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RESEARCH AND ENGINEERING DEVELOPMENT

KELLOGG

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

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APPROVED:

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I. SUMMARY

This Progress Report is the thirty-seventh since the awarding of the contract. It is concerned with the first phase of the contract and summarizes the progress that has been made in the three principal areas now being studied: Process Research, Chemical Engineering Studies and Mechanical Development.

Additional experiments were performed to determine the amount of sulfur in the coal which will wind up in the effluent from the gasifier. Within the limits of analytical accuracy these experiments indicated that all of the sulfur will be retained by the melt and that the gasifier effluent will be practically sulfur-free.

In order to further clarify what happens to sulfur in the melt system, two additional experiments were carried out in which 1% mixtures each of sulfur dioxide and hydrogen sulfide were bubbled through the melt at 1740°F. Within detection limits (99.7% removed), no sulfur compounds were found in either of the runs. Even when the gases were allowed merely to impinge on the quiescent melt surface, complete sulfur removal was obtained.

In cooperation with the Mechanical Development Group, attempts have been made to prepare an uncontaminated melt sample for use in ash removal studies by actually gasifying coal (bottom-feed) for an extended period of time. Due to the small size of the coal feed tube, considerable plugging difficulty was encountered. However, two important observations were made while the unit was operating. First, no sulfur could be detected in the off gases from the gasifier thus verifying the aforementioned conclusions. Second, there was no significant breakthrough of tars when the coal was bottom-fed indicating complete gasification of the volatile matter.

Several modifications were made to the pilot plant flow sheet in order to reduce its cost and to take into account recent laboratory findings. One minor change was to reduce the pressure of the ash thickener from approximately 15 psig to atmospheric pressure in order to reduce its cost. Modifications are currently under way to change the slipstream withdrawal from the combustor to the gasifier. This has been done in order that the sulfur in the coal can be removed as sodium sulfide rather than sodium sulfate since the sulfate is more water soluble than sodium carbonate and would prohibit the rejection of sulfur from the system without an undue sodium loss. On the other hand, the sulfur can be recovered quite easily from sodium sulfide by reaction with carbon dioxide in the carbonation tower.

Estimated capital savings in sulfur removal equipment due to the retention of sulfur in the melt is about $7,000,000. This corresponds to a reduction of about 2¢/MSCF in pipeline gas selling price. An additional 1.5¢/MSCF savings can be realized if the sulfur is recovered via the Claus Process. The combined effect of these savings corresponds to a reduction in pipeline gas selling price to 47 to 49¢/MSCF depending on whether or not by-product power is credited.

New Monofrax A specimens have been cut from a Diamond Cut Lug block in preparation for new corrosion tests. In addition, testing of the Insulag insulating material has been begun.

Computer programs have been developed to enable the calculation of the stresses in the internally insulated carbonate transport lines to be made.

Preliminary sketches have been transmitted to Design Engineering for the preparation of a planning study of the gasification section. The purpose of this study is to determine engineering solutions to all serious design problems prior to release of the project for final engineering design.

II. PROCESS RESEARCH

A. Accomplishments

1. Sulfur Content of Gasifier Effluent:

The initial attempt to determine whether sulfur as hydrogen sulfide will be evolved from the gasifier was performed in an alumina tube with a melt containing 1% sulfur as sodium sulfate, 8% ash and 4% carbon from 12/20 mesh anthracite. This melt was brought to 1740°F with carbon dioxide for agitation, and the melt sampled for sulfur analysis which indicated 1.06% sulfur. In order to simulate steady state, 30% steam in a prepared product gas (26.2% CO_2, 50.7% H_2, 9.5% CO, and 13.6% N_2) was passed through the melt for one hour and the melt resampled. Although no hydrogen sulfide was detected in the off-gas from the reactor tube, the melt analysis showed 0.46% sulfur, representing a significant loss of sulfur. This was rationalized as either due to segregation in the bed or to sulfur pickup by the Inconel sampler.

A repeat of the above run was made and at the end of the one hour, instead of sampling and running a chance of sulfur loss, the whole melt was frozen, ground and sampled for analysis. The original melt analyzed 1.13% sulfur (1.05% sulfur was calculated from mix) and the final sample analyzed 0.95% sulfur (1.04% sulfur was calculated for the mix). Again exit gases did not contain any hydrogen sulfide.

Considering the accuracy of the sulfur analysis, the conclusion has been reached that sulfur was not lost from the melt and that the product gas from the gasifier will be practically sulfur-free. The chemistry of carbonyl sulfide was studied and the conclusion reached that it will not be present in the gasifier product gas.

2. Additional Experiments on Sulfur in Melts:

A melt containing 8% ash, 2.5% sodium sulfide, and about 1-2% carbon from anthracite was held at 1740°F in an alumina tube and a gas mixture of 1% sulfur dioxide in nitrogen was bubbled through the melt using an alumina tube as an inlet. The superficial gas velocity was 0.5 ft./sec. After one-half hour the exit gas was analyzed by gas chromatography and found to be free of sulfur dioxide. The limit of sulfur dioxide detection was 0.025%.

The 1% sulfur dioxide in nitrogen gas was replaced with 1% hydrogen sulfide in nitrogen and bubbled through the melt at 0.5 ft./sec. for one-half hour. Again complete absorption of the sulfur in the gas occurred and the exit gas was free of hydrogen sulfide. Limit of detection was 0.025%.

The sensitivity of gas chromatography detection was increased ten fold and once again bubbling 1% sulfur dioxide in nitrogen gas at 0.5 ft./sec. through a sodium carbonate melt at 1740°F absorbed all the sulfur dioxide. Hence at least 99.7% of the sulfur dioxide was removed. A smell test on the exit gas indicated no sulfur dioxide, and this limit of detection has been reported as 5 parts per million.

Instead of bubbling the sulfurous gases through a melt, they were allowed to merelyimpinge on the quiescent surface. Retention of both SO_2 and H_2S by the melt as analyzed by the highest sensitivity of gas chromatography was at least 99.7%.

3. Preparation of 8% Ash in Sodium Carbonate:

In order to prepare an uncontaminated 8% ash in sodium carbonate melt, starting from coal which could be used for determination of sulfur distribution and recovery, sodium recovery and ash removal, an alumina container and alumina tubes have been utilized. The Mechanical Engineering Group has undertaken the preparation of this melt.

An initial attempt to bottom feed the high-volatile bituminous coal failed due to agglomeration in the inlet tube. Mild oxidation of this coal was performed to prevent caking in this tube. Although this helped a great deal, plugging in the small diameter tube still prevented completion of the experiment. During the operable part of the run, samples of the exit gases were analyzed and found to be free of sulfur gases thus verifying the sulfur removal-melt experiments reported above. Also of considerable note was the lack of any significant breakthrough of tars and volatile matter from injecting the coal at the bottom of the melt. Complete gasification of the volatiles and tar appeared to occur in the melt.

A further attempt feeding anthracite in the above metal-free reactor system will be made in order to produce an 8% ash melt.

B. Projections

After preparation of an uncontaminated 8% ash melt the analytical and process research will be performed as indicated.

III. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

A. Accomplishments

1. Pilot Plant:

Several modifications were made to the pilot plant flow sheet in order to reduce its cost and to take into consideration recent laboratory findings.

One minor change involved flashing the quenched melt solution fed to the ash removal section to atmospheric pressure rather than the 17.1 psig indicated in the Proposal. The reason for doing this is to allow the use of an atmospheric pressure thickener rather than a considerably more expensive pressure device (particularly in the commercial plant). Of course, this now necessitates adding a slurry pump prior to the ash filter.

Another modification has been made as a result of the recent data concerning the disposition and type of sulfur in the melt system. It has been found that essentially all of the sulfur in the coal will remain in the melt - none will leave in the gaseous effluents. This sulfur will be present as sodium sulfide in the gasifier and sodium sulfate in the combustor. Since sodium sulfate is even more soluble in water than sodium carbonate, sodium recovery of this portion of the melt in the ash removal section would be impossible. However, the sodium sulfide has been found to react with CO_2 under conditions of the carbonation tower to produce hydrogen sulfide. Thus, in addition to eliminating a potential pollution problem (SO_2), and to reducing sulfur removal costs downstream, the sulfur is ultimately recovered in a form wherein it can easily be converted to elemental sulfur.

The estimated reduction in investment due to the elimination of the sulfur removal equipment in the gas purification section is approximately $7,000,000 for the pipeline gas case. This, in turn, would result in a decrease in gas selling price of about 2¢/MSCF. In addition, if the sulfur were recovered via the Claus Process and could be sold at $30/ton, an additional savings of 1.5¢/MSCF could be realized. The combination of these reductions in the case of bituminous coal would result in a pipeline gas selling price in the range of 47 to 49¢/MSCF (depending on whether or not by-product power can be credited).

However, in order to achieve the above savings, the melt slipstream to ash removal must be changed from the combustor to the gasifier. This change is currently being made and the pilot plant flow sheet correspondingly modified.

2. Flow Sheet Studies:

Estimation of the investment for the 250,000,000 SCFD synthesis gas plant is nearly complete. It is anticipated that this estimate will be available by mid-September.

B. Projections

1. Pilot Plant:

Work will continue on modifying the pilot plant flow sheet to take into account the new findings on sulfur disposition. In addition, more consideration will be given to the control scheme to be used in the pilot plant in order to aid in the eventual definitive design work.

2. Flow Sheet Studies:

It is anticipated that the investment for the synthesis gas plant will be completed during September. When it is, gas manufacturing cost using bituminous coal will be calculated.

IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Mechanical Characteristics Testing:

During this report period the major effort was in connection with preparing a sample of melt that had experienced actual gasification conditions and that had contacted only alumina. This work was done at the request of the Chemical Research Group, and the results will be reported by them.

2. Corrosion Testing of High Temperature Materials:

New specimens of Monofrax A have been cut and testing will resume shortly. These new specimens were cut from a DCL (Diamond Cut Lug) block and were inspected to insure the soundest possible specimens.

In addition, testing of the INSULAG insulating material previously described has begun.

3. Design Studies:

A computer program for finding the influence coefficients, stresses and deflections in a short conical shell subject to arbitrary axial and radial (through-thickness) temperature distributions was developed. An existing cylindrical shell program is being modified to permit the same determinations. With these two programs, it will be possible to determine the stresses in the internally insulated carbonate transport lines if the temperature distribution is given.

Preliminary sketches were transmitted to the Design Engineering Department for the preparation of a planning study of the coal gasification section. The purpose of this study is to determine engineering solutions to all serious design problems prior to release of the project for final engineering design. Fairly complete drawings of the major vessels have been completed, and details of instrumentation and control for the gasification section are currently under review.

B. Projections

1. Mechanical Characteristics Testing:

No further melt preparation is currently comtemplated at this time, but the final decision will be made by the Chemical Research Group based on analysis of the current sample.

2. Corrosion Testing of High Temperature Materials:

The new Monofrax A specimens will be measured and the test program restarted. The INSULAG testing will continue.

3. Design Studies:

Work on the planning study and instrumentation and control review will be continued.