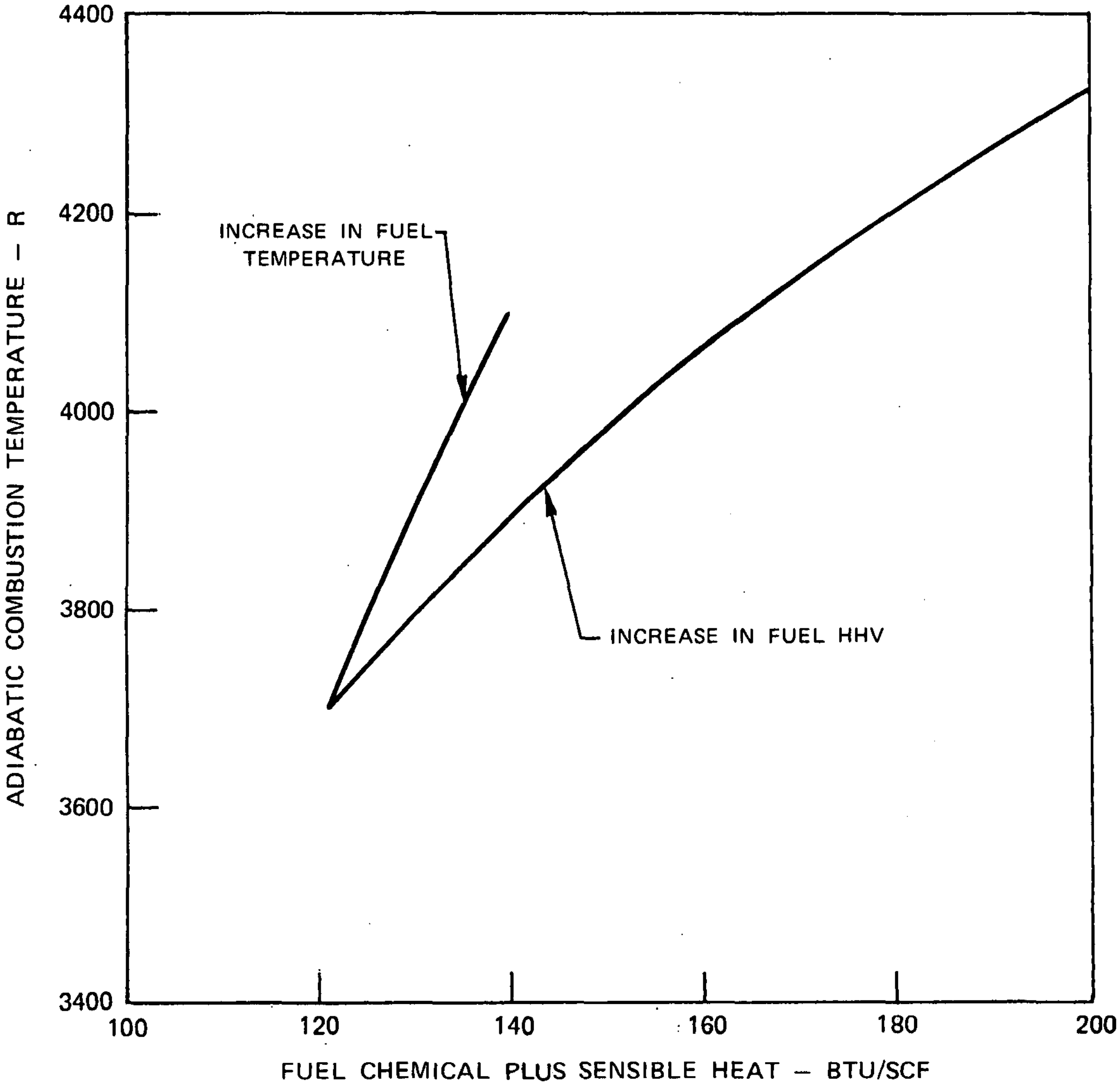

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FIG. 42

NITRIC OXIDE FORMATION IN GAS TURBINE BURNER

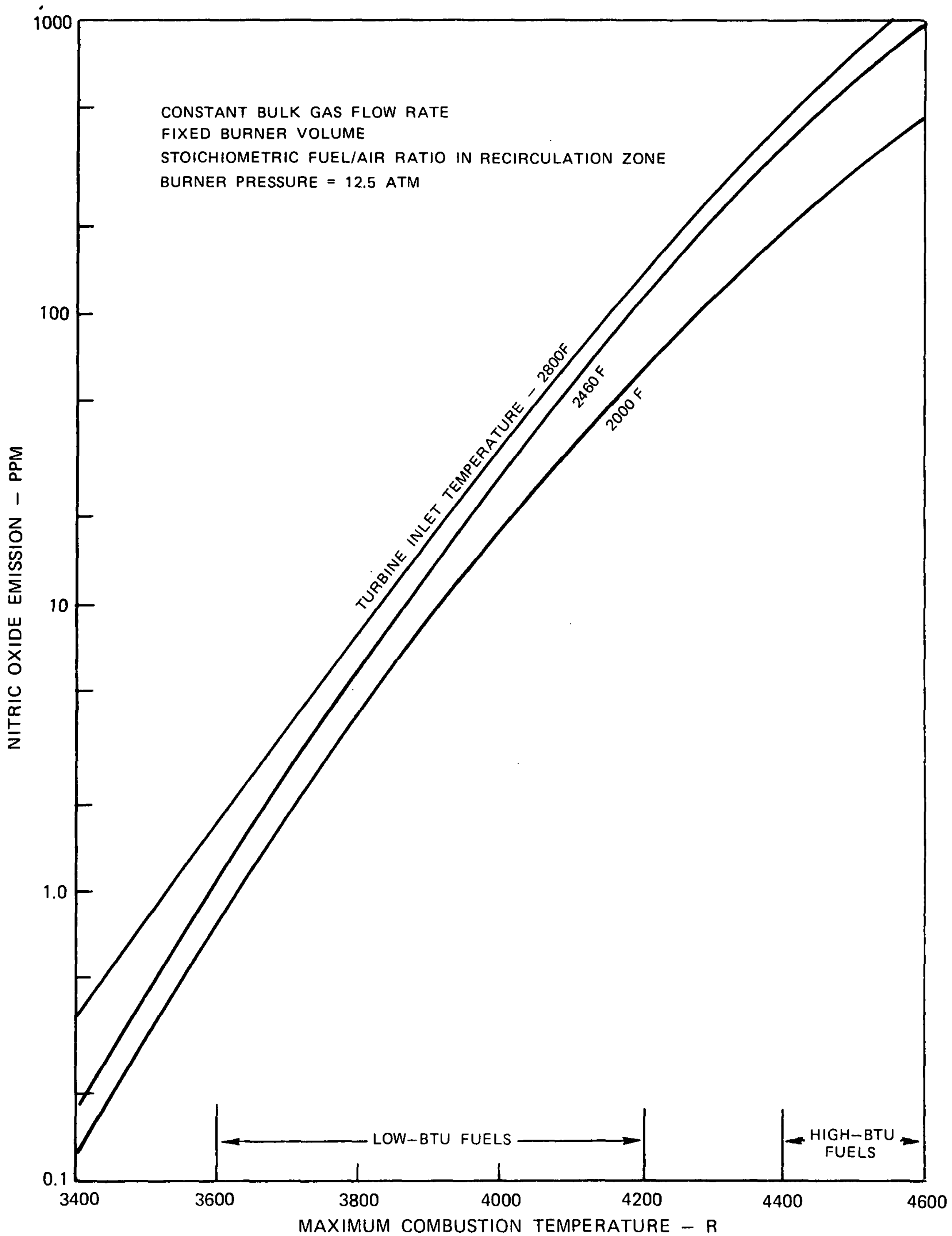

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TABLE 55

COMBUSTION TEMPERATURES FOR FUEL GAS

System	BuMines/Selexol	BCR/Selexol
Fuel Gas Heating Value, Btu/SCF (HHV)	141.7	156.5
Fuel Gas Temperature, F (Regeneratively heated)	252	1000
Air Temperature, F	755	903
Combustion Temperature, F (Fuel at 80 F, Air at 825 F)	3450	3580
Correction for Fuel Temperature, F	+ 64	+ 360
Correction for Air Temperature, F	- 41	+ 46
Approximate Combustion Temperature, F	3475	3980
Turbine Inlet Temperature, F	2200	2600
NO_x Emission, ppm	13	500
NO_x Emission, lb/MMBtu (as NO_2)	0.04	1.42

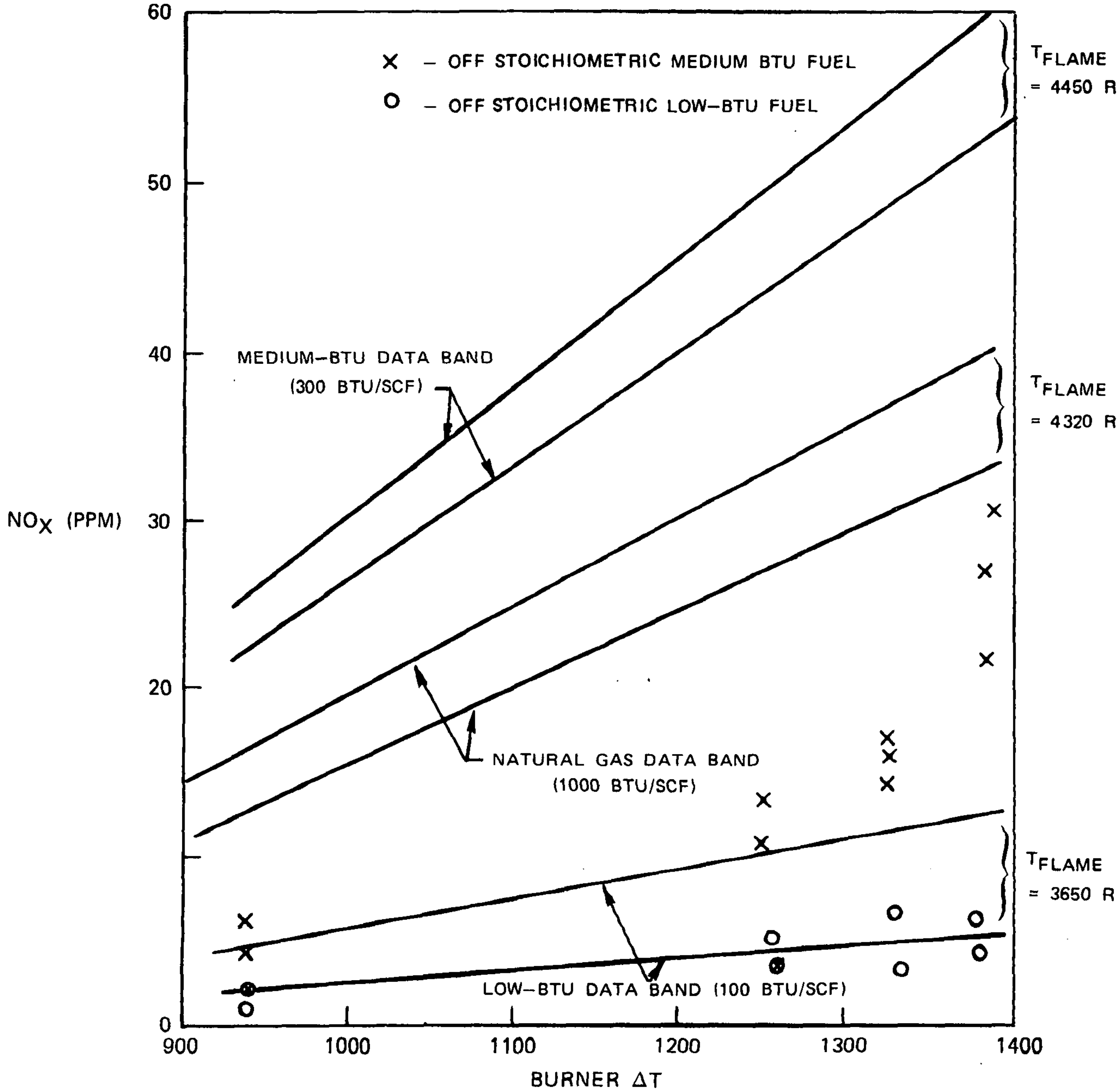
0.25 lb/MMBtu. However, without the regenerative fuel heating, the overall performance of the system would decrease approximately five percent. When the fuel-bound nitrogen is added, the total NO_x emission would be (90 percent fuel-bound nitrogen conversion) approximately 0.33 lb/MMBtu. If the regulation of 0.7 lb/MMBtu were to be equaled, then the regeneration would be limited to approximately 750 F.

There is a second approach to reducing the thermal NO_x. This approach involves combustor modification. While the details of these modifications are beyond the scope of the present study, briefly they are aimed at burning at off-stoichiometric conditions, i.e., at lower than stoichiometric flame temperatures. The Turbo Power and Marine Systems subsidary of United Technologies Corporation has been carrying out a series of tests on low- and medium-Btu buel gases produced by an experimental gasifier at the Texaco Development Company's Montebello, California research facility. Of particular interst are the results of the use of premixed (fuel and air mixed prior to the introduction into the combustion) burners. Figure 43 shows the NO_x emissions as a function of source temperature rise for several values of fuel chemical heating value. In the test series, the fuel gas was delivered at essentially ambient temperature. The theoretical stoichimetric temperatures are given. Also shown in Fig. 43 are the approximate emissions for burners having premix conditions. While no significant reduction was noted for low-Btu gas (the emissions were already low), use with the medium-Btu gas indicated a large reduction. The reduction as a function of equivalence ratio (local fuel/air ratio divided by stoichiometric fuel/air ratio) is shown in Fig. 44.

While it will require experimental verification at the appropriate operating conditions, it appears that a potential thermal NO_x reduction of approximately 80 percent may be realized by premixing. Unfortunately, premixing cannot be applied to fuel gases much above 1200 F because of self ignition. However, the lower temperature gases may be regenerated to 1000 F and premixed at off-stoichiometric conditions thereby allowing high performance without undue NO_x problems. Because these values need to be experimentally verified, the NO_x emissions of Table 53 do not reflect any of the improvements felt possible.

Unfortunately, the fuel-bound nitrogen does not appear to be as ameanable to treatment by combustor modification. As was done in the previous study(1), the assumption of 90 percent conversion of the ammonia to NO_x was made. Thus, the values of NO_x given in Table 54 indicate higher than acceptable levels of NO_x from those combinations of gasifiers and cleanup systems not having sufficiently high-operating temperature to decompose ammonia or without an aqueous scrubbing system.

NO_X PRODUCTION FROM COMBUSTORS BURNING LOW–BTU AND MEDIUM–BTU GAS



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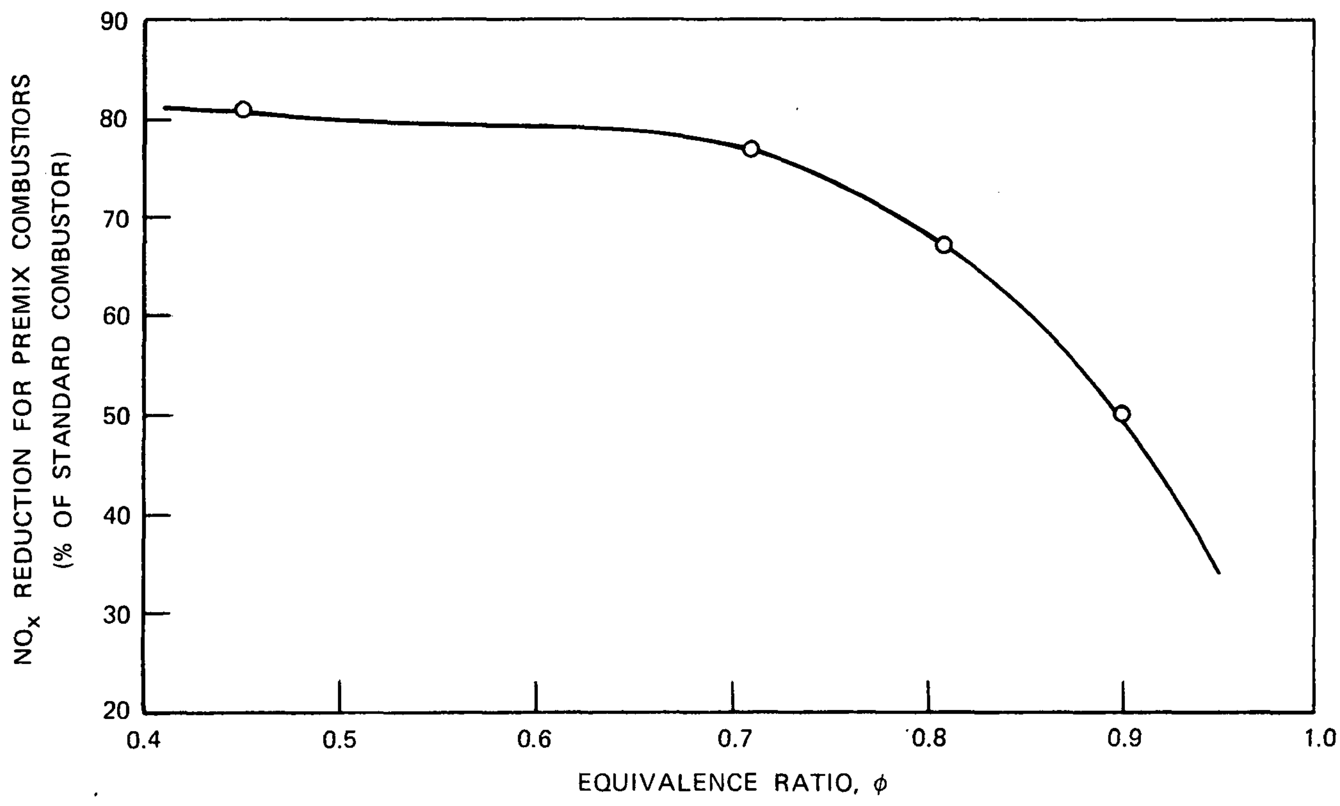
THE EFFECT OF EQUIVALENCE RATIO ON NO_X EMISSIONS



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Particulates - It was stated in an earlier portion of this report (Section 2) that the ability of the turbine to operate satisfactorily for reasonable periods of time was very much a function of particulate removal. It was also pointed out that because there is very little interfacing between the particulate removal device (either high- or low-temperature) and the remainder of the system, little definition of operating characteristics is necessary. Thus, based upon data reported previously[1] for systems having aqueous scrubbing, particulate carry-over in the fuel gas meets the stringent turbine requirements given previously, and in turn would easily meet the 0.1 lb/MMBtu EPA limit.

Based upon the limited data available on high-temperature and high-pressure cleanup systems, these systems are capable of removing small particles to levels approaching the turbine requirements. For example, small-scale cleanup systems at Argonne National Laboratory[40] operating at 8-10 atm and 1500 F - 1700 F shows that grain loadings of < 0.001 gr/SCF could be attained. This was accomplished with two stages of cyclones and two stages of final mesh filter. Submicron particulates were removed. It should be noted that metallic trace elements such as Pb, Na, Ca, etc. which are harmful to gas turbines tended to agglomerate on the fine particulates and, thus, were removed from the process stream with the particulates. While this removal feature has yet to be demonstrated on a large scale for high-temperature (1600 F) cleanup, it is hoped that this phenomena will continue to occur.

WATER EFFLUENTS

As a preliminary to any discussion on wastewater treatment, it is necessary to identify the sources of discharge, to characterize the water to be treated, and to define the end use of the treated water. To address the last problem first, it is generally agreed that in the context of minimizing water consumption, all effluent water streams should be treated and reused within the boundaries of the plant. As a corollary, utilization/treatment schemes should not be primarily designed to return water to a river or to the land in any other way.

Coal contains many trace impurities, which if concentrated are toxic. Our knowledge of the trace elements is imperfect, and regulations relating to the discharge of many elements do not exist at this time. Faced with a lack of regulatory guidance and an incomplete picture with regard to the dangers that might be associated with liquid waste streams, the disposal of waste material should be, as far as possible, under controlled conditions. Every effort should be made to remove wastes as solids. This is not an absolute requirement, but an ideal against which various water treatment schemes can and should be rated. Since all coal conversion processes are net consumers of water which leaves the plant as vapor, hydrogen gas or as hydrocarbons, total wastewater reuse is theoretically possible.

Waste Water Sources

Wastewater effluents produced by a low-Btu coal gasification combined-cycle electric power plant can result from a number of unit operations. Some wastes are discharge continuously as long as the plant is operating. Some wastes are produced intermittently on a fairly regularly scheduled basis, such as daily or weekly, but are still associated with the production of electrical energy. Other wastes are also produced intermittently, but at less frequent intervals and are generally associated with either the shutdown or startup of coal processing or electricity generating units. Additional wastes generated are essentially unrelated to production, but depend on meteorological or other factors.

Wastewaters are produced relatively continuously from the following sources (where applicable): gasifier raw gas cleanup systems, cooling water systems, ash handling systems, wet scrubber air pollution control systems, and boiler blowdown. Intermittently, but on a regular basis, wastewater is produced primarily by water treatment operations which utilize a cleaning or regenerative step as part of their cycle such as ion exchanger regeneration, filter backwashing, and clarifier blowdown.

Wastewater effluents are also produced by the cleaning of major units of equipment on a scheduled basis either during maintenance shutdown or during startup of a new unit. The efficiency of coal gasification and electricity generating plants is largely dependent on the cleanliness of their heat transfer surfaces. Internal cleaning of this equipment is usually done by chemical means and requires strong chemicals to remove deposits from these surfaces. Moreover, the cleaning is not successful unless the surfaces are cleaned to bare metal which in turn means that some metal has to be dissolved in the cleaning solution.

Finally, rainfall runoff results in drainage from coal piles in the storage area, from floor and yard drains, and from construction activity.

Process Condensates - Process condensates is the name given to wastewaters that have contacted coal or tar. They are produced in the raw gas cleanup system when the gas is cooled and cleaned to remove impurities and by-products associated with the gasification of coal or oil. Process condensates are generated only from processes which utilize low-temperature gas cleanup systems. When a high-temperature gas cleanup system is used, only sulfur containing compounds and entrained solid impurities are removed (unless a future high temperature nitrogen compound removal system is used); the remainder is discharge to the atmosphere after the product gas and combustible impurities have been oxidized in the turbines (unless additional cleanup proves necessary).

Low-temperature gas cleanup systems, on the other hand, are designed to remove all the materials generated in the gasification that are not compatible with the product gas. Since such systems operate at or below the ambient temperature, condensible materials are removed from the gas stream and are discharged from the process as liquid effluents. The organic phase which consists primarily of tar and oil is returned to the process, whereas the aqueous phase is conveyed to the wastewater treatment plant for by-product recovery and water purification.

Low-temperature gas cleanup systems have the greatest potential for water pollution. The gasifier output may contain all of the products commonly associated with pyrolysis, carbonization, and coking of coals in addition to oxygenated products associated with partial combustion. Hence a broad spectrum of heavier materials present may be classified as tar, including phenols and cresols, pyridines, anilines, dihydric phenols, intermediate and high boiling aromatics, saturates, olefins, and thiophenes. Another grouping termed light oil and/or naphtha, include B-T-X, naphthalene, thiophene, and condensible hydrocarbons and carbon disulfide. Ammonia, hydrogen cyanide, coal, char, ash fines and trace metals will also be present.

The particular distribution of compounds which will be present in the raw fuel gas will, of course, depend on the composition of feed coal and on the particular conditions of the gasification. The composition of the raw gas will determine the characteristics of the wastewater effluents. In general, gasification processes are classified into three categories according to their operating temperatures. These include the low-operating-temperature fixed-bed gasifiers, the intermediate-operating-temperature fluidized-bed gasifiers, and the high-operating-temperature entrained-bed gasifiers. Since the amount and variety of undecomposed organic matter that will escape with the raw gas are largely dependent on the gasifier operating temperature, it is evident that fixed-bed gasifiers generate the "dirtiest" raw gas. Table 56 shows the chemical characteristics of wastewater effluents produced by the raw gas cleanup systems of the Synthane, Lurgi, and Bureau of Mines coal gasification processes. The numerical values of the Bureau of Mines/Selexol effluent were estimated and represent water which has been steam stripped to recover ammonia. For comparison purposes, Table 56 also shows a representative chemical analysis of weak ammonia liquor from a coke plant.

Trace elements which are present in coal may be volatilized during the gasification process and subsequently scrubbed out in the water washing steps. An indication of the elements likely to be found in the water stream is given by the analysis of Illinois coals[41] and of the process condensate from gasification of an Illinois No. 6 coal via the Synthane Process[42] (Table 57). These data were presented previously[1] and are repeated here for convenience. Of particular concern are those elements identified by the EPA as hazardous to human health: beryllium, fluorine, arsenic, selenium, cadmium, mercury, and lead. These elements are all volatile and can be expected to appear in the raw gas and ultimately in the wastewater stream.

It should also be noted that some of the polynuclear hydrocarbons which may be present in raw gas have exhibited carcinogenic properties in animal studies. Control of such materials will generally be required in connection with evaporation from the wastewater treatment system, in plumes from cooling towers if leakage from the process train occurs, in the direct handling of separated tar or oil products, and in the flue gases from coal or tar combustion.

Cooling System Blowdown - In the operation of a closed cooling system, the bulk of the warm circulating water returning to the cooling system is cooled by the evaporation of a small fraction of it. The amount of water lost due to evaporation is a function of the temperature difference of the water between the inlet and outlet of the cooling system.

Table 56. CHEMICAL CHARACTERISTICS OF PROCESS CONDENSATE[1]

COMPONENT	COKE PLANT	SYNTHANE	LURGI	BuMINES/SELEXOL
Total ammonia	1800-4300	7000-10,000	1050	200-400
Total sulfur	0-50	1400		
phenol	410-2400	2600-6600	500	500
Thiocyanate	100-1500	20-200		100
cyanide	10-37	0.1-0.6		1-10
Fatty acid			1750	
chloride		500	500	500
carbonate	1200-2700	17,000		250
COD	2500-10,000	15,000-38,000		
BOD_5				2500
sulfides				10-100
Heavy metals				10-20
pH	8.3-9.1	8.6-9.2		9

1. Values are ppm except for pH and do not represent a complete characterization of the condensate.

Table 57. TRACE ELEMENT ANALYSIS OF ILLINOIS COAL

ELEMENT	ILLINOIS COAL[1]	WASTEWATER[2]
Al	1.29%	1000 ppb
Ca	0.77	4000
Cl	0.14	
Fe	1.92	3000
K	0.16	160
Mg	0.05	2000
Na	0.05	
Si	2.49	
Ti	0.07	
As	14.0 ppm	30 ppb
B	102.0	
Be	1.6	130
Br	15.4	
Cd	2.5	6
Co	9.6	2
Cr	13.8	6
Cu	15.2	20
F	60.9	
Ga	3.1	
Ge	6.6	30
Hg	0.2	
Mn	49.4	40
Mo	7.5	
Ni	21.1	30
P	71.1	90
Pb	34.8	
Sb	1.3	
Se	2.1	360
Sn	4.8	20
V	32.7	3
Zn	272.3	60
Zr	72.5	

1. Mean value for 101 coals analyzed.(41)
2. Process condensate from gasification of Illinois No. 6 coal.(42)

Roughly, evaporation losses amount to approximately one percent of the circulating water for each 10 F drop assuming a latent heat for water of 1000 Btu/lb. Additional water is lost to the atmosphere as a result of entrainment of water in the air draft (drift loss). The amounts of drift losses depend on the cooling system used varying from up to five percent of the circulating water for spray ponds to approximately 0.1 percent for forced draft cooling towers. Because of the water losses due to evaporation, the remaining water becomes more concentrated with dissolved solids. If the concentration level of any of the soluble salts exceeds its solubility level, the salt will precipitate. Some of the salts are characterized by reverse solubility, that is, their solubility decreases with increasing temperature. When cooling water saturated with such a salt is heated in the process condensers, the salt will deposit as a scale on the condenser tube walls and hinder heat transfer across the tubes.

Scale formation is usually controlled by discharging a portion of the circulating water from the cooling system to prevent a buildup of high dissolved solids concentration. This bleeding process, which is referred to as cooling system blowdown, is carried out either continuously or intermittently. The amount of blowdown is a function of the number of concentration cycles, that is, the ratio between the content of the critical component in the circulating water and the makeup water. This is also known as the number of concentrations. If it is assumed that all components in the feedwater must leave the system in the blowdown and enter only through the makeup, then the makeup flow, M_1 times its critical component concentration must equal the blowdown, B_1 times its critical component concentration. This results in the following relation where C, the number of concentrations is equal to the ratio of critical component concentration in the blowdown to its concentration in the feed:

$$C = \frac{M}{B} \tag{17}$$

The makeup, M_1 is the sum of the water lost due to evaporation, drift and blowdown. Blowdown can be calculated as the sum of water withdrawn for that purpose plus drift losses although this latter quantity is quite variable and in practice a conservative value of zero drift may be assumed.

A variety of chemical additives may be used to treat water circulating in the cooling system to control scaling, erosion, and fouling. These additives will appear in the blowdown along with matter originally present in the makeup stream. Biological growth in the circulating water is usually inhibited by chlorinating the water. Cooling waters are very often acidified with sulfuric acid to increase the solubility of the dissolved solids, and subsequently, to lower the makeup requirements due to blowdown. Pentachlorophosphate is cometimes added to cooling water to inhibit fungi attack on wooden cooling towers.

There may be particular problems associated with leakage into the cooling system from the high pressure gas processing train. Such leakages, if they occur, will also be present in the cooling system blowdown.

Steam Cycle Blowdown - A major problem associated with the operation of boilers or waste heat recovery systems is the formation of scale. The primary cause of scale formation is the reverse solubility of many of the scale forming salts. The higher the temperature and pressure of boiler operation, the more insoluble the scale forming salts become. Calcium and magnesium salts are the most common ingredients of boiler scales. Calcium deposition is primarily due to the thermal decomposition of calcium bicarbonate according to the following equation:

$$Ca(HCO_3)_2 = CaCO_3(S) + CO_2 + H_2O \tag{18}$$

Deposits of iron oxide, copper oxide and other metallic oxides are frequently found in boilers operating with very pure feed water. The source of these deposits is corrosion caused by the action of dissolved oxygen and carbon dioxide.

Boiler blowdown is the most widely used control method against scale formation. The amount of blowdown required is a function of the allowable concentration of scale forming or other undesirable components in the boiler and the degree to which the makeup water is cleaned. As for the cooling towers, the rate of allowable concentrations to makeup concentration of the critical component determines the number of concentration cycles which defines the ratio of makeup to blowdown (Eq. 17). High pressure boilers have quite stringent limits on contaminants. For example, the allowable concentration of silica varies from 125 ppm at pressures under 300 psig down to 0.5 ppm at pressures in excess of 2000 psig. As a result, C, the allowable number of concentrations can be quite low in a high pressure steam system. At pressures above 600 psi, silica ($Si\ O_2$) percent in the boiler will vaporize along with other contaminants and escape with the steam. To eliminate this condensation and resultant fouding of the turbine, it is necessary to maintain extremely low silica concentrations in the boiler which can result in a high amount of blowdown. Other methods, such as steam washing can be used to reduce the contaminant vapor content of the steam permitting higher boiler water concentrations and reducing the required blowdown quantity or makeup water quality.

Boiler blowdowns contain all of the additives to boiler feedwater as well as the soluble matter originally present in the boiler feedwater. Scale formation is usually inhibited by adding chemicals such as phosphates which precipitate scale forming salts to form sludge. Chelating agents which complex with scale forming metal ions, thus increasing their solubility, are also widely used. Sodium sulfite or hydrazine are often added to boilder feedwater in order to inhibit corrosion from dissolved oxygen.

Boiler blowdown is alkaline with a pH of 9.5 to 10 for hydrazine treated water and a pH of 10 to 11 for phosphate treated water. Hydrazine treated boilers produce blowdowns containing up to 2 ppm ammonia and those treated with phosphate may contain up to 50 mg/ℓ phosphate and up to 100 mg/ℓ hydroxide alkalinity.

Water Treatment Wastes - Water treatment waste streams are usually described by three parameters: pH, suspended solids concentration, and concentration parameters typical of processes involved or toxic elements involved in the process.

Clarification wastes consist of clarifier sludge and filter washes. Clarifier sludge could be either alum or iron sludge from coagulant chemicals. If the clarifier is a lime softener, the sludge would containd calcium carbonate and magnesium hydroxide. Filter washes would contain suspended solids either as light carryover floc from the clarifier or naturally occurring in unclarified raw water.

Ion exchanger wastes are either acidic or alkaline except for sodium chloride solutions which are neutral. Usually, such wastes do not contain suspended matter. They may, however, contain calcium sulfate and calcium carbonate precipitates because of the common ion effect.

Equipment Cleaning Wastes - A variety of cleaning formulations are used to clean scale and corrosion deposits from boilers and condensers. The cleaning program is usually dependent on the composition of the surface adhering materials. Cleaning solutions are usually grouped in three principal categories according to their composition. The first category includes the alkaline cleaning mixtures with an oxidizing agent for copper removal. These solutions contain an oxidizing agent and copper chelating compound, usually ammonia. The oxidizing compound converts metallic copper deposits to divalent copper ion which then reacts with ammonia to form a soluble complex. The wastewater effluents from such cleaning contain ammonium ion, oxidizing agents, and high levels of dissolved copper and iron, andhave high alkalinity.

The second category includes acidic cleaning mixtures. These mixtures are effective in removing scale due to water hardness. They contain a strong acid and a fluoride salt to remove silica. Waste streams from such mixtures may contain phosphates, fluorides, BOD, and acidity as well as large quantities of iron, copper and hardness forming salts.

The last group of formulations include solutions containing alkaline chelating agents and anticorrosion additives. These cleaning mixtures may be used alone or after acid cleaning to neutralize residual acidity and to remove additional amounts of scale forming materials. Their use generates wastewater containing alkalinity, BOD, phosphate and scale forming components.

In addition to these three categories, there are a large number of proprietary formulations which have been developed and are manufactured by companies specializing in cleaning chemicals. Most of these chemicals are similar to those described earlier and the resulting wastes contain: alkalinity, BOD, phosphate, ammonium compounds, and scale forming compounds such as iron, copper, and hardness.

Coal Pile Runoff - Coal pile runoff is the water drainage from the coal storage area which occurs during periods of rain. Such runoffs present a potential danger of water pollution if allowed to drain into waterways or to seep into ground aquifiers. The nature of coal pile runoffs depends on the type of coal used. Generally, there are two groups of coal pile runoffs. The first has a neutral or slightly alkaline pH and contains ferrous ions. Such runoffs are obtained from coal containing large amounts of alkaline materials or small amounts of pyrite. The second group of runoffs is highly acidic containing large amounts of dissolved iron and aluminum. These runoffs are produced from pyrite rich coal. Pyrites, or iron sulfides, are oxidized by atmospheric oxygen and hydrolyzed to form ferrous sulfate and sulfuric acid according to the following reaction:

$$2F_e S_2 + O_1 + H_2O \rightarrow 2F_2 SO_4 + 2H_2 SO_4 \qquad (19)$$

Additional sulfuric acid may be formed if the ferrous ions are further oxidized to the ferric state. When rain falls on coal piles, the acid is washed out and eventually winds up in the coal pile drainage.

At the low pH produced, other metals, such as aluminum, copper, manganese, zinc, etc., are also dissolved to further degrade the water.

Floor and Yard Drains - The floor drains, generally, contain dust and fines, and floor scrubbing detergents. This stream also contains lubricating oil or other oils which are washed away during equipment cleaning, oil from leakage of pump seals, and oil collected from spillage around the storage tank area of oil processing gasifiers.

Water and Wastewater Treatment

Treatment Technology - The water treatment scheme adopted in this study is designed for maximum water reuse and zero water discharge. The process was developed for the Bureau of Mines/Selexol system, but is also applicable, with only minor modifications, to the other processes. The principal difference between the various gasification processes, as far as the wastewater treatment is concerned, is the chemical characteristics of the process condensates generated in the raw gas cleanup systems. The chemical nature of the remaining streams are expected to be identical for all processes because each of the stream will originate from a unit which is common to all processes. Moreover, except for process condensates and water used for slag quenching the characterisitcs of the various wastewater effluents will be similar to those produced from a conventional coal-fired power plant.

Table 58 shows the chemical characteristics of process condensates produced in the various processes and potential control techniques. Of the eight integrated systems studied, four utilize a high-temperature cleanup system and therefore, will not generate process condensates. The remaining four processes will produce process condensates from the raw gas cleanup system, but of different water qualities. Condensates produced by the BCR and Koppers-Totzek gasification systems, because of their high operating temperatures, are expected to be free of organic matter. Such condensates will contain suspended solids, ammonia, sulfides and possibly small quantities of cyanides. In the partial oxidation/Selexol process naphtha can be used to remove soot from the gas water wash and, therefore, the condensates from this process can contain small amounts of organic matter. The most contaminated wastewater effluent will be generated by the Bureau of Mines/Selexol system. Condensates from the BCR or the Koppers-Totzek gasification systems can be treated by air stripping at pH 11 to remove ammonia followed by clarification to remove suspended matter. The offgas from the stripping tower may require incineration to prevent air pollution. The clarified effluent can be used as cooling water makeup. Condensates from both the partial

TABLE 58. CHEMICAL CHARACTERISTICS OF PROCESS CONDENSATES AND POTENTIAL CONTROL SYSTEMS

Processes	Pollutants	Treatment
BCR/Selexsol	ammonia, sulfides, cyanides, suspended solids	air stripping at pH 11, clarification
BCR/CONOCO	no condensate	
BuMines/Iron Oxide	no condensate	
BuMines/ Selexol	ammonia, sulfides, cyanides, suspended solids, penoles, tar, oil, dissolved inorganics	biological oxidation
K-T/Selexsol	ammonia, sulfides, cyanides, suspended solids	air stripping at pH 11, clarification
K-T/Iron Oxide	no condensate	
Oil /Selexsol	ammonia, sulfide, cyanides, naphtha	biological oxidation
Oil /CONOCO	no condensate	

oxidation/Selexol and the BuMines/Selexol gasification systems will require a treatment step for the removal of organic compounds. Condensates from the partial oxidation/Selexol process can be treated in an oxidation pond, whereas those generated by the BuMines/Selexol process would require a far more extensive treatment. This is discussed in the subsequent paragraphs.

It should be emphasized that the treatment of wastewater effluents can be accomplished by a great number of processes. However, in order to select and implement an efficient waste management program it is necessary to evaluate the control and treatment techniques against specific factors applicable to each case. Table 59 is a list of control techniques for potential pollutants from coal gasification plants. The information in Table 59 is based, in part, on a work plan for environmental study[43] of coal conversion processes prepared by Hittman Associates for the Federal Energy Research and Development Agency. The table contains information relevant to the principles of the methods, their limitations, the concentration range of their applicability, the efficiency of the methods and the extent of their industrial usage. It should be emphasized, however, that many of the listed methods have been developed specifically for the purpose of product recovery and as such are not applicable to pollutants present in the wastewater in low concentrations.

Process Description

Figure 45 shows a simplified flow diagram of a water treatment process for the Bureau of Mines/Selexol combined-cycle power plant. The chemical composition of the raw water[44] is shown in Table 60. The analysis represents the upper limits of the concentration rangeof the constituents in 95 percent of the fresh surface water in the United States. The water balance for the process is shown in Table 61.

Raw water is initially pumped to a storage reservior which also serves as a flow equalizer and a clarifier for removal of naturally occurring suspended solids. The water withdrawn from the storage pond is split into two streams, one of which is conveyed to the cooling system as makeup after the water has been chemically conditioned to control scaling, corrosion, and fouling. The second stream is demineralized by ion exchangers and deaerated to remove dissolved oxygen and carbon dioxide. The demineralized water is conveyed to the various boilers and waste heat recovery systems for steam generation.

Table 59. POTENTIAL CONTROL TECHNOLOGY FOR COAL CONVERSION WASTEWATER

Pollutant		Treatment Method	Limitations	Applicable Concentration Range	Level After Removal	Industry Usage
Hexavalent chromium	(1)	Reduction to chromium (III) with SO_2, $NaHSO_3$ or $FeSO_4$ at pH below 3 followed by precipitation at pH 8.5-9.5	Reduction is not complete. Rate depends on pH, reducing agent and contact time	100-500 mg/l	0.05-1 mg/l	Common
	(2)	Adsorption on anion exchanger	Recovery process	$<$ 200 mg/l	Removal to 0.05 mg/l	Moderate
	(3)	Evaporative recovery	Recovery process	$>$ 500 mg/l		Not Practiced
Cyanide	(1)	Oxidation to cyanate with chlorine at pH above 10		100-1000 mg/l		Not Practiced
	(2)	Oxidation to cyanate with chlorine at pH above 10 followed by acid hydrolysis to CO_2 and N_2 at pH 2-3	Increases total dissolved solid and treatment costs		Removal to 0.1 mg/l	Moderate
	(3)	Decomposition to CO_2 and N_2 via cyanate with chlorine at pH 8-8.5	Toxic cyanogen chloride may be liberated, a large excess of chlorine is required	100-1000 mg/l	Complete removal	Common
	(4)	Electrolytic decomposition to CO_2 and N_2 via cyanate at 200°F	Interference by sulfate	$>$ 1000 mg/l	0.1-0.4 mg/l after 7-18 days	Common
	(5)	Ozonation	Only partial decomposition to CO_2 and N_2	100-1000 mg/l	Complete removal	Moderate

Table 59. (Continued)

Pollutant	Treatment Method	Limitations	Applicable Concentration Range	Level After Removal	Industry Usage
	(6) Storage of waste at ambient temperature	Incomplete treatment	100-1000 mg/l	70-90% reduction after 4-8 days storage	Practiced by coking industry
	(7) Precipitation as ferro ferricyanide with iron salt	Incomplete treatment	100-1000 mg/l	0.5-12.3 mg/l depending on the concentration in influent	Not practiced
	(8) Adsorption on activated carbon	Incomplete treatment	100-1000 mg/l	0.6-1.4	Not practiced
	(9) Biological treatment		> 100 mg/l	70-90% removal	
	(10) Oxidation with hydrogen peroxide to cyanate (Kastone process)	Proprietary information	100-1000 mg/l		
Fluoride	(1) Precipitation with lime as calcium fluoride at pH 11	Slow rate of precipitation	720 mg/l	10-20 mg/l	Common
	(2) Coagulation by alum	Applicable only to low hardness water	<20 mg/l	Removal to 1 mg/l	Not practiced
	(3) Adsorption on hydroxylapatite bed	Presence of chlorine increases cost of bed regeneration	<20 mg/l	0.5-1.5 mg/l	Water treatment

Table 59. (Continued)

Pollutant		Treatment Method	Limitations	Applicable Concentration Range	Level After Removal	Industry Usage
	(4)	Adsorption on aluminum saturated cation exchanger	Expensive	<20 mg/l		Not practiced
	(5)	Adsorption on activated alumina bed	4% of bed is lost in each re-generation cycle	<20 mg/l	Removal to 1 mg/l	Not prac-ticed-water treatment technology
Iron (II)	(1)	Oxidation to Fe(III) by aeration followed by precipitation as $Fe(OH)_3$ at pH 7			Below 0.5 mg/l	Common
	(2)	Oxidation to Fe(III) by chlorine followed by precipitation as $Fe(OH)_3$ at pH 7			Removal to 0.5 mg/l	Moderate
	(3)	Deep well disposal		Concentrated waste		Practiced by steel industry
Tar and Oil	(1)	Gravity separation	Does not remove emulsion	Primary treatment	60-99% of floated oil	Common
	(2)	Centrifugation		Secondary treatment		Common
	(3)	Heating		Secondary treatment		Not practiced

Table 59. (Continued)

Pollutants		Treatment Method	Limitations	Applicable Concentration Range	Level After Removal	Industry Usage
	(4)	Precoat filtration		Secondary treatment	5-20 mg/l	Common
	(5)	Coagulation or demusification with chemicals, followed by air flotation or settling	Addition of alum forms sludge which are difficult to dewater	Secondary treatment	50-90%	Common
	(6)	Biological treatment		Secondary treatment	Removal to 15 mg/l	Common
pH Control	(1)	Neutralization with chemicals	Cost depend on buffer capacity of waste		Neutral pH	Common
Phenols	(1)	Benzene-caustic dephenolization process		> 500 mg/l	210-240 mg/l	Common
	(2)	Counter-current extractor (Chemizon process)		> 500 mg/l	Removal to 100 mg/l	Common
	(3)	Pulsed column extractors		> 500 mg/l	Removal to 30 mg/l	Common
	(4)	Phenosolvan dephenolization (Lurgi)		> 500 mg/l	4.5-10 mg/l	Common
	(5)	IFAWOL dephenolization (Carl still)		> 500 mg/l	Removal to 40 mg/l	Common
	(6)	Light oil extraction (Koppers)		> 1500 mg/l	10-30 mg/l	Common
	(7)	Incineration		> 7000 mg/l	Complete	Not practiced

Table 59. (Continued)

Pollutants	Treatment Method	Limitations	Applicable Concentration Range	Level After Removal	Industry Usage
	(8) Oxidation ditch		50-500 mg/l	99%	Common
	(9) Trickling filter		50-500 mg/l	98%	Common
	(10) Activated sludge		50-500 mg/l	99%	Common
	(11) Oxidation with ozon	Expensive when waste contains more than 5 mg/l	<50 mg/l	Removal to 0.35 mg/l	Limited usage
	(12) Activated carbon bed		<50 mg/l	Removal to 0.005 mg/l	Common
	(13) Oxidation with chlorine		<50 mg/l		Common
Dissolved Solids	(1) Concentration and evaporation		>50000 mg/l	Complete removal	Not generally in use-de-salination technology
	(2) Reverse osmosis	Efficiency depends on membrane condition		50-95%	Not prac-ticed-de-salination technology
	(3) Distillation			60-90%	Not prac-ticed-de-salination technology

Table 59. (Continued)

Pollutants		Treatment Method	Limitations	Applicable Concentration Range	Level After Removal	Industry Usage
Suspended Solids	(1)	Sedimentation			90-95%	Extensive
	(2)	Chemical coagulation			95-99%	Moderate
	(3)	Filtration			95%	Not Practiced-water treatment technology
Ammonia	(1)	Stripping at pH of 10-11	Water adsorbs CO_2-may lead to scale formation		50-90%	Extensive
	(2)	Biological nitrification	Nutrient may be required	$<$1250 mg/l	Removal to 2 mg/l	Extensive
	(3)	Ion exchange			80-95%	Not practiced
Chloride	(1)	Deep well injection		$>$60 g/l	Ultimate disposal	Moderate
	(2)	Evaporation ponds	Limited by geographical location and land availability		Complete removal	Extensive
Sulfide	(1)	Biological oxidation to sulfate			Complete oxidation	
Thiocyanate	(1)	Biological oxidation	Excess ammonia lower efficiency		90%	Moderate
	(2)	Ion exchange	Excess ammonia lower efficiency		90%	Not practiced

WATER AND WASTE WATER TREATMENT FOR THE BUREAU OF MINES/SELEXOL PROCESS

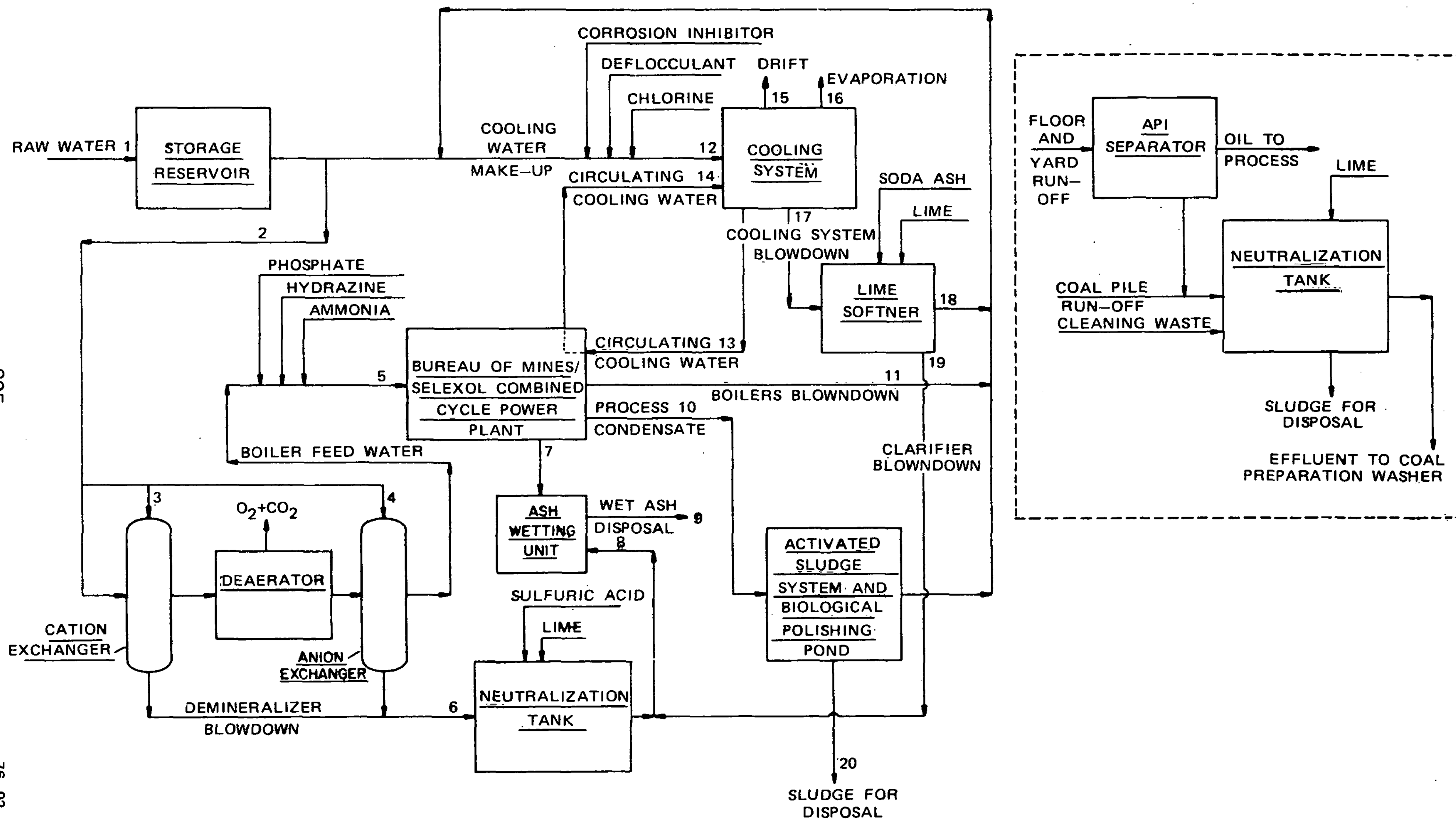

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FIG. 45

Table 60. RAW WATER ANALYSIS

pH	7.6	
Total dissolved solids	400	mg/l
Bicarbonate (HCO_3^-)	180	mg/l
Sulfate (SO_4^{2-})	90	mg/l
Chloride (Cl^-)	170	mg/l
Nitrate (NO_3^-)	4.2	mg/l
Calcium (Ca)	52	mg/l
Magnesium (Mg)	14	mg/l
Sodium and Potassium (Na, K)	85	mg/l
Iron (Fe)	0.7	mg/l
Silica (SiO_2)	8.8	mg/l
Dissolved Oxygen (O_2)	9.8	mg/l
Ammonia (NH_3)	2.5	mg/l
Specific conductivity at 25°C	1.1×10^{-3}	mho

Table 61

WATER BALANCES FOR THE BUREAU OF MINES/SELEXOL PROCESS

Stream No.	Description	Flow lb/hr
1.	Raw water input	2,635,784
2.	Raw water to demineralization unit	611,435
3.	Acid regenerant and rinse water	14,604
4.	Alkaline regenerant and rinse water	14,604
5.	Boiler feed water to process	582,227
6.	Demineralizer blowdown	29,208
7.	Ash from gasifier	114,132
8.	Water for ash wetting	52,704
9.	Wet ash for disposal	166,836
10.	Process condensate	174,686
11.	Boilers blowdown	40,906
12.	Cooling water makeup	2,910,280
13.	Cold cooling water	108,546,280
14.	Warm cooling water	108,546,280
15.	Drift losses	108,546
16.	Evaporation losses	2,099,165
17.	Cooling system blowdown	702,569
18.	Softened Water	679,073
19.	Clarifier blowdown	23,496
20.	Biological treatment unit blowdown	8,734

The blowdown from the demineralizer consists of the waste regenerants and rinses from both the cation and anion resins. These streams are combined and conveyed to a neutralization unit where the pH is adjusted to within the range of 6.0 to 9.0, on a batch basis, by the addition of sulfuric acid or sodium hydroxide as required. The neutralized waste will be used to wet the ash from the gasifier prior to its disposal.

The blowdowns from the boilers and the waste-heat recovery systems are high-quality waters and, therefore, can be used as a supplement for almost every water input to the plant. These waters are combined and conveyed to the cooling system as part of the cooling water makeup.

The cooling water blowdown is of the same chemical quality as the water circulating in the condenser cooling system. Limits on the water quality in that system are governed by the need to remain below concentrations at which scale forms in the condenser. The blowdown is lime softened and recycled back to the cooling system after clarification. The clarifier blowdown will also be disposed of with the coal ash.

The water condensate from the gas cleanup system is highly polluted containing a variety of organic and inorganic compounds. Some of the pollutants, such as phenols and cyanides, are highly toxic to living organisms. However, indications are that the concentration of the toxic compounds is below the tolerance limits of the micro-organism population used in biological based treatment processes. The water condensing from the Selexol cleanup system is treated in a two-stage biological treatment unit. The first stage is an activated sludge system whereby zoogleal bacteria and other aerobic organisms are mixed with the wastewater and aerated. The activated sludge is subsequently separated from the treated waste by sedimentation and the treated effluent is conveyed to a polishing aeration basin, where residual organic matter is further biodegraded. The sludge from both stages is collected and a portion is returned to the aeration basin as required to maintain biological activity.

The rest is sent to the ash disposal area for drying and disposal. The purified water from the polishing-settling basin is filtered and sent to the cooling system. It should be indicated that the reuse of process condensate as cooling water may cause odor problems since the chlorination of the water effluent may result in the formation of highly odorous chlorophenolic compounds. The biological treatment unit can also be used to treat domestic wastewater and any other waste stream containing biodegradable organic matter. It may be necessary to add nutrient elements to the wastewater influent if such deficiency occurs in order to maintain the efficiency of the process and to prevent process upset due to the high load of toxic substances.

The treatment of periodic wastes which are not connected with coal gasification or electrical power generation can be accomplished in a single treatment system. The wastewater effluents from equipment cleaning operations, coal pile, floor and yard drainage are collected in a storage pond. Floor and yard runoffs are usually passed through an API oil separator located ahead of the storage pond to remove nonemulsive oil. The disposal of the combined waste can be accomplished by evaporation if the land is inexpensive and the rate of evaporation is higher than the rate of precipitation. Alternatively, the wastewater effluent is neutralized with lime to a pH of 6 to 9 and the water is clarified to remove precipitated salts and suspended solids. It may be necessary to add coagulant in order to remove emulsive oil and colloidal suspensions. The water effluent can be used in the washing operation of the coal preparation section of a nearby mine. The solid effluent from the clarifier is disposed of with other solid wastes.

Chemical Treatment of Circulating Cooling Water

Cooling waters are treated to inhibit scale formation, corrosion, and fouling. Scale is an adherent layer of foreign material formed on the water side of the heat exchanger surface. The scale acts as an insulator reducing the rate of heat transfer, and consequently, the thermal efficiency of the process. In addition, scale formation restricts the rates of water flow in the condensers by increasing the hydraulic friction of the tubing.

Scale is formed as a result of precipitation of inorganic salts which occur in all natural water. Because of the continuous loss of cooling water due to evaporation and the addition of makeup to supplement these losses, the concentration of dissolved solids in the circulating cooling water gradually increases. If the solubility of any combination of cations and anions exceeds their solubility product, the salt will precipitate. The formation of scale can be controlled by increasing the solubility of the salts or by precipitating them as sluge and removing the sludge with the blowdown. The solubility of the salt can be increased by lowering the active concentrations of the ions. For example, the concentration of the carbonate ion can be reduced by lowering the pH of the water. Alternatively, the addition of chelating agents which form complexes with calcium reduces the concentration of the free calcium ion. By lowering the concentration of the ions the cooling system can be operated at a higher concentration cycle and consequently, with smaller blowdown.

Precipitation of scale forming salts as sludge is achieved by adding dispersants which prevent the agglomeration of solid material. Recent developments have centered around the use of polyelectrolytes which adsorb onto the surface of the growing salt crystals and enter the crystalline structure. This prevents deposition of a uniform adherent scale causing layer. Instead, irregularly shaped crystals are formed which are easily sheared or broken off from the surface scale.

Chemical treatment is used most often for corrosion control. Chromates and polyphosphates are used either separately or together to inhibit corrosion in cooling water recirculating systems. Chromate, being a strong oxidizing agent, forms a thin passive layer of oxides on the anodic surface which protects the metal against further oxidation. When used alone, chromates require concentrations above 700 ppm as Na_2CrO_4, otherwise corrosion may be even more severe than if no inhibitor had been used. If, on the other hand, chromates are used in combination with polyphosphate, the concentration of sodium chromate required is approximately 20 ppm. However, the pH of the cooling water must be carefully controlled to prevent precipitation of calcium phosphate or calcium carbonate. Other anodic inhibitors are silicates, ferrocyandies, and nitrites. Cathodic inhibitors include zinc, nickel, manganese, and trivalent chromium salts. These inhibitors are also used in combination with chromates and polyphosphates.

Fouling refers to the deposition of foreign matter on process equipment surfaces. Fouling can result from deposition of inorganic matter such as silt and clay or can be caused by algal and bacterial growth. The latter is by far the most serious source of fouling. Fouling is most commonly controlled by chlorination, usually in combination with nonoxidizing biocides such as thiocyanates, copper salts, or chlorinated phenolic compounds. The deposition of inorganic suspended solids is controlled by dispersants such as organic polymers which prevent agglomeration and subsequent settling.

Boiler Feedwater Treatment

The treatment of water for the purpose of making boiler feedwater can be viewed as a two-step process. The first is the external treatment whereby the raw water is demineralized by ion exchangers, reverse osmosis, or softening to lower its dissolved solids content. The second step is the internal treatment involving the addition of various chemicals to the water to inhibit scale formation and corrosion. Scaling is controlled by the same methods used for cooling water, that is, either by precipitating the scale forming cations as a sludge, usually as salts of phosphate, and removing the sludge with the blowdown, or by chelating these ions with complexing agents such as EDTA to increase their solubility. Corrosion is controlled by chemical deaerators which are essentially strong reducing agents. These compounds react with dissolved oxygen to form inert and noncorrosive products. Sodium sulfite is usually used in low-pressure boilers but not in high-pressure boilers because it is oxidized to sulfate, an undesirable component in high-pressure boilers. Oxygen corrosion in high-pressure boilers is controlled with hydrazine which decomposes upon reacting with dissolved oxygen to water and inert nitrogen.

Cost Estimates For The Water System of the BuMines/Selexol Process

This section discusses cost estimates for the production of process and cooling water, and for the treatment and reuse of wastewater for the BuMines/Selexol integrated combined cycle power plant. The cost estimates were determined from published reports dealing with water and wastewater treatment technologies, and with the capital and operating costs of such technologies. This is only a preliminary study which lacks detailed designs of the various processing units involved in the treatment of water and wastewater, and therefore, the costs should be considered only as first estimates. The calculated values were determined from cost estimates of units processing similar flow rates and chemical compositions of water and wastewater. Very often, however, such information was not available and the cost estimates were determined from published data which have been extrapolated to adjust for differences in both flow rates and chemical compositions. The cost estimates, so determined, were then revised to adjust for escalation using the Chemical Engineering Index. The results are listed in Table 62 as the estimated capital costs and annual operating and maintenance costs for mid-1975.

In calculating the cost estimates, it was assumed that the lime softening system includes a clarifier, a rapid sand filter, and a slugde removal system. The demineralizer was assumed to include separate cation and anion exchangers each consisting of four columns, one of which is being regenerated at all times. The raw water storage system includes a pumping station at the raw water source and a storage pond with a 30-day storage capacity. The latter was assumed to be paved with reinforced concrete to prevent losses due to water infiltration. In calculating the cost estimate for the cooling water treatment system, it was assumed that the principal cost is that associated with the chlorination of the water effluent from the biological treatment system. This effluent was assumed to have a 5 ppm phenol content and the chlorine

TABLE 62

CAPITAL AND ANNUAL OPERATING COSTS OF A WATER SYSTEM FOR THE BuMINES/SELEXOL PROCESS

Unit	Capital Costs	Annual Operating Costs
Lime softening system	$ 713,000	$ 152,000
Demineralizer	$1,024,000	$ 429,000
Raw water storage system	$3,312,000	$ 5,000
Cooling water treatment system	$ 50,000	$ 392,000
Neutralization system	$ 24,000	$ 3,000
Activated sludge system	$ 500,000	$ 46,000
Total	$5,623,000	$1,027,000

requirement was based on total destruction of the phenol to prevent odor problems. The neutralization unit was assumed to be completely automated, neutralizing water effluent of pH 4 with lime. The neutralized slurry is conveyed to the ash disposal system for ash wetting. The activated sludge system consists of an aeration unit, clarifier, and an aerated polishing pond with a 24-hour capacity. The latter is also paved with reinforced concrete to prevent water infiltration.

SOLID RESIDUALS

Summary of Solids Produced

Ash - Only first-generation (low-temperature) gasifiers such as the BuMines gasifier produce ash, because they operate below ash fusion temperatures (1500°F). The ash is a refractory material present in the coal and has no fuel value. Ranges of typical ash composition from boilers are given in Table 63.

Slag - Slag is produced by second-generation (high-temperature) gasifiers, because they operate at slagging temperature (2200°F) and cause the mineral matter to melt. The slag is quenched and removed from the gasifier and may contain some dissolved gases. A typical gasifier slag composition however, would probably be quite similar to a typical gasifier ash composition.

Spent Limestone (Scrubber Sludge) - If a non-regenerable flue gas scrubber is used with any of the systems to reduce SO_2 emissions, a scrubber sludge is produced. If a lime/limestone scrubber is used, the scrubber sludge consists of $CaSO_3$ and $CaSO_4$. This is dewatered and stabilized by conversion to $CaSO_4$ before disposal.

Spent Dolomite - Spent dolomite is produced in the CONOCO desulfurization processes. The spent dolomite is removed from the regenerator and consists of $CaCO_3 \cdot MgO$ and $CaS \cdot MgO$. This is further treated with H_2O and CO_2 to convert it completely to inert $CaCO_3 \cdot MgCO_3$ which is then disposed of.

Elemental Sulfur - In all the systems utilizing Claus sulfur recovery with a regenerable scrubbing process, elemental sulfur is produced. The sulfur is typically 99 percent pure, and, when in solid form, is usually flaked for bulk shipment to market.

Miscellaneous - Particulates recovered from the fuel gas by particulate removal devices consist of fly ash, dust and unburned carbon. Processing steps used to concentrate SO_2 in off gases produce a solid waste consisting of Na_2SO_3, which must be oxidized to Na_2SO_4 before disposal. Other solids produced in smaller quantities, include the spent catalysts which use alumina supports on which the catalyst is impregnated. Spent iron-oxide from the Bureau of Mines and B&W iron-oxide processes has to be regenerated and stabilized before disposal.

Table 63

CONSTITUENTS OF COAL ASH[1]

Constituent	Percent
SiO_2	30-50
Al_2O_3	20-30
Fe_2O_3	10-30
TiO_2	0.4-1.3
CaO	1.5-4.7
MgO	0.5-1.1
Na_2O	0.4-1.5
K_2O	1.0-3.0
SO_3	0.2-3.2
C and volatiles	0.1-4.0
P	0.1-0.3
B	0.1-0.6
U and Th	0.0-0.1
Cu	trace
Mn	trace
Ni	trace
Pb	trace
Zn	trace
Sr	trace
Ba	trace
Zr	trace

[1]Composition is representative of a fully oxidizing conventional boiler. Residue from gasification would tend to be in a less oxidized and possibly sulfided form.

Identification of Types of Solids Produced by Water and Wastewater Treatments

Solid wastes are a major by-product of many of the processing steps involved in the treatment of water and wastewater. All water supplies contain varying amounts of naturally occurring suspended solid matter and dissolved chemical salts. Therefore, raw water must be treated for removal of the mineral salts and suspended matter before being used in the process. Very often, such treatment produces solid wastes as by-products. The treatment of wastewater also results in the formation of solid wastes.

Solid wastes from water and wastewater treatment processes are usually referred to as sludge. They are formed by the precipitation of slightly soluble salts, or due to coagulation and subsequent sedimentation of suspended matter. They are collected and removed from the water treatment system in clarifiers as slurries with various contents of suspended solids.

The nature and composition of the sludges depend on the characteristics of the treated water and the type of treatment used. Clarifier sludge from water treatment processes could be either alum or iron salt sludge, from coagulant chemicals. Alum sludge is a bulky gelatinous substance composed of aluminum hydroxide, inorganic particles such as clay or sand, color colloids, micro-organisms including plankton, and other organic matter removed from the water. The major constituent in sludge from a lime soda softening clarifier is calcium carbonate. Other constituents which may be present are magnesium hydroxide, hydroxides of aluminum or iron, insoluble matter such as clay, silt or sand, and organic matter such as algae or other plankton removed from the water. The nature and characteristics of the excess sludge from the biological treatment system will depend to a large extent on the chemical composition of the waste and the species of micro-organisms that can climatise themselves to this type of waste. Generally, such waste will contain dead cells of bacteria and algae, partially decomposed organic matter and inert soluble and insoluble inorganics. Excess activated sludge is usually golden brown and flocculent. Uncontrolled disposal of such sludge may result in the development of septic conditions due to the decomposition of the residual organic matter by anaerobic organisms. Sludge is also formed when coal pile runoff and floor and yard drainage are neutralized. The constituents of such sludge are calcium carbonate and hydroxides of iron, aluminum, chromium, zinc and manganese. Oil may be present as well as fines of coal and dust. Sludge may also be formed as a result of the neutralization of waste regenerants and rinses from the demineralization system. Since sulfuric acid is used to regenerate the cation exchanger, calcium sulfate may precipitate due to the common ion effect.

The lime sludge from the softening unit will be mixed with the ash to wet it prior to its transport to the disposal site. The sludges from the activated sludge and demineralizer units would probably be disposed of with conventional disposal techniques. The activated sludge would be dried, usually by vacuum filtration, and then subsequently incinerated. The sludge from the demineralizer, primarily calcium sulfate, can be dewatered and disposed of in land fill.

Disposal Options and Their Implications

As with any process or power plant that produces solid waste, there are several options available for disposing of these residuals, each depending on a number of site-specific and residual-specific considerations. These options range from the sale of the residual to the storage of the residual in an environmentally acceptable manner. The storage may take the form of on-site and off-site burial or surface storage. The following deals with the power plant solid residuals, the disposal options that would likely be implemented and their implications, vis-a-vis cost and environmental considerations.

Ash and Slag - Activities in the area of ash and slag utilization probably predate those of any of the other solid residuals one might expect from low-Btu gasifiers. As a result, the area of by-product utilization is probably more advanced for ash and slag than that of any of the other solid residuals. The impetus for this developmental work was the result of the dominance of coal as an energy source from the beginning of the Industrial Revolution through the 1940's. An annotated list of references on ash utilization published in the Proceedings of the Second Ash Utilization Symposium sponsored by the National Coal Association includes an entry for a U.S. patent covering the production of alumina from coal ash which was obtained as far back as 1932.

The major use of fly ash is as a concrete additive which serves both as a mechanical filler supplementing or replacing fine aggregate and as a pozzolan supplementing or partially replacing cement. There are numerous other, quantitatively less significant, existing uses for fly ash, bottom ash, and slag. They include use in abrasive cleaning, refractories, oil well cementing, grouting, snow sanding, mine fire control, subsidence control, pipe coatings, sand blast grit, etc. Additionally, the Bureau of Mines (now ERDA) has sponsored several studies which evaluate the use of fly ash in mined-land reclamation as well as ash utilization from lignite gasification. Most significantly, the cost per acre for mined-land reclamation can be reduced by a factor of 3 to 5 compared with the conventional methods.[45] It should be noted, however, that the economics of producing a commercial product from ash or slag must be examined very carefully in comparison with the storage or fill alternative, since the necessary equipment and operating staff required to convert the ash to a commercial product can significantly increase the cost of ash disposal.

In 1971, 12 percent of the fly ash, 16 percent of the bottom ash, and 75 percent of the slag produced in the United States were utilized in the applications previously mentioned.[46] As can be seen from these figures, especially those for fly and bottom ash, the major portion of the ash produced in the United States ultimately ends up in disposal areas. These disposal options generally consist of ponding and landfilling.

With ponding, ash is transported in the form of a slurry either to an off-site or on-site ash settling pond, where the ash settles out of the slurry and the water is removed via weirs or standpipes, thus allowing continuous operation of the pond unti it is full of ash. The cost for this method of disposal is in the range of $0.56 to $2.04 per ton of ash.[46] This figure includes the operating costs which incorporate transport and other pond operation expenses. A nationwide survey[47] conducted in 1970 of 22 utilities disposing of ash in off-site ponds showed that it was costing $0.034 to $1.23 per ton (average of 25 plants equal to $0.51 per ton) to sluice ash to the disposal area. Trucking the ash off-site was being done at a higher cost, in the range of $0.12 to $1.49 per ton, or at an average of $0.57 per ton for the 10 plants that utilized truck hauling.

The cost of constructing the pond would depend on a number of site and design related factors, e.g., the nature of the soil at the pond location, the size of the pond and the type of liner used. The cost for a five to ten acre pond with no providions for drainage can range from $5,000 to $20,000 per acre for a pond with a clay or stabilized pozzolan base lining.[48] On the other end of the scale, the cost of a drained pond with a plastic liner can range from $25,000 to $30,000 per acre.[48]

Generally speaking, the viability of this alternative is a function of the availability of suitable sites at or in close proximity to the plant.

In the case of the Bureau of Mines Gasifier and Selexol Unit integrated power plant, production (392×10^3 tons/year based on a 0.70 load factor) of bottom and fly ash would require about 360 acres of storage for ponding the ash associated with 20 years of production, if the ash is ponded to a depth of 10 feet and compacted to a density of 100 lb/ft^3.

Some plants do not have adequate space for a disposal pond and must resort to transporting the ash to a land disposal site. In some instances this site might be within the plant boundaries, but this is usually not the case. Care must be taken in the selection of these sites, since there appears to be some potential for the leaching of contaminants from the ash causing problems with groundwater. Although there are no verified instances of groundwater pollution due to leaching of contaminants in fly ash used in landfills, greenhouse studies have shown that the application of fly ash to soils does increase the availability of boron, molybdenum, potassium, zinc and phosphorous.[46,49] Also, the constituents of ash from a gasifier may behave diffferently.

As is the case with ponding, the economics of a landfill can vary widely depending on the distance to the disposal site, the amount of ash to be disposed of, the type of transportation used and the landfilling technique used. The reported range in cost for operating a landfill is from $0.56 to $2.24 per ton, not including the cost of reclamation.[46] Significantly, studies sponsored by the Bureau of Mines (ERDA) have shown a potential benefit to plant growth through the controlled addition of fly ash to agricultural soils.[50] Data developed at the Morgantown Energy Research Center show that approximately 200 tons of fly ash can, on an average, reclaim an acre of surface mined land. Landfilling spent surfaces coal mines might provide a utility, assuming it is conveniently situated, with a convenient and environmentally acceptable disposal alternative. Using the figure developed at the Morgantown Research Center, it should be noted that the fly ash associated with one year of operation of a Koppers-Totzek gasifier, of the size addressed in this study, could have reclaimed approximately three percent of the land disturbed by surface mining for coal in the Central States in 1970.[45]

<u>Sulfur</u> - With the advent of environmental regulations limiting the amount of sulfur that can be discharged to the environment, in particular the discharge of sulfur oxides resulting from the combustion of fossil fuels containing sulfur, quantities of sulfur are becoming available that will far outstrip the demand. As a result, a number of government and private research groups are currently exploring new applications for elemental

sulfur. These applications generally fall into three major groups: (1) sulfur containing fertilizers, (2) sulfur based construction and paving materials, and (3) sulfur foams.

Although about 50 percent of the sulfur presently consumed goes into fertilizer production, the Sulfur Institute foresees an annual added potential of 2.8 million tons per year of sulfur as a crop nutrient in the United States and Canada. In addition to its use in fertilizer as a crop nutrient, sulfur is currently being studied as a coating to urea for its application as a slow-release fertilizer. Since it is estimated that the sulfur coated urea can be produced for only about 35 percent more than the cost of regular urea, it would be much cheaper than other controlled release products now on the market.[51]

With regard to the utilization of sulfur as a road paving material, it has been used as a substitute for limestone as the bulk aggregate. Shell Canada Limited, has been experimenting with the addition of molten sulfur to hot-mix asphalt paving materials. They claim that this addition increases the mix workability so that the mix may be placed without densification. As the mix cools, the sulfur solidifies and imparts a high degree of mechanical stability to the mix so that high quality mixes may be produced from poorly graded aggregates and even one-sized sands. By incorporating sulfur in asphalt mixes, high quality paving materials can be manufactured using inexpensive, poorly-graded sands. These sand-asphalt sulfur mixes may be used to construct road bases, surfaces, curbing, and sidewalks to build platforms over weak subgrades and for castings of various shapes.

A spray material containing sulfur, talc, fiberglass, and dicyclopentadeiene has been used by the Bureau of Mines to construct block buildings as part of a demonstration program. In the demonstration, the blocks were surface bonded together for structural stability by spraying with the mixture. This demonstration program was an attempt to show the feasibility of sulfur in coatings as well as in structural materials.

Sulfur foam, as a subsurface insulation, could potentially have an even higher volume highway application than its use as an aggregate. Sulfur foam may some day be widely used as roadway or runway subsurface insulation, either to protect the road subbase from freezing or to protect a permafrost subbase from thawing. In either case, the foam would be buried approximately one foot below the surface, deep enough not to be affected by the daily temperature cycling on a surface. Sulfur foam might also be used as subbase insulation for homes or cold storage warehouses.

Miscellaneous Solids - The sodium sulfite resulting from the purge of the Bureau of Mines Iron Oxide cleanup system is a compound that has already found some commercial application. Since it s a compound that is easily oxidized, it can and is being used where a gentle reducing agent is desired. These applications include its use as a bleach for wool and silk; as an antichlor after the bleaching of yarns, textiles and papers; as a preservative for food stuffs; and to prevent raw-sugar solution from coloring upon evaporation. This material also has wide application in the preparation of photographic developers, as a preventative of the oxidation of hydroquinone and other agents. To a smaller degree, it has found acceptance in the field of medicine as an antiseptic and as an antizymotic for internal use. Recent interest in sodium sulfite has centered around the discovery that its addition to boiler feedwater will remove oxygen from the water, and thus help prevent corrosion and scale formation. In general, the surplus of this material not utilized in the previously mentioned applications would probably be sold to the sulfate pulp mills.

The spent dolomite that is produced by the Conoco half-calcinated dolomite cleanup system might present a disposal problem. Some investigators(51) believe that the spent material will consist of a calcium carbonate which would not be a particularly troublesome material to dispose of by storage or landfilling. However, the calcium sulfide inner core component liberates hydrogen sulfide gas very slowly on exposure to moist air, creating an odor problem and ultimately yielding sulfur dioxide, sulfite, and sulfate pollutants. Calcium sulfite is, however, utilized in industry as a depilatory in the tanning industry and in cosmetics. In a finely divided form, it is employed in luminous paints.

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APPENDIX A

EQUILIBRIUM MODEL FOR COAL GASIFIERS

The equilibrium composition of solids and gases provides a good estimate for the product gas composition of certain coal gasifiers. If the gasifier operates at a high temperature (i.e. 3000 F) with the gasifier size such that there is enough residence time for reactions to go to completion and if stratification may be neglected within the gasifier then the equilibrium composition will provide a good estimate of the gasifier product gas composition. Examples of gasifiers for which equilibrium is a good assumption are the Koppers-Totzek and Kellogg molten salt gasifiers. It should be emphasized that for gasifiers with strong stratification and limited residence times, e.g., fluid beds, and for gasifiers with low temperatures and short residence times, e.g. BCR's upper stage, the product gas composition is kinetic limited and not equal to the equilibrium composition. The equilibrium composition does, however, provide an important guideline for environmental studies. If the pollutant equilibrium concentration is much lower than the concentration in the product gas, then catalytic acceleration of reactions involving the pollutants toward their equilibrium level can reduce the pollutant concentration to an acceptable level.

Computer programs to calculate the equilibrium composition of mixture of gases or gases and a solid have now been in wide use for many years following the pioneering work of Brinkley (52-56), who developed very elegant computational procedures for arbitrary mixtures of elements to solve the basic thermodynamic equations developed by Gibbs (57). These computer programs were first used in the late 1950's, with Brinkley as a consultant, and have been updated and improved since then. Recently the necessary modifications were made to input coal, char, steam, transport gases and air to the model and to have it compute the equilibrium composition. Included are solid phase ash and carbon as well as an arbitrary number of gas compounds and the option to specify set yields (for kinetic limited products). In Gibbs' model the solids are assumed to be finely divided and dispersed among the gases--surface effects are not included. The gases are assumed to follow the perfect gas law.

The input to the equilibrium program includes the atoms per unit weight of each element and either the temperature and pressure, the enthalpy and pressure, the entropy and temperature, the enthalpy and entropy, the density and pressure, the temperature and density or the internal energy and density. The unspecified thermodynamic properties are calculated as well as the gas mixture molecular weight and mole fractions of the mixture of gases and the solid ash and carbon weight concentrations. The list of compounds to be considered is specified as input and may be, in principle, arbitrarily long. Of course, the computer time goes up - quadratically - as the number of compounds.

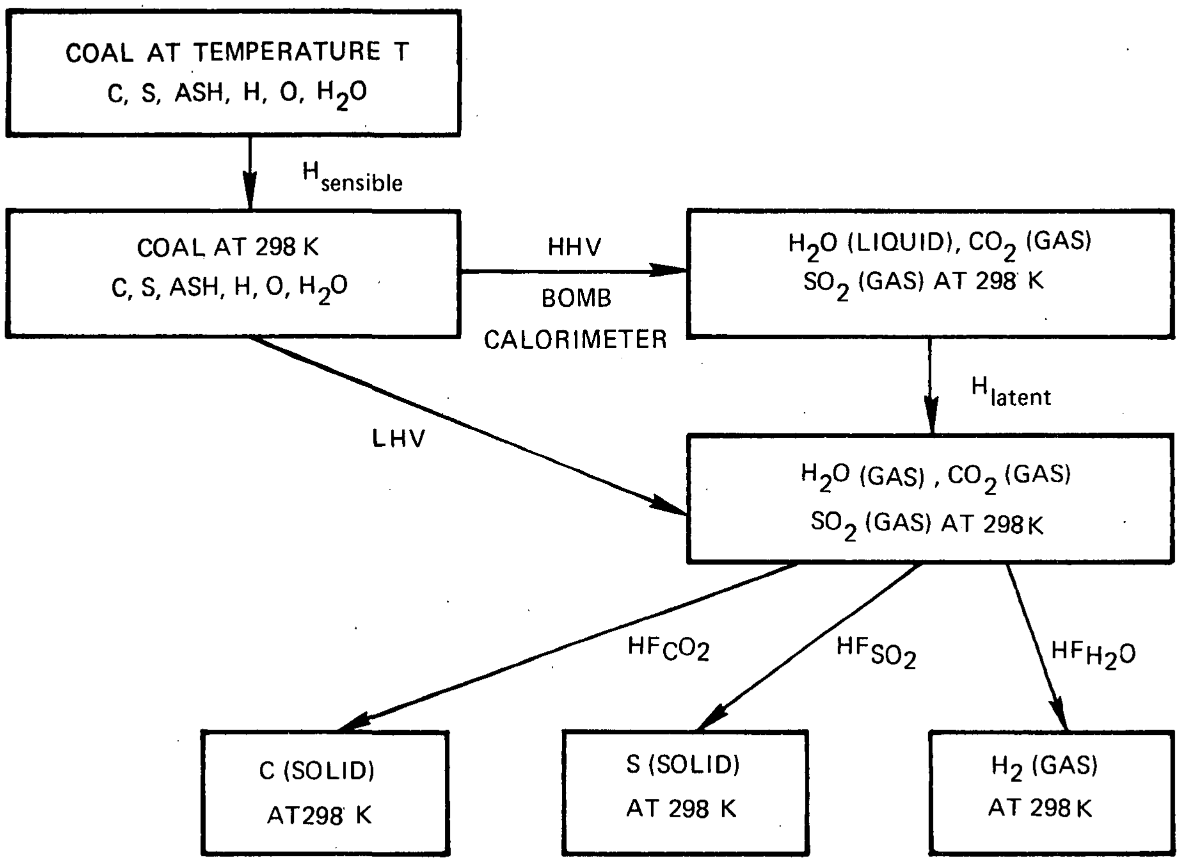
In simulating coal gasifier operation, the input quantities are coal, air (or oxygen), steam and possibly transport gases. The enthalpy of the air and transport gases can be calculated easily using the same reference states (C (solid), H_2 (gas), N_2 (gas), O_2 (gas) etc. have zero enthalpy) and reference temperature (298 K) as for the product gas using heat of formation and specific heat curves based on JANAF data. Steam enthalpies can be obtained from the literature[58] and converted to the reference temperature used in the JANAF tables.

Coal enthalpies involve a slightly more complicated procedure. A heating value for the coal studied may be determined from a bomb calorimeter test of the coal. Alternatively a version of Dulong's formula with appropricate coefficients for the coal can be used. If the coal is heated prior to its entry into the gasifier, then the specific enthalpy must be determined by tests on the coal. Specific note should be made as to whether the coal is superheated so that the energy cost of vaporizing the moisture in the coal is accounted for external to the gasifier. Finally, the specific heat and higher heating value of the coal must be converted to equivalent enthalpies for C (solid), ash (solid), S (solid), H_2 (gas) and O_2 (gas) to be consistent with the other data. This is done following the scheme in Fig. 46. The bomb calorimeter test results in products of H_2O (liquid), CO_2 (gas) and SO_2 (gas) at 298 K as well as ash (solid) and excess O_2 (gas). After accounting for the latent heat of the water and converting the higher heating value (HHV) to a lower heating value (LHV) the heats of formation of CO_2, SO_2, and H_2O (all gases) may be computed using the JANNAF data heats of formation. Thus the total enthalpy of the coal (with respect to the reference temperature and reference states used in the JANNAF data) equals the sensible heat plus the higher heating value of the coal less the latent heat less the heat of formation of CO_2, SO_2, and H_2O. It has been noted that the total enthalpy is not zero because of the specific heat and because of the energy contained in exceedingly complex coal carbohydrates' chemical bonds. The question of what enthalpy should be used for char is best

FIG. 46

FLOW CHART FOR COAL ENTHALPY CONVERSION

SCHEME FOR CONVERTING COAL SPECIFIC ENTHALPY PLUS HIGHER HEATING VALUE TO ENTHALPIES OF C (SOLID), ASH (SOLID), S (SOLID), H_2 (GAS) AND O_2 (GAS)



$$H_{total} = H_{sensible} + HHV - H_{latent} - HF_{CO_2} - HF_{SO_2} - HF_{H_2O}$$

OR

$$H_{total} = H_{sensible} + LHV - HF_{CO_2} - HF_{SO_2} - HF_{H_2O}$$

WHERE

$HHV = LHV + H_{latent}$

HF = HEAT OF FORMATION

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answered by combusting a sample of the char in a bomb calorimeter. If the carbon in the char were simply fixed carbon, the higher heating value will simply be the heat of formation of CO_2. If the higher heating value exceeds the heat of formation of CO_2, then energy containing chemical bonds between carbon atoms were still present in the char. It should be noted that the variation of the higher heating value of a coal, or char, determined from bomb calorimeter tests may vary by 100 to 200 Btu/lb input.

The results of a computer model used by Koppers Co. and the UTRC model are shown in Table 64. In this case the coal temperature (160°F) and HHV, steam enthalpy (from Ref. 7) and oxidizer temperature (98 percent O_2 at 220°F) together with the composition and weight flows yielded the mixture enthalpy as well as the element weight flows. The equilibrium program then calculated the equilibrium temperature and composition of the mixture. As shown in Table 61 the predicted temperature was 85°F below the K-T model temperature. Therefore, the equilibrium model was adjusted to the K-T model specified temperature with the resultant gas composition as shown in Table 64. The agreement is very good except for the water-gas reaction components. Therefore, the water-gas shift equilibrium constant was calculated from both the mole fractions given by K-T and the equilibrium model and compared with values at that temperature (2732°F) calculated directly from the JANNAF data for Gibbs free energies. The water-gas shift equilibrium constant calculated for the K-T results is 2.62 and from both the equilibrium model and Gibbs free energies at 2732°F is 3.68. This leads to the conclusion that K-T has modified the results of an equilibrium calculation to reflect operating experience. This question has not been pursued since this study did not focus on the Koppers-Totzek gasifier.

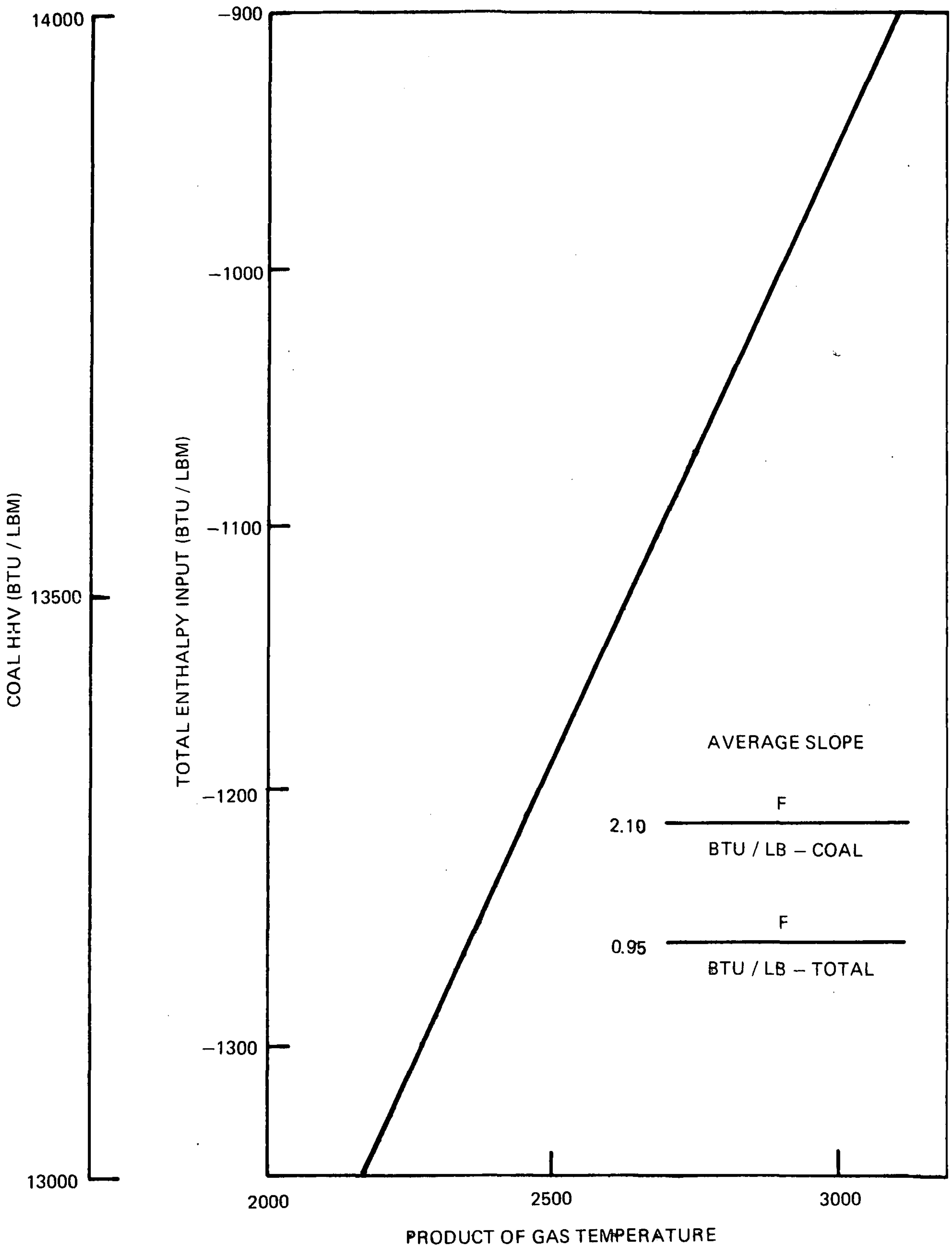
An additional point in using equilibrium gasifiers is the high sensitivity of the operating temperature to the enthalpy input--in particular to the coal heating value. Varying this parameter for the Koppers-Totzek gasifier shows the strong dependence, approximately 2.1 F.Btu/lb total (0.95 F/Btu/lb-coal) of gasifier operating temperature on coal HHV input (Fig. 47). (The coal amounted to approximately 45 percent of the weight input.) The strong dependence is typical of reducing atmospheres, as opposed to oxidizing atmospheres where a more typical dependence is 0.5 F/Btu/lb. Figure 47 illustrates that inaccuracies of 100 Btu/lb in coal HHV can lead to differences of 95°F in predicted gasifier product gas temperatures. Since the coal HHV is usually only determined to this accuracy, the resulting difference in product gas temperature should be included in system planning.

Table 64

COMPARISON OF RESULTS FROM KOPPERS-TOTZEK
AND UTRC GASIFIER MODELS

	Koppers-Totzek Model	Equilibrium Model	
		Enthalpy Specified	T Specified
T (F)	2732	2647	2732
Enthalpy (Btu/lb)	-1082	-1122	-1082
Product gas (mole fractions)			
CO	.4969	.5055	.5070
CO_2	.0631	.0538	.0522
H_2	.3179	.3093	.3078
H_2O	.1056	.1149	.1164
N_2	.0096	.0096	.0096
H_2S & COS	.0069	.0066	.0064
Others (HS, etc)	0	.0022	.0005
Others (H, etc)	0	.0001	.0001
Solids Output (weight fractions)			
Ash	.0317	.0317	.0317
C	.0171	.0171	.0170

DEPENDENCE OF PRODUCT GAS TEMPERATURE ON ENTHALPY INPUT UNDER EQUILIBRIUM



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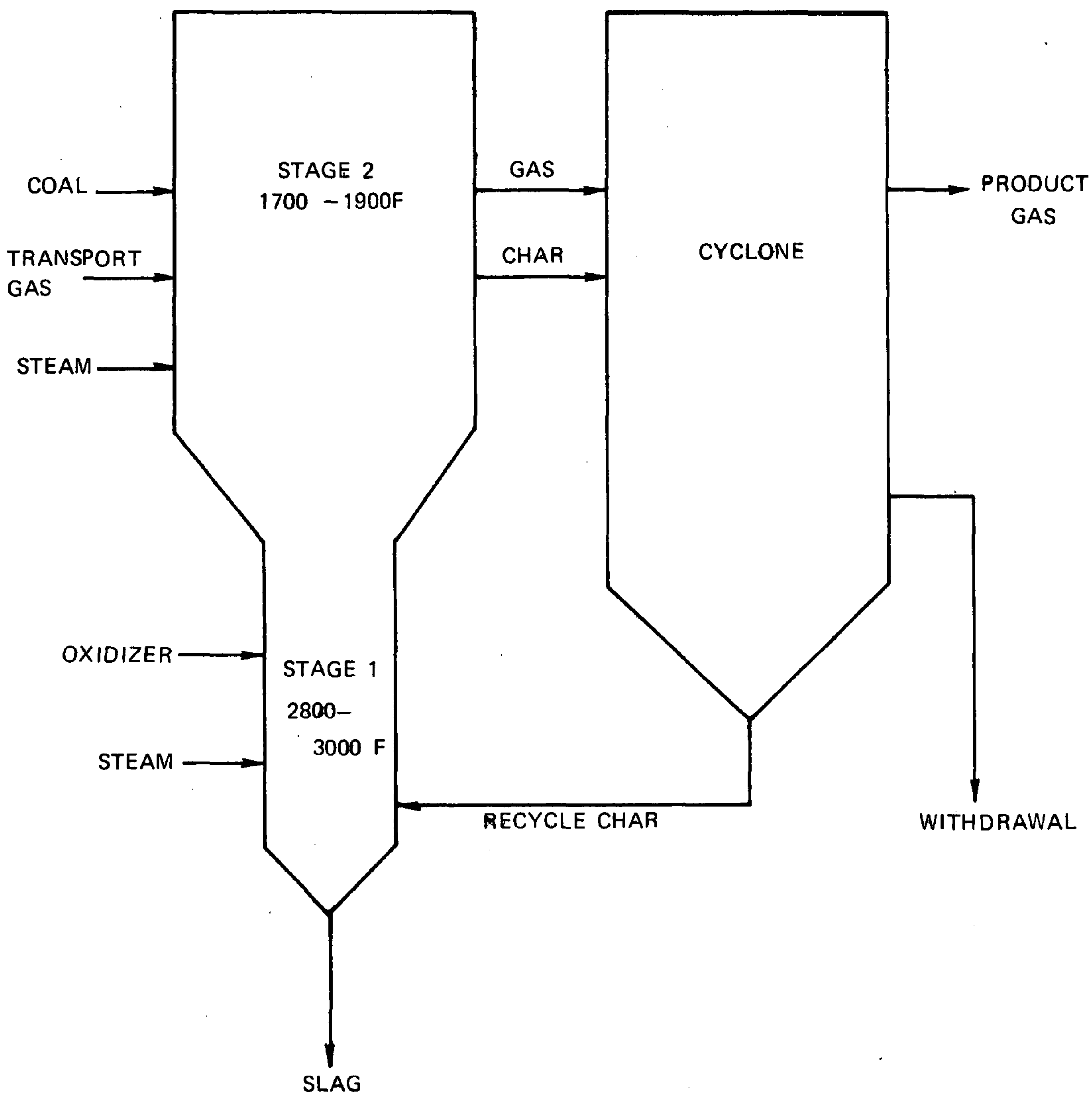
APPENDIX B

BITUMINOUS COAL RESEARCH, INC. (BCR) TWO-STAGE GASIFIER MODEL

It had been planned to use the equilibrium model described in Appendix A as a basis for developing a model of the two-stage BCR gasifier. When the basic equilibrium model was developed and tested on a single-stage gasifier, contact was made with BCR in order to obtain the data necessary to proceed with further modeling. After some preliminary discussions, BCR consented to make available their computer model of the two-stage gasifier together with advice as to its use contingent upon the approval of ERDA under whose auspices the model had been developed. ERDA's subsequent approval is a good example of the benefits of intra-government cooperation in the energy area. With the availability of the BCR model, further work on the equilibrium model was suspended and efforts focused on implementing the BCR model. Following is a description of this model and of the assumptions necessary to use it.

The model of the two-stage gasifier is based on limited experimental results of the rapid devolatilization of coal in stage 2 (the upper stage) in a 100 lb/hr Process Equipment Development Unit (PEDU). Stage 1 has not yet been tested. A diagram of the design is given in Fig. 48. Coal, carried by a transport gas, and steam are fed into Stage 2 where they encounter hot gases and char rising from Stage 1. The coal is rapidly devolativlized, with a high methane yield, at relatively low temperatures (1700-1900 F) and the resultant gases and char are swept out to a series of cyclone separators. The clean product gas, possibly with some particulate matter (char), indicated as "withdrawal" in Fig. 48 is sent to the sulfur cleanup system. The precipitated char from the cyclones is then recycled into Stage 1 of the gasifier where it is burned. An oxidizer (oxygen or air) and steam are fed in to provide oxygen to combust the char at high temperatures (2800-3000 F). The steam acts as both a temperature moderator and source of hydrogen since the methane yield in Stage 2 is strongly a function of the partial pressure of hydrogen[59,60]. Ash is slagged out of Stage 1, possibly with the aid of a limestone catalyst (not shown) and the gases and unburned char are swept up into Stage 2 completing the cycle. The steam in Stage 1 is used mainly as a

SIMPLIFIED MASS FLOW DIAGRAM FOR THE TWO-STAGE BCR GASIFIER



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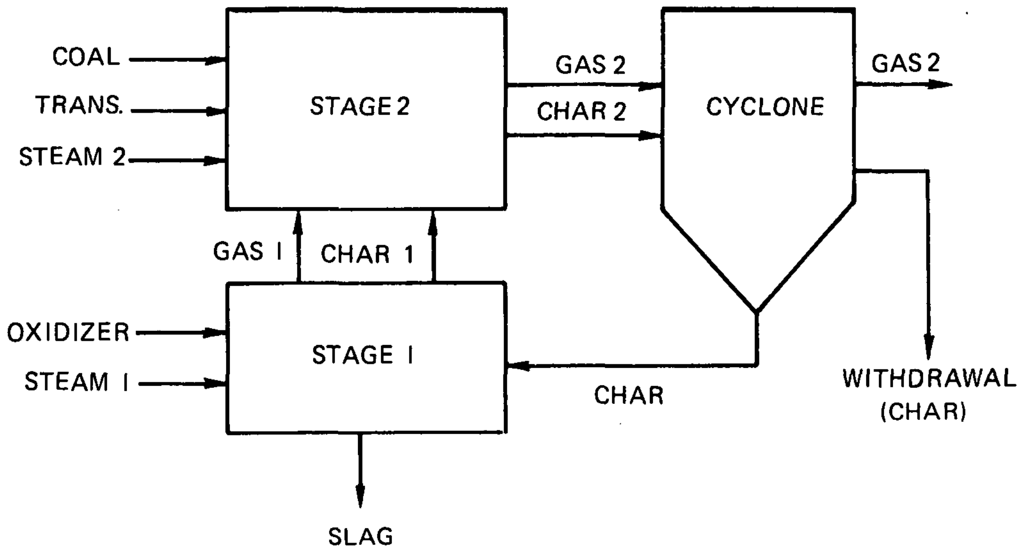
temperature modulator, with a secondary effect on the methane yield via the hydrogen partial pressure.

Experience at BCR with the PEDU has shown that the product gas produced in Stage 2 is limited by process kinetics, i.e., the gases produced are very different from the equilibrium mixture at the operating temperature. In order to estimate the product gas composition BCR specifies the yield of methane and oxidized carbon (CO, CO_2) from Stage 2 based upon empirical curves derived from both their own experiments with their PEDU and experiments of other researchers[61-63]. The amount of carbon which is combusted in Stage 1 is also specified usually at a conservative value of 60 or 70 percent. The water-gas shift reaction is the only reaction assumed to go to equilibrium in both stages. All sulfur is assumed to go to H_2S, although Foster- Wheeler has modified this slightly by introducing a specified H_2S to COS ratio.

These specifications determine algebraically a surprising amount of the composition of the gas and char streams, as is shown in Fig. 49. The gas and solid stream in Fig. 48 are the same as those in Fig. 49 with the addition of the gas and solid streams from Stage 1 to Stage 2. The term "YCH4" is the weight fraction of the C input in the COAL stream which is converted to CH_4 in Stage 2. The term "YCO" is the weight fraction of the C input in the COAL stream which is oxidized to CO and/or CO_2 in Stage 2. The C in the CHAR 1 stream from Stage 1 is assumed not to react. (This fixed carbon has survived exposure to both Stage 2 and Stage 1 at least once without reacting.) The term "WDRAWL" is the fraction of CHAR 2 which is not separated out in the series of cyclones, i.e., it is contained in the product gas. For use in an integrated power system the 1 percent or less of CHAR 2 would be removed in the subsequent fuel gas cleanup system. The term "YC" is the fraction of C in CHAR which is oxidized to CO and/or CO_2 in Stage 1. Algebraic solution of the element mass balances of the solids streams gives a complete solution for all of the solids streams in terms of the COAL stream input. Similarly, except for the water gas shift, the gas stream mass balances can be solved algebraically. It then remains to adjust the mass flows "OXIDIZER", "STEAM 1" and, if included, "STEAM 2" to achieve the desired operating temperatures in Stages 1 and 2. This is accomplished in an iterative manner by first adjusting the STEAM 1 flow rate until the desired Stage 1 temperature is achieved and then adjusting the OXIDIZER flow rate until the Stage 2 temperature is achieved. The energy balances (enthalpy in equals enthalpy out) in the two stages are the dependent functions and the flow rates of OXIDIZER and STEAM 1 are the variables for the iterative solution process.

FIG. 49

BREAKDOWN OF MASS FLOWS IF YIELD IS SPECIFIED
(MASS FLOWS, LB/HR., YCO, YCH4, YC AND WDRAWL ARE FRACTIONS)



WHERE CHAR CONSISTS OF

C IN CHAR = C IN COAL X (1– YCO – YCH4) X (1– WDRAWL)/D

ASH IN CHAR = ASH IN COAL X (1– WDRAWL)/D

SLAG CONSISTS OF

ASH IN SLAG = ASH IN COAL X (1– WDRAWL) X YC/D

CHAR 1 CONSISTS OF

C IN CHAR 1 = C IN COAL X (1–YCO – YCH4) X (1–WDRAWL) X (1– YC)/D

ASH IN CHAR 1 = ASH IN COAL X (1– WDRAWL)(1–YC)/D

CHAR 2 CONSISTS OF

C IN CHAR 2 = C IN COAL X (1– YCO–YCH4)/D

ASH IN CHAR 2 = ASH IN COAL/D

WITHDRAWAL CONSISTS OF

C IN WITHDRAWAL = C IN COAL X (1–YCO –YCH4) X WDRAWL/D

ASH IN WITHDRAWAL = ASH IN COAL X WDRAWL/D

WHERE D = 1–(1–WDRAWL)(1–YC)

YC = FRACTION OF C IN CHAR OXIDIZED IN STAGE 1

YCO = FRACTION OF C IN COAL OXIDIZED IN STAGE 2

YCH_4 = FRACTION OF C IN COAL CONVERTED TO CH_4 IN STAGE 2

WDRAWL = FRACTION OF CHAR2 CARRIED OVER IN PRODUCT GAS (GAS2)

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Using the foregoing to estimate the energy and mass balances and operating temperatures, the gasifier operation is reduced to specifying YC, WDRAWL, YCH4 and YCO. As mentioned above, YC, the fraction of the carbon in the char which is oxidized in Stage 1, is conservatively estimated by BCR at 60 or 70 percent. When operating data for Stage 1 becomes available this will be set accordingly. WDRAWL depends on the number and efficiency of cyclone separators. Since excessive carryover results in both operating inefficiencies and potential downstream damage, it is preferrable to use high-efficiency cyclones to recycle essentially all of the char from Stage 2; hence, WDRAWL is 1 percent or less. The methane yield, YCH4, depends intimately both on the partial pressure of hydrogen in Stage 2 and on the Stage 2 temperature and has been the subject of much study at BCR and elsewhere because of the interest in using coal gasifiers to synthesize conventional pipeline gas. The BCR method of selecting YCH4 is given below. The value of YCO which determines how much carbon in the coal does not react, i.e., "fixed carbon", may be expected to be such that YCH4 + YCO = C in the volatiles in the coal (approximately). In running the model YCH4 + YCO equals C in the volatiles within about 30 percent. At the same time, additional carbon may be formed due to the chemical kinetics toward carbon formation from the gases. To account for this, consideration must be given to the Boudouard reaction equilibrium.

It may be noted that YCO provides a conceptually useful and informative link between the two gasifier operation regimes currently under consideration -- the low temperature, rapid devolatilization scheme in the BCR gasifier and the high-temperature equilibrium scheme in Koppers-Totzek gasifier. If YCO is simplistically increased from 15 percent to 80 percent, the gasifier goes from a favorable region of operation -- high product gas HHV, low steam and oxidizer requirements -- over a "hill" or unfavorable regime -- low product gas HHV, high steam and oxidizer requirements -- to another favorable region. The latter region in which all the C in the coal is gasified (equilibrium) is the region used for many years by Koppers-Totzek and others. The efficiency advantage of the BCR gasifier is due to, 1) the existence of the first favorable region of gasifier operating having rapid devolatilization and low YCO (Stage 2) in which only part (essentially the volatiles) of the coal is gasified, and 2) recycle of the char (the uncombusted C in the coal plus ash) to furnish the energy (Stage 1) and thereby closing the gasifier operation loop.

The specification of YCH^4 is based upon the BCR PEDU experiments and other laboratory data on the rapid devolatilization of coal at high pressures[66,64]. The conclusion is that YCH^4 can be estimated empirically as follows:

$$YCH^4 = \frac{a + b \cdot P_{H_2}}{1 + b\, P_{H_2}} \tag{20}$$

where

$a = .08$

$b = b_1 \exp[-\frac{b_2}{T}]$ where b_1 and b_2 are constants and T is temperature

P_{H_2} = partial pressure of hydrogen

There are several methods of determining the values of b_1 and b_2 using both theoretical kinetics arguments and experimental data. Fortunately, values of YCH^4 found from these various methods are in relatively close agreement as can be seen in Figs. 50a and 50b.

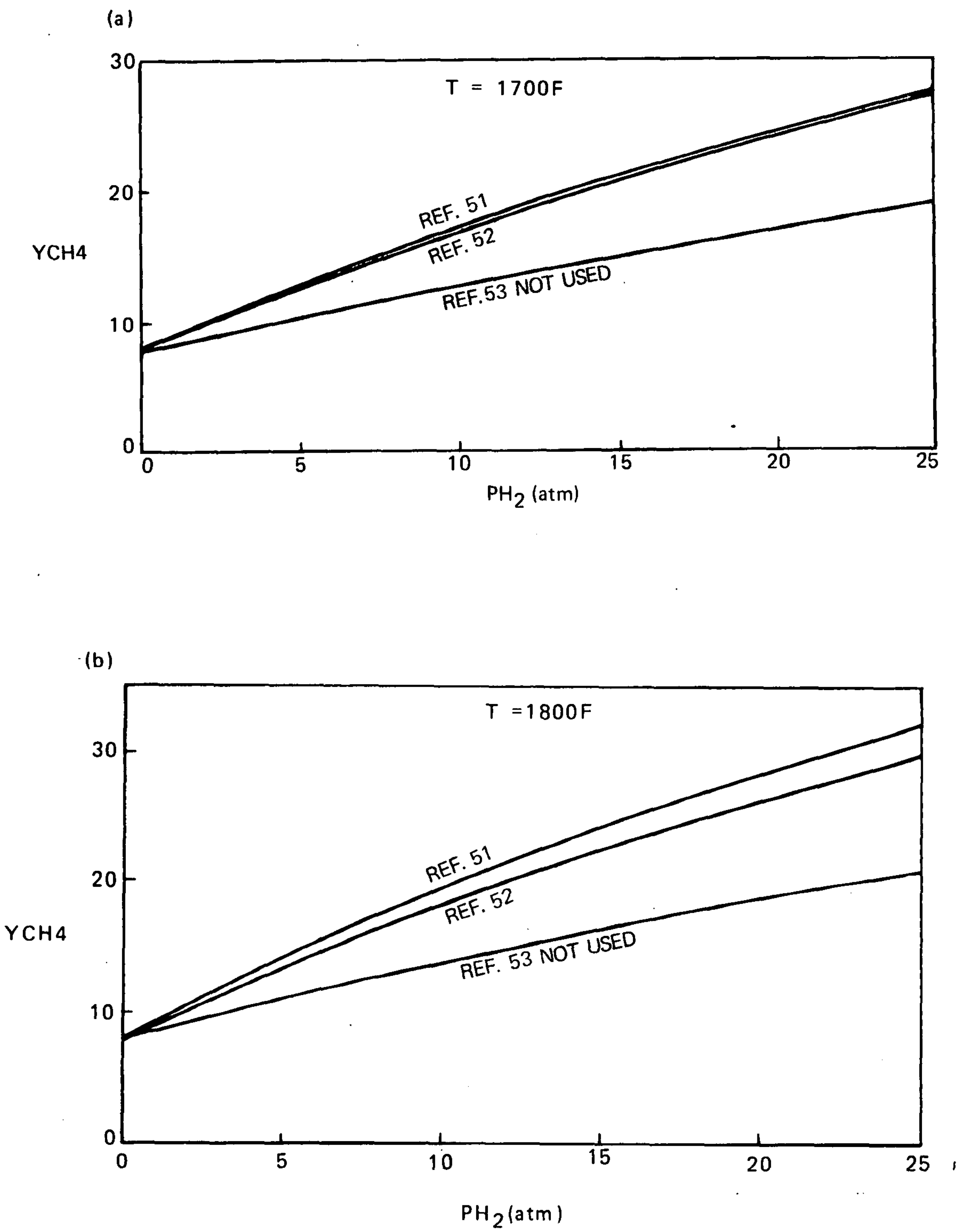
Estimates of YCH^4 for the temperatures and hydrogen partial pressures of interest reveals quite close agreement between the curves based upon Refs. 59 and 60. The curve based on Ref. 61 is somewhat different. Since this curve is based upon experiments at very high hydrogen partial pressures (up to 500 atm) and the operating conditions for the typical air blown cases in this study have hydrogen partial pressurs of only 5-10 atm, the curve based on Ref. 61 was not used. In this study the methane yield YCH^4 was assumed to lie between the two curves determined from the data in Refs. 59 and 60.

YCO is specified according to the Boudouard reaction

$$2\ CO \rightleftarrows CO_2 + C\ (\text{solid}) \tag{21}$$

This reaction does not actually occur directly but may occur in two steps (56). It nevertheless serves as a touchstone to determine whether the specification of the amount of carbon gasified is correct for the assumed operating conditions. The basic assumption is that the mole fraction of CO, x_{CO}, in the gas being formed in Stage 2 uniformly increases during the course of the chemical reactions occurring there. Then, x_{CO} may be compared to its equilibrium value according to the Boudouard reaction. If YCO is too high, then x_{CO} will be above Boudouard reaction equilibrium and the Boudouard reaction would suggest that solid carbon is being formed. During the rapid devolatilization of Stage 2, one would not expect the carbon in the coal to oxidize and then revert

METHANE YIELD VERSUS PARTIAL PRESSURE OF HYDROGEN



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into solid carbon again, i.e., one would not expect x_{CO} to overshoot its equilibrium value. Rather, the question is whether x_{CO} even reaches its Boudouard reaction equilibrium value. The BCR approach is to choose YCO such that x_{CO} is below Boudouard reaction equilibrium (CO_2 amd C tend to form CO) but that YCO yields x_{CO} as close to equilibrium as possible. During the course of this study hundreds of runs with the BCR model resulted in only about one-half dozen cases having the Boudouard reaction constant (see below) below equilibrium (toward solid C), while concurrently achieving a mass and energy balance in the gasifier under the specific operating temperatures and pressure. In general, several values of YCO above equilibrium (toward CO) were possible and the value closest to equilibrium was chosen in order to determine whether x_{CO} and x_{CO_2} were above or below Boudouard reaction equilibrium. It is instructive to calculate an equilibrium constant and determine whether the gasifier would "operate" at values for x_{CO} and x_{CO_2} such that the CO or CO_2 were above equilibrium. By classical thermodynamics at equilibrium

$$\frac{x_{CO_2}}{p x_{CO}^2} = \exp \frac{2 \cdot \mu_{CO}^o(T) - \mu_{CO_2}^o(T) - \mu_C^o(T)}{RT} \qquad (22)$$

where

x_{CO}, x_{CO_2} = mole fractions of CO and CO_2
p = pressure in atmospheres
μ_{CO}^o, $\mu_{CO_2}^o$, μ_C^o = Gibbs free energies (chemical potentials) of CO, CO_2, and solid C
T = temperature
R = gas constant

Thus a simple way to check the Boudouard reaction equilibrium is to calculate

$$K = \frac{[x_{CO_2}/(p \cdot x_{CO}^2]\text{actual}}{[x_{CO_2}/(p \cdot x_{CO}^2)]\text{equilibrium}} \qquad (23)$$

where the denominator is determined from the equation above and the numerator from the values calculated by the mass and energy balance in the BCR gasifier computer model. If $K \geq 1$, then x_{CO} is below equilibrium and the reaction is tending away from solid C formation. If $K < 1$ the Boudouard reaction tends toward solid C formation. In this study YCO was chosen to make K as close to 1 as possible, but always greater than 1. As mentioned above, very few conditions were found with $K < 1$.

In addition to adapting the BCR model to our computer system and carrying out numerous parametric cases, additional modifications were made. Enthalpy and Gibbs free energy curves from the UTRC library were used. Specific heat curves for SiO_2 were used for ash. Also added were a check on the Boudouard constant, K defined above, and a check to see if the specified YCH^4 fell between the two curves based on the empirical data which was supplied by BCR. This addition will allow an automatic iterative procedure to be used when the gasifier model is eventually incorporated into the SOAPP(1) program used at UTRC.

Further work is needed to determine how far from equilibrium the gasifier can operate, in terms of the Boudouard constant K, defined above. It was found during parametric analyses that as the operating conditions were varied from the design point, values of K became several hundred then several thousand. Clearly, this is inconsistent with the assumption of water gas shift equilibrium, but it is not clear what the K cutoff point value is. At design point, K was typically 3-6.

APPENDIX C

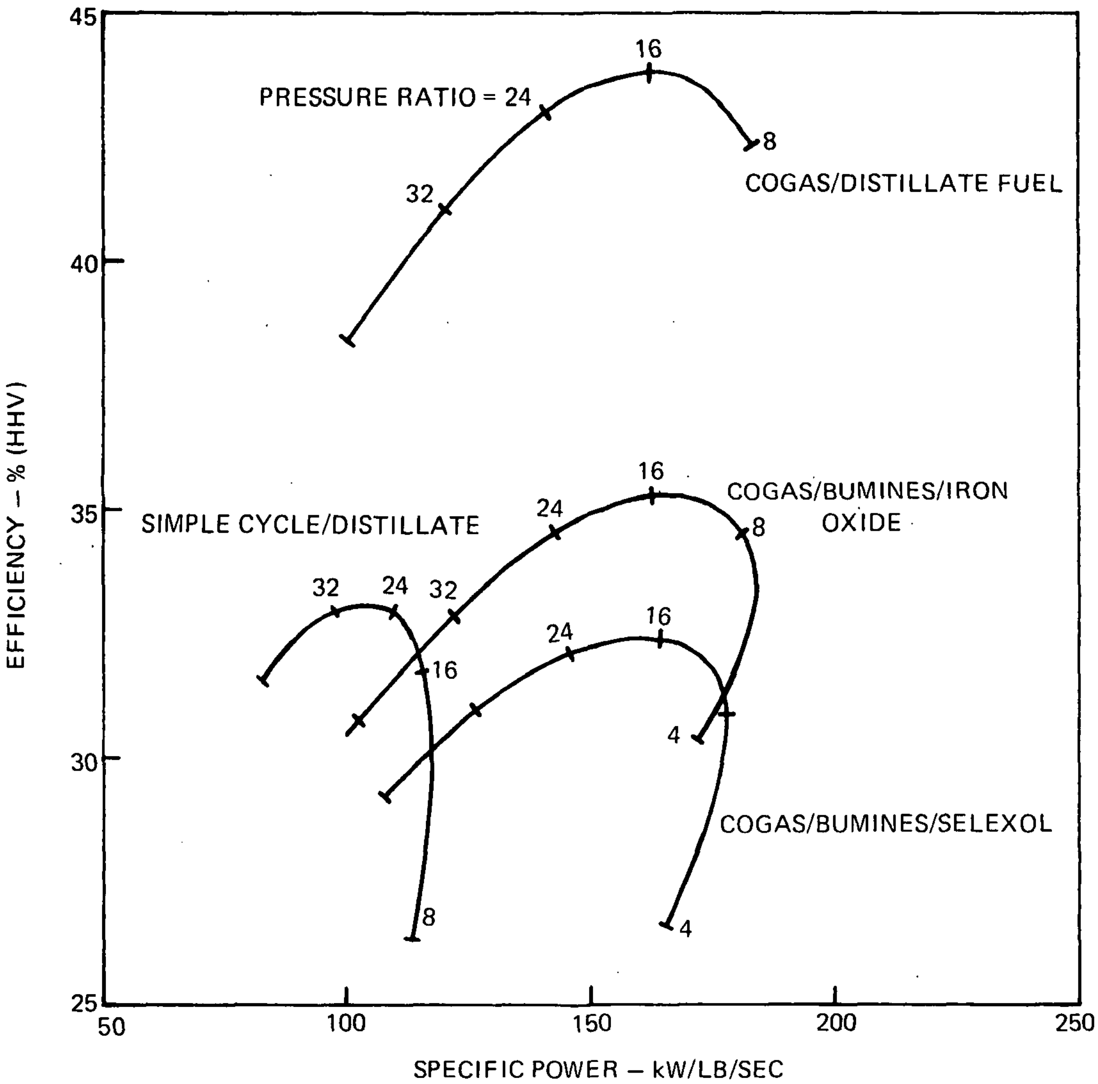
During the initial phase of the program, first and second generation power system characteristics were defined. First generation systems use conventional cooling techniques with a turbine inlet temperature of 2200°F. Second generation systems use ceramic vanes with conventionally cooled blades with a turbine inlet temperature of 2600°F. In each case a turbine pressure ratio was selected to give high specific power (kW output per unit air flow) while not compromising system performance. This selection was made initially on the basis of data for distillate fired systems considered. For the revised systems presented in this report, the effect of pressure ratio on both first and second generation systems was again evaluated. The results are presented in Figs. 51 and 52. They show little change from the previous curves and the selection appears to remain valid.

FIG. 51

FIRST GENERATION SYSTEM PERFORMANCE

TURBINE INLET TEMPERATURE = 2200F

CONVENTIONAL AIR COOLING



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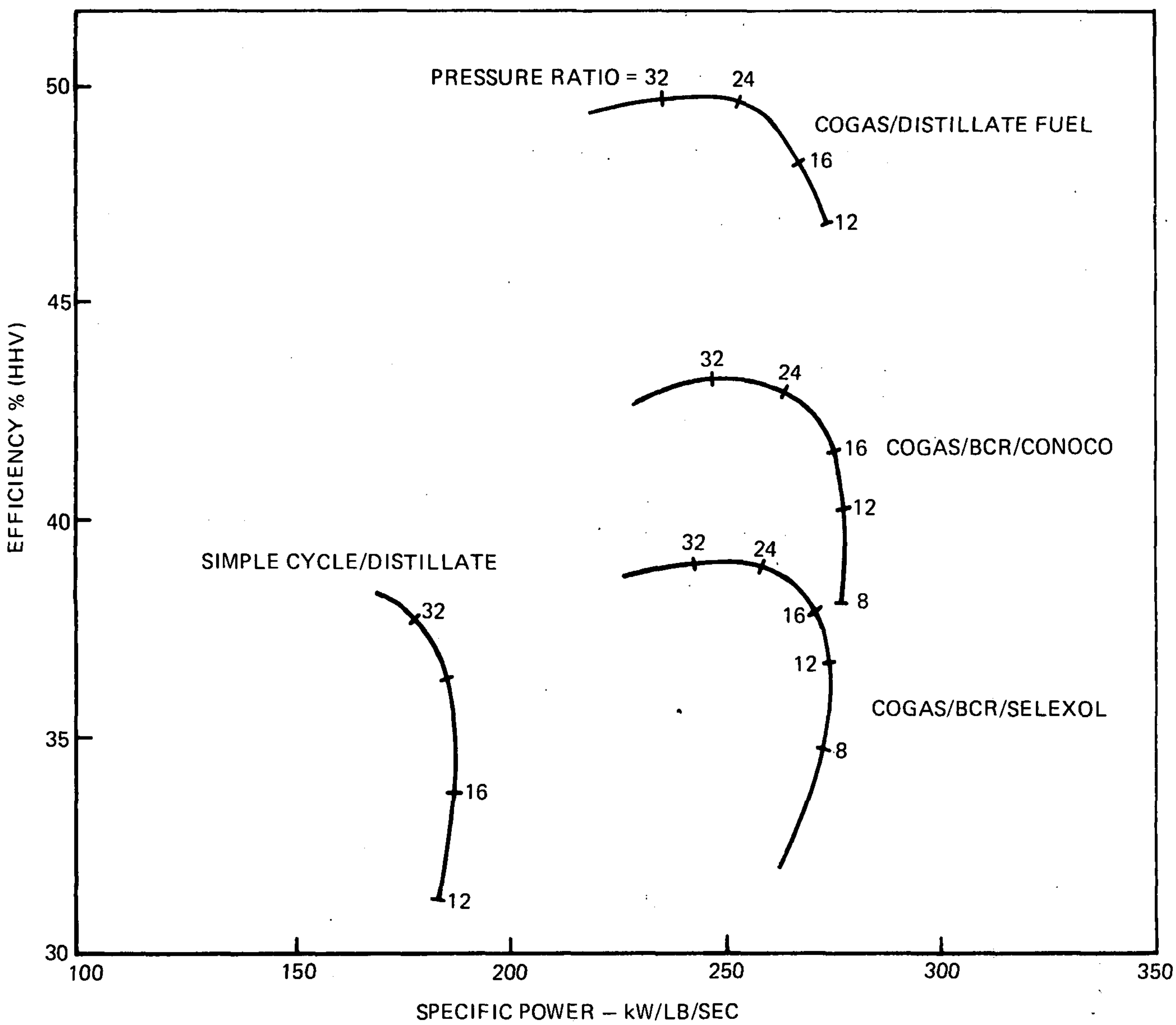
SECOND GENERATION SYSTEM PERFORMANCE

TURBINE INLET TEMPERATURE = 2600F

CERAMIC VANES, CONVENTIONAL BLADES



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16. ABSTRACT As they relate to combined cycle power generation, the report gives results of an evaluation of the technical and economic considerations of atmospheric-pressure, oxygen-blown coal gasifiers (Koppers-Totzek) and pressurized, air-blown, partial-oxidation residual-oil gasifiers (Shell/Texaco). Also presented are refinements of systems reported in an earlier phase report, EPA-600/2-75-078. The objective of the report is to help define the environmental impact of combinations of: (1) fossil fuel gasification systems, (2) low- and high-temperature fuel gas cleanup processes, and (3) advanced cycle power systems.

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Fuels	Gasification	Stationary Sources	21D	
Gas Purification		Fuel Gas	07A, 13H	
Fossil Fuels		Environmental Impact		
Coal Gasification		Combined Cycle Power Generation	10A	
Electric Power Generation		Emission Control		

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