BASIC FEATURES OF THE CO_2 ACCEPTOR GASIFICATION PROCESS

D. R. Mosher, U. D. Marwig, and J. A. Phinney

Stearns-Roger Corporation, P. O. Box 1469, Rapid City, SD 57701
Consolidation Coal Company, P. O. Box 1687, Rapid City, SD 57701
Consolidation Coal Company, Research Division, Library, PA 15129

INTRODUCTION

The Rapid City plant embodies a unique chemical, fluidized bed system originally conceived by Consolidation Coal in the 1940's. The plant is located where there is easy access to various sources of lignite in the huge Western lignite field. The scale of the plant was chosen to permit obtaining precise engineering data and scale-up information for commercial facilities.

At this point, the laboratory work is complete, plant construction is complete (except for insulation and painting) and preliminary operations have started.

PROCESS DESCRIPTION

The production of pipeline gas by gasification of lignite using the Consol process has four main steps. The overall steps are shown in Figure 1. They are coal preparation, gasification, gas purification, and methanation. Coal pretreatment is also shown; however, this step is unnecessary when lignite is gasified. To handle sub-bituminous coal, it is necessary to use a pretreatment step comparable to that employed in other gasification processes.

The key reactions that take place in the CO_2 Acceptor Process are summarized in Table I. The reactions of carbon, carbon oxides, steam and hydrogen are the same in all gasification processes. The reactions shown that involve calcium oxide, calcium carbonate, and carbon dioxide are unique to the Consol process. Through these reactions, heat is transported between the gasification and combustion sections and simultaneously carbon dioxide is removed from the product gas.

In the coal preparation step, the lignite is crushed to approximately 8 mesh in a mill and simultaneously dried from a total moisture content of 35% to 5% using hot gas.

As a final step in preparation, lignite is preheated in a fluidized bed to 572°F, which also drives off some bound moisture and possibly some CO_2. This step will be modified to a pretreatment when sub-bituminous coal is used.

Lignite is a non-caking coal; and as a result, the dried and ground material leaving the fluidized bed heater is ready for gasification.

The gasification section of the process, as incorporated in the pilot plant, is shown in Figure 2. The crushed and dried lignite powder is introduced to a lockhopper system. Pressure in the hopper is increased to gasification pressure of 150 to 300 psig, and the powder is then fed through a rotary feeder into the first reaction vessel called the devolatilizer.

In the devolatilizer, the lignite reacts with a hydrogen-rich stream from the gasific at 1500°F. The introduction point of lignite is at the bottom of the bed and the volatil matter from the lignite leaves the top of the bed as methane, carbon monoxide, and hydrog The configuration of the vessel and operation conditions are such that there is essentiall no condensable hydrocarbon in the product gas.

The devolatilized lignite (which we can now refer to as char) flows by gravity from the devolatilizer. It is then lifted into the gasifier (the vessel on the right in Figure 2) using superheated steam as a motive gas. In the pilot plant, we have the flexibility of recycling gas to the gasifier through a cleanup and compressor system. This is also true of gases from the other reactors. This capability is included in the pilot plant to permit studying alternative operating schemes.

Carbon in the char is gasified by reaction with steam in the gasifier. Residual char, containing about 35% of the original carbon in the lignite, flows out of the gasifier by gravity and is lifted pneumatically to the regenerator using a very small stream of gas recycled from the regenerator as the motive gas.

In the regenerator, the residual carbon is burned at approximately 1900°F to supply the heat needed for the reversal of the carbonation reactions that take place in the devolatilizer and gasifier vessels (see Table I). The residual ash, containing about 5 absolute per cent of the original lignite carbon content, is entrained in the outlet gas from the gasifier. This residue, together with fines from the dolomite cycle which will be described next, is removed from the regenerator offgas in a cyclone. In the pilot plant at Rapid City, these solids will be lockhoppered out of the system into a tank where they will be slurried with water and pumped to a settling pond.

The dolomite cycle carries heat from the combustion in the regenerator to the gasification and devolatilization as was mentioned earlier. This is the key to the CO_2 Acceptor Process. Thermodynamic considerations associated with this cycle will be described later. In the regenerator vessel, calcium carbonate is calcined to calcium oxide adsorbing heat, and this heat is released when the calcium oxide is converted back to calcium carbonate by reaction with CO_2 in the other reactors.

The regenerator runs essentially full of fluidized dolomite. Char from the gasifier enters the bottom and is elutriated out the top after combustion with air. Calcined dolomite from the regenerator flows into the other two vessels by gravity.

In the gasifier and the devolatilizer, the top bed is essentially all fluidized char. Dolomite is introduced at the top and comes out of the char bed from a second fluidized bed in the small section at the bottom of each vessel. The small sections are called boots. There is little char in the dolomite boot section.

Dolomite from these boots flows by gravity to an engager pot from where it is lifted back into the regenerator. Air will be used as the motive fluid in commercial plants. The pilot plant is also equipped to use recycled gas from the outlet of the regenerator.

The product gas finishing and methanation steps are not included in the Rapid City Pilot Plant. The techniques will be similar to those used for other gasification processes.

STATUS

At this point, bench-scale research on the CO_2 Acceptor Process is finished and the pilot plant is complete except for insulation and painting. Some components of the plant, mostly standard designs, have been tested. Training of operating personnel will be completed by mid-October, at which point dry runs will begin. These runs will test the gasification controls, the special mechanical features, and the fluo-solid transfer between the reactor beds. These tests represent a start at completing the future developments numbered "1" and "2" in Table II.

We expect to begin gasification starting in February, and at that time, we will begin acquiring knowhow for commercial operation (Item 3 in Table II).

Presently the plans for the pilot plant involve testing the least severe process concepts first and gradually working toward more difficult combinations. Each test will bring us closer to achieving the three future developments in Table II.

GENERAL REMARKS REGARDING OPERABILITY PROBLEMS IN GASIFICATION PROCESSES

- The price for synthetic gas from coal is highly influenced by charges related to the investment of the plant. This capital intensity is dependent on the nature of the feedstock.

As compared to petroleum or the usual petrochemical raw materials, coal has properties which uniquely influence a processing plant investment. Some of these properties are:

1. Coal is a solid with varying and only partially predictable thermoplastic properties.
2. It contains mineral matter of varying composition.
3. It has varying chemical and petrographic compositions, and an undefined complex chemical structure.
4. It is thermally unstable and decomposes to yield a wide spectrum of gases, oils, and solids, the properties of which are influenced by the conditions of pyrolysis.

In addition to the problems created by these unique raw material properties, there is the basic necessity of supplying the large quantities of heat required for the endothermic gasification reaction at the high temperature levels needed for acceptable reaction kinetics.

Thus, the following potential operational problems are common to all coal gasification processes:

1. Feeding.
2. Caking.
3. Handling of volatile matter.
4. Supply of process heat.
5. Deposit formation.
6. Ash removal.

In the evaluation of chemical processes, the judgment usually culminates in a comparison of the projected process economics. When this is done for commercially proven processes, the operability is already established and the result of such an evaluation is reliable.

For conceptual processes, however, with only bench-scale results available, judgment of alternative processes using cost estimates is a rather risky venture, especially in the field of coal gasification.

While the individual concept may feature a different degree of difficulty in each of the problem points listed above, it is obvious that processes with the most straightforward solution to these problems have the best chance to become commercialized. In judging concepts, one should, therefore, examine the chances for operability first of all. Many concepts based on sound chemistry have failed because some of the problems have turned out to be insurmountable.

The CO_2 Acceptor Process will be examined in the following paragraphs in each of the areas that create operational problems.

FEEDING PROBLEMS

A problem exists whenever a large quantity of solids has to be introduced at a continuous and controlled rate into a pressurized high temperature reactor. The three principal means for accomplishing this step are a lockhopper system, pumping coal as a slurry, or a piston feeding device.

The lockhopper system was chosen for the CO_2 Acceptor Process for the following reasons:

1. Operability commercially established.
2. Low investment and operating cost for the pressure level desired.
3. Carbon dioxide can be used for pressurizing.
4. Amenable to automation.

In the pilot plant, the system consists of two hoppers, each with a capacity of one hour operation at 1.5 tons (Figure 3). The hoppers are operated alternately. While one of them is connected with the system and feeding, the other one is blocked off while it is depressurized, filled with coal, and finally repressurized with CO_2.

Operation is semi-automatic by electrically operated valves and push buttons. The feedrate is controlled from the main control room by variable speed rotary feeders, and the amount is measured by a system of loadcells and transmitters.

The lockhoppers are continuously purged with a small flow of CO_2 to keep hot process gas out during the feeding period and to prevent air from entering during the filling operation. Total CO_2 required for pressurizing and purging, 1300 SCFH, is small compared to other processes. The reason for this is that the lockhoppers are operated with 500 to 600°F preheated coal which tends to decrease pressurizing and purge gas requirements.

CAKING PROBLEMS

The CO_2 Acceptor Process is primarily designed to process lignite and sub-bituminous coals. While the lignite does not present a problem, normally non-caking sub-bituminous coal displays weak caking properties at high partial pressures of hydrogen. Although we do not expect agglomeration of the fluid bed, the "popcorn"-shaped (cenospheres) char produced by pyrolysis of caking coals can cause operational problems.

The plant is equipped to pretreat caking coal by operating the fluidized preheater at oxidizing conditions.

The preheater system (Figure 4) of the pilot plant is designed for atmospheric pressure. It is sized for eight hours retention time of the coal in order to serve as a surge between the drying system and the gasification section.

The system consists mainly of a natural gas-fired furnace, a fluidized bed vessel, and a venturi scrubber. In operation as an oxidizer, the furnace is fired with excess air. As tempering gas, we have the option to use either steam or flue gas from the regenerator of the gasification section. The outlet gas is quenched and scrubbed in the venturi scrubber and released to the atmosphere.

Because of the eight hour retention time, mild oxidizing conditions are sufficient. It is intended to operate at 500 to 600°F and up to 6% O_2 in the inlet gas with sub-bituminous coals.

In a commercial plant, this system would be modified for operation at a shorter retention time, and consequently, stronger oxidizing conditions.

HANDLING OF VOLATILE MATTER

Each coal evolves volatile matter during thermal treatment. The amount and the composition of these volatiles are determined by the rank of the coal as well as by the conditions of this treatment. In addition to fixed gases, hydrocarbons ranging from heavy tar to light distillates of aliphatic or aromatic nature are usually present as vapors in the raw gas.

Separation of these condensables from the raw gas which usually carries more or less dust can present a problem. The degree of difficulty and the numbers of steps required for cleanup is in proportion to the range of the hydrocarbon spectrum present in the gas.

We came to the conclusion that liquid hydrocarbon byproducts should be avoided by all means if the process configuration provides the possibility. Even though they have a high BTU price, the return would neither justify an additional process complication nor the investment for additional separation and refining equipment.

It was found that a minimum temperature of 1500°F and a retention time of the vapors in the reactor bed of at least 17 seconds in the presence of steam and hydrogen would break the volatile matter down to permanent gases, mainly methane, a trace of ethane, and some carbon oxides.

The devolatilizer reactor was designed for these conditions. Fresh coal is fed into the bottom of the fluidized bed, and the bed height provides sufficient retention time for the ascending vapors to react with steam and hydrogen present in fluidizing gas.

As a result, our gas clean-up system is rather simple (Figure 5). It consists of a quench tower with disc and doughnut internals, a quench separator, and a venturi scrubber.

The quench water is recycled to the tower from the separator and indirectly cooled. Excess water from condensation of undecomposed steam carries the precipitated solids out of the system. We have provided a baffle in the quench separator to handle light oil which might occur at upset conditions or startup. In the venturi scrubber, traces of dust are removed from the gas before it enters the recycle compressor.

As mentioned before, our gas treatment is limited to these steps because we did not install equipment for methanation and associated preparatory treatment.

SUPPLY OF PROCESS HEAT

The method of heat supply has a great impact on the economy of a gasification process. Problems are usually associated with the requirement to supply the heat at relatively high temperature levels to the reaction zone.

If consideration is limited to systems producing essentially nitrogen-free water gas, coal gasification processes can be categorized in terms of the methods of supplying heat to the gasification zone; i.e.,

1. Oxygen-blown systems.
2. Cyclic processes.
3. Indirectly heated processes (electrical heat, nuclear energy, etc.).
4. Heat carrier processes.

The CO_2 Acceptor Process falls in the last category. However, it is distinguished from other solids recirculation processes by the fact that most of the heat is liberated by chemical reaction.

As described before, calcined dolomite at 1950°F is introduced to the top of the reactor beds in granular form. Because of their higher gravity, the particles shower through the beds. On their way down, they react with CO_2 which is always present in devolatilization and gasification zones.

At the bottom of each reactor, the carbonated dolomite is collected in a bed of smaller diameter and a higher fluidizing velocity. From these small beds it is transferred to the regenerator for calcination at 1950°F (see Figure 2). This reaction requires heat which is supplied by combustion of residual char from the gasifier. After this treatment, the dolomite is ready for another cycle.

The average acceptor particle will undergo about 50 cycles of calcining and recarbonation until it is replaced by dolomite makeup. This replacement rate of 2% is necessary to maintain a reasonable activity level in the circulating inventory. We expect that under these conditions between 30 and 40 mol per cent of the circulating dolomite will participate in the recarbonation reaction.

Figure 6, a T-H diagram, shows that only 27.5% of the heat carried with the dolomite is sensible heat and that the major portion of 72.5% is heat of reaction. This diagram is for one mol of dolomite at 40% activity and 1950/1500°F temperature differential. The total heat supplied to the process by one mol of dolomite under these conditions is about 40,000 BTU.

About three and one-half times as much dolomite would be required at the same temperature differential for the same heat supply if all the heat were supplied by sensible heat. All solids which have been used in this service as heat carriers such as sand or char, etc., have roughly the same specific heat as dolomite. In the CO_2 Acceptor Process, the weight ratio of circulated dolomite to coal fed is between 3 and 4; whereas other gasification processes with chemically inert heat carriers have to circulate a burden of 10 to 15 times their coal feed. Since increased solids flow in a process means more investment, the acceptor process should be more economical than other processes of the heat carrier category.

DEPOSIT FORMATION

Deposit formation is a problem common to all gasification processes. Considerable time was spent in studying this problem in the CO_2 Acceptor bench-scale studies. It was found that deposits can occur in all three reactors. The mechanism of formation is different in each process vessel.

Devolatilizer deposits are formed by interaction between sodium sulfate, pyrite and SiO_2, while in the gasifier only the last two components are involved. There are no obvious means of preventing these deposits. The bench-scale data indicates, however, that with most Western coals, commercial operating periods of at least six months can be achieved without descaling the reactors. Obviously, however, coals having high sodium sulfate and pyrites contents should be avoided. In passing, it should be noted that the devolatilizer and gasifier deposits are not related to the presence of the dolomite acceptor; all gasification processes utilizing Western coals will encounter this problem.

In contrast, the deposits found in the regenerator are unique to the CO_2 Acceptor Process and can be much more severe. It was found that the formation mechanism is based on sulfur reactions in regeneration and that the deposition can be prevented by controlling the conditions in the regenerator.

Calcined dolomite is as good an acceptor for sulfur compounds as for CO_2. The sulfur forms CaS, mainly in the devolatilizer but also in the gasifier. In the regenerator the CaS content of the acceptor is oxidized in the $CaSO_4$ by either of the following reactions:

$$1/4\ CaS + CO_2 \longrightarrow 1/4\ CaSO_4 + CO$$

$$\text{or}\quad 1/4\ CaS + 1/2\ O_2 \longrightarrow 1/4\ CaSO_4$$

When CaS and $CaSO_4$ exist together in the absence of carbon oxides, sulfur is rejected and the calcium is converted to CaO by the reaction:

$$3/4\ CaSO_4 + 1/4\ CaS \longrightarrow CaO + SO_2$$

This last reaction is the sum of various intermediate steps. As an intermediate in the reaction, at temperatures above 1750°F, a transient liquid phase occurs which collects and solidifies on the regenerator walls.

In studying the problem, it was found that a slight partial pressure of carbon monoxide in the regenerator would prevent the diffusion of the transient liquid to the surface of the acceptor particles and thereby avoid its deposition on the walls of the vessel. The amount of CO required depends primarily on the total amount of sulfur fed to the regenerator and must be determined individually for each coal or set of operating conditions.

There is a price tag associated with this solution; namely, the rejection of carbon in the regenerator, which means loss in overall efficiency. Approximately 5% of the original carbon of the coal must be sacrificed.

ASH REMOVAL

This problem generally involves three steps:

1. Separation of ash from the process.
2. Removal from the pressure system.
3. Disposal.

Separation of ash from the process takes place in the regenerator. The particles, while reacting with air, move upwards through the interstices of the dolomite bed. The ash particles are stripped out of the bed because they are much finer than dolomite particles.

Separation of entrained ash from the gas takes place in a cyclone and the rest is removed in a wet scrubber. Before entering the cyclone, the gas/solid mixture is cooled from 1900 to 1000°F by means of a water-jacketed pipe.

The removal from the pressure system is accomplished by alternately operating lock-hoppers of a configuration similar to those described for coal feeding.

The residue from the lockhoppers contains about 80% of the sulfur content of the feed coal. Because it is present as CaS, this material cannot be disposed of by dumping Rain would gradually liberate H_2S causing a bad odor in the vicinity of the dump area.

In the pilot plant, the ash lockhoppers are discharged into an agitated tank and slurried with water. The slurry is reacted with CO_2 to release H_2S which is incinerated The innocuous solid residue is then pumped into a settling pond.

Disposal in a commercial plant would be accomplished in a similar manner, except that the liberated H_2S would be converted to sulfur. Investigations are under way to find commercial use for the residue.

CONCLUSION AND SUMMARY

The construction of the Rapid City Pilot Plant is almost completed. After initial cold runs, gasification tests will be started in February of next year.

The process was examined with respect to the six main problems commonly associated with coal gasification.

For the problems of feeding, caking, and ash removal, the process configuration offers the possibility of straightforward solutions, while the problem with condensable hydrocarbons can be eliminated completely by appropriate process steps.

The process embodies a unique solution to the heat supply problem wherein the heat is transported chemically. The required solids circulation rate is only a fraction of that which would be required if all the heat were supplied as sensible heat.

The formation of ash deposits in the devolatilizer and gasifier is expected with Western coals in all gasification processes. Bench-scale data indicate that with most Western coals, commercial operating periods of at least six months can be achieved without scale removal.

Deposit formation in the acceptor regenerator is a potentially serious problem. The problem was eliminated in bench-scale tests at the expense of a loss in process efficiency.

TABLE I

PERTINENT REACTIONS IN CO_2 ACCEPTOR PROCESS

	HEAT OF REACTION BTU/MOL at 298.16° K
$C + H_2O\ (g) \rightarrow CO + H_2$	56,500 Endothermic
$CO + H_2O\ (g) \rightarrow CO_2 + H_2$	17,700 Exothermic
$CaO + CO_2 \rightarrow CaCO_3$	76,200 Exothermic
$CaCO_3 \rightarrow CaO + CO_2$	76,200 Endothermic
$2C + H_2 + H_2O\ (g) \rightarrow CH_4 + CO$	24,300 Endothermic

TABLE II

MOST SIGNIFICANT PAST AND FUTURE DEVELOPMENTS

PAST	FUTURE
1. Concept of Using Acceptor in Commercially Feasible Process	1. Confirmation of Practical Operability and Plant Capacity
2. Correlations for Dolomite-Char Fluid Systems and for Reaction Rates	2. Obtain Information for Precise Engineering Scale-Up
3. Methods for Avoiding Agglomeration and Slagging	3. Acquire Knowhow for Commercial Start Up and Operation

PIPELINE GAS FROM COAL

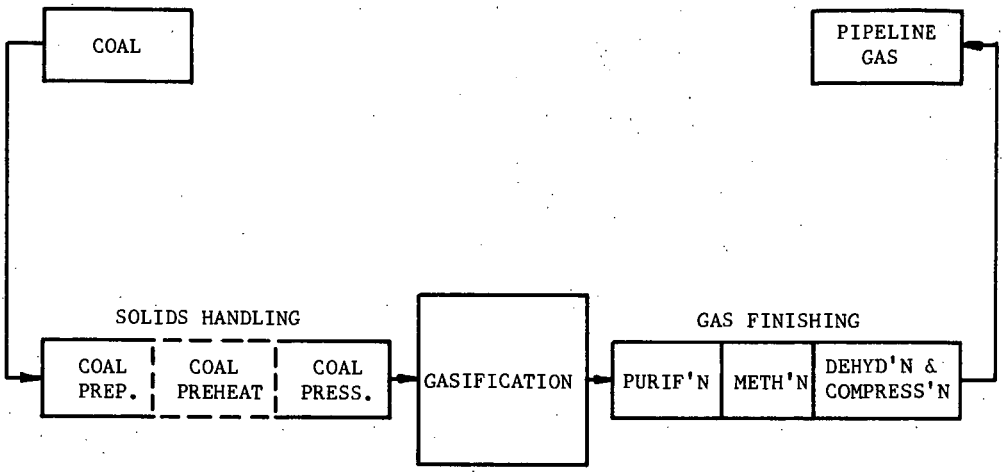

FIG. 1

CO_2 ACCEPTOR PROCESS
RAPID CITY PILOT PLANT- GASIFICATION SECTION

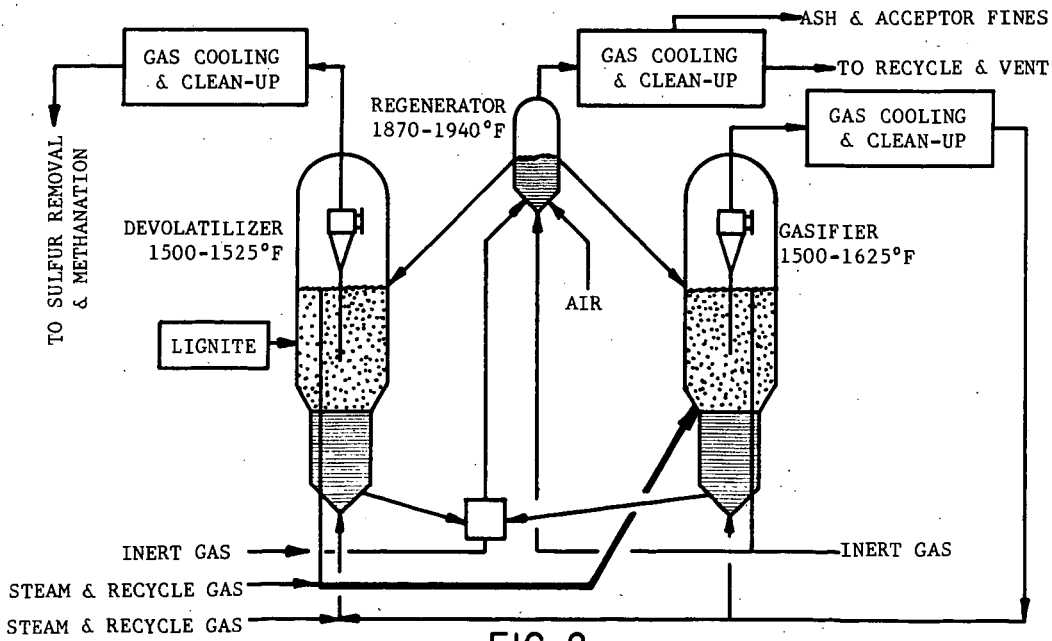

FIG. 2

LOCK HOPPER SYSTEM

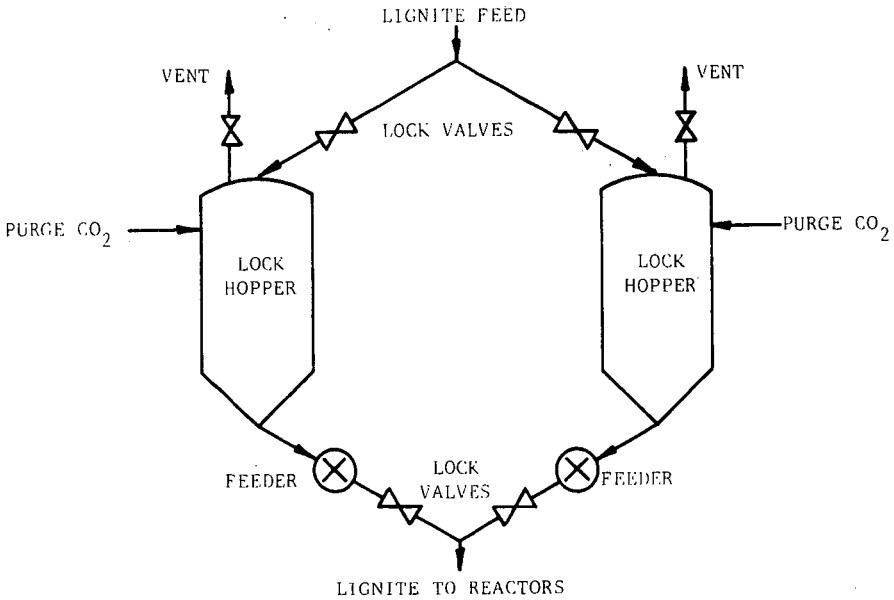

FIG. 3

PREHEATER SYSTEM

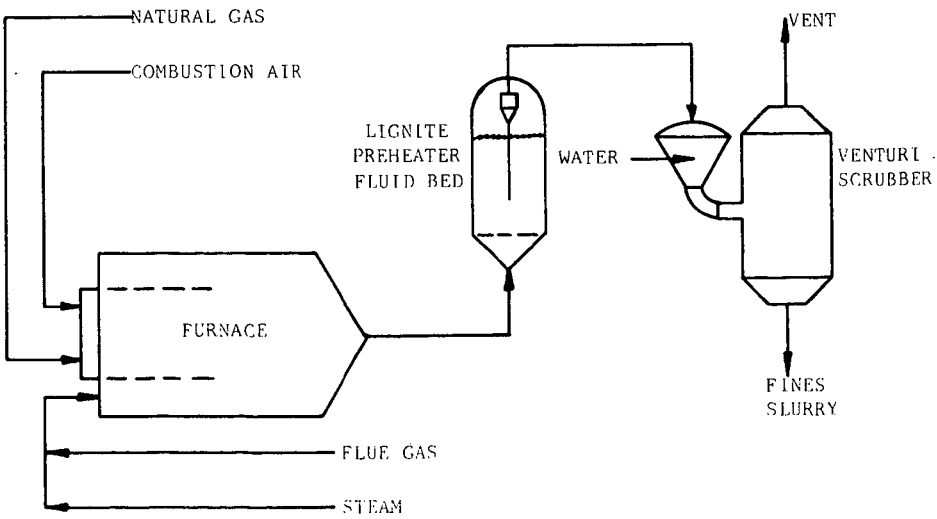

FIG. 4

GAS CLEAN-UP SYSTEM AT PILOT PLANT

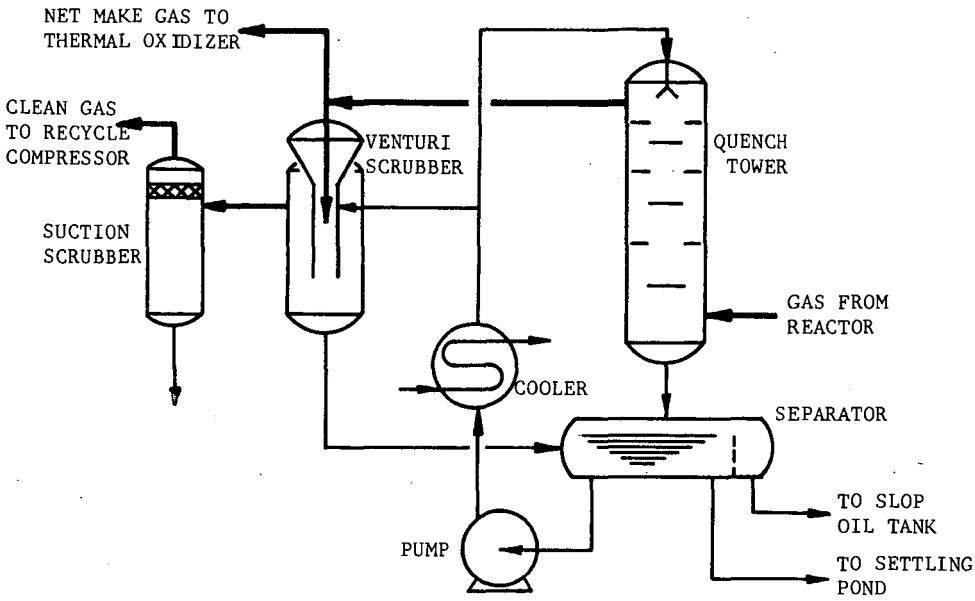

FIG. 5

HEAT SUPPLY OF ACCEPTOR AT 40% ACTIVITY

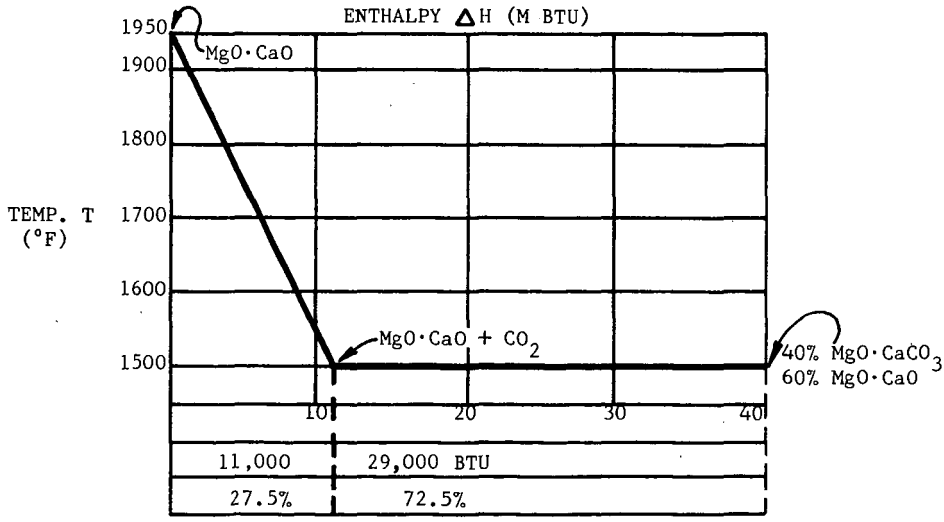

FIG. 6