MWK-MPR-20

RESEARCH AND DEVELOPMENT DEPARTMENT —— KELLOGG

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

March 31, 1966

Progress Report No. 20

APPROVED: George T. Skaperdas
Project Manager

[signature]
DIRECTOR
Chemical Engineering Development

[signature]
MANAGER
RESEARCH & DEVELOPMENT DEPARTMENT

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I. INTRODUCTION

The objective of this contract with the Office of Coal Research is to develop the Kellogg Gasification Process to the point where it will be able, on a commercial scale, to convert coal into pipeline gas at a cost of 50¢/MSCF or hydrogen at 25¢/MSCF. Five raw materials are to be studied -- an anthracite, a high-volatile bituminous coal, a sub-bituminous coal, a lignite, and a char. Although Kellogg's experimental work will not extend beyond the production of raw synthesis gas, the overall project must make engineering evaluations for four ultimate end products -- pipeline gas, hydrogen, synthesis gas, and transport gas.

Basis for the Kellogg Gasification Process is the reaction between steam and fine coal in a molten salt bath to form synthesis gas, a mixture of hydrogen and carbon monoxide, according to the reaction:

$$\underset{\text{(coal)}}{C} + \underset{\text{(steam)}}{H_2O} + \text{heat} \longrightarrow \underbrace{H_2 + CO}_{\text{(synthesis gas)}}$$

The necessary heat of reaction is supplied by circulating a heated molten salt stream. In addition, the molten salt mixture is chosen to catalyze the gasification reaction so that it may be carried out at a relatively low temperature.

The program is divided into three phases of study extending over a five-year period. Phase I, which is now in progress, involves several concurrent efforts:

1. Bench-scale process research -- to investigate melt properties, reaction kinetics, and the effect of process variables.

2. Chemical engineering studies and development -- to determine the optimum process flowsheet and operating conditions and to coordinate experimental work with overall project objectives.

3. Mechanical development -- to find acceptable materials of construction and develop techniques for handling the molten salt and powdered coal.

Phase I will be concluded by the design of a pilot plant to gasify 24 tons of coal per day, if it is found that a pilot plant program is justified by the bench-scale experimentation and economic studies.

Phase II will be devoted largely to the construction and operation of a pilot plant to convert a variety of raw materials into raw synthesis gas. The effect of operating variables found to be significant in Phase I will be investigated to obtain data for design of a commercial plant.

Phase III will involve the detailed process design of a commercial plant to produce 250 million standard cubic feet a day of product gas, including cost estimates and projected economics for those areas of the country that appear to offer commercial possibilities.

II. SUMMARY

This progress report is the twentieth 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.

Gasification tests have been conducted in the 4 1/4-inch-diameter corrosion test reactor to study the effect of melt depth, vessel diameter, and bottom feeding of coke. The first run at 6-inch bed depth, 1 ft./sec. superficial velocity, atmospheric pressure, 1740°F, and 2% ash in the melt was successful. Rate of gasification compared favorably with that to be expected in the 2-inch unit under the same conditions. Succeeding runs at higher bed depths were not successful because of melt frothing up into the gas outlet tube or failure of heating elements.

Experiments were then undertaken in an open-top, 2-inch-diameter tube to try to understand the bed expansion and frothing problems that seem to be occurring under gasification conditions. A number of tests made with varying bed depth, superficial gas velocity, ash concentration, carbon concentration, and feed gas composition permitted the following conclusions:

1. An 8-inch bed containing 8% ash and 4% carbon will expand at least three-fold when steam is introduced at 1 ft./sec. superficial velocity in a 4-inch-diameter tube.

2. Introduction of coke into the same melt in nitrogen atmosphere (no steam) produces much less initial bed exapansion.

3. Ash concentration in the melt significantly affects the extent of bed expansion. Under conditions such that expansion is 3-fold with 8% ash present, it is only 2 1/4-fold at 2% ash.

4. The effect of superficial velocity on bed expansion under gasification conditions is small. Bed height increases by about 10% as superficial velocity is raised from 0.5 to 1.0 ft./sec.

5. Previously-reported rate constants for 8-inch beds, which showed a 20-25% decrease from those in 4-inch beds, are suspect. The decrease may have been due, not to bed height per se, but to expansion out of the heated reactor zone to a cooler area where the rate is smaller because of the known effect of temperature.

Efforts will be continued to operate the 4 1/4-inch reactor successfully with a deeper bed to establish the effect--if any--of bed depth. The effect of top vs. bottom feeding of coal will also be studied, if this is feasible. Results from the 2-inch and 4 1/4-inch reactors will be compared to discover any apparent effects of reactor diameter. A gasification experiment at 10 atmospheres will be tried in the 2-inch unit to permit further definition of the pressure effect reported last month.

Conceptual designs for producing pipeline gas from bituminous and sub-bituminous coals have been completed. Process flowsheets, material balances, and utilities summaries are being prepared for presentation, and capital cost estimating is now in progress.

The economic consequences of quenching hot synthesis gas and/or flue gas from the reactor with a water spray were investigated. It was concluded that quenching both streams to 1500°F, which could serve to freeze any entrained melt droplets, or quenching the synthesis gas to 400°F to condense vaporized tars would have relatively minor consequences; product gas cost would change by only a few cents per thousand cubic feet. However, if the flue gas had to be quenched to 400°F the result would be catastrophic. The loss of power otherwise generated by expanding the hot flue gas would add 18¢/MSCF to product gas cost.

Consideration of the economic effect of changes in other design bases or assumptions will continue.

Oxidation Test #3, intended as a long-term test of several materials of construction at 1840°F in a simulated combustion atmosphere, was continued during the month. Monofrax A showed an average overall corrosion rate of 0.03 inches per year after 500 hours and is confirmed to be an excellent choice for the intended use.

Design of a 5 3/4-inch-ID by 6-foot-long reactor, to be used to investigate bed expansion and the effect of deeper beds, was started during the month. A larger furnace needed for heating this reactor was placed on order.

III. PROCESS RESEARCH

A. Accomplishments

A decrease of 20 to 25% in reaction rate constant, as a result of changing bed height in the 2-inch diameter Inconel reactor from 4 to 8 inches, precipitated the desire to modify the Mechanical Engineering Division's 4.25-inch diameter corrosion test reactor for gasification runs. A possible reason for the rate loss was a wall effect, which should be decidedly less in the larger-diameter reactor. It was necessary to suspend the Process Research effort in order to set up the analytical equipment at this unit.

The initial run in the 4.25-inch diameter reactor was made with a 6-inch bed of sodium carbonate containing bituminous coal ash, using a 1 ft./sec. superficial velocity of 90% steam in nitrogen at atmospheric pressure. Desired reaction temperature was 1740°F, but due to the large volume of the reactor and the limited capacity of the available furnace, temperature averaged 1712°F, with a range from 1740 to 1685°F. Although the weight balance of 80% on carbon was low, the reaction rate constant of 1.1 appeared to be normal.

The next attempt, at a 12-inch bed height, failed because the outlet of the reactor plugged. Temperature control here was much poorer and would have made comparison of the data difficult. A further attempt to run with an 11-inch bed height and with additional heaters placed above the furnace but still on the reactor, also failed because of outlet line plugging. To supplement the limited furnace capacity, direct winding of the reactor with nichrome heating wire on porcelain beads was tried. Unfortunately, the wire burned out twice while heating up the reactor.

Normal operating procedure has involved charging coke to the molten bath with steam and nitrogen flowing at the desired rate. To decrease the foaming and expansion of the bed which occurs within the minute or so after the coke goes in, the introduction of the coke into steam-free nitrogen at 0.1 ft./sec. was investigated in an open-tube, 2"-diameter, Inconel reactor. Coke was added in five 4-gram increments at one minute intervals to a melt containing 2% ash with only nitrogen flowing at 0.1 ft./sec. The first coke addition caused an approximate maximum expansion from 4 to 12 inches and then the bed settled to a lower level. Further additions of coke and, later, steam at 0.9 ft./sec. did not cause any higher expansions of the bed.

While waiting for the 4.25-inch reactor to be wound, another attempt was made to run an 8" bed depth in the 2" reactor using a melt containing 8% ash and the technique described above for adding coke in steam-free nitrogen. The reactor was moved 5 inches lower in the Kanthal furnace to keep the expanded bed within the heating zone. Thus, it was necessary to test a 4" bed of 8% ash melt at 3 atmospheres, 1740°F, and 1 ft./sec. velocity. The reaction rate constant for this run was 1.9 as compared to 1.8 on the standard curve. When attempting to test the 8" bed at the same conditions, introduction of only half the coke caused foaming which plugged the outlet.

Additional open tube (2" diam.) experiments were then performed to get visual confirmation of the above bed height effects. An 8-inch bed of melt containing 8% ash at 0.1 ft./sec. nitrogen flow expanded to a maximum of 14 inches when steam was introduced at 0.9 ft./sec. After this initial expansion the melt settled back to about 10-12 inches. Steam was cut off and an addition of 19 grams of coke (2% C in melt) caused the bed to expand until it overflowed the 24" length of tube. After this settled down, addition of further increments of coke (still without steam) showed: 1 g. produced no noticeable rise, 5 g. produced a 2" rise, 14 g. produced a 4" rise, and 5 g. gave no rise. After the bed settled back, introduction of 0.9 ft./sec. of steam caused the bed to foam to the top of the Inconel tube (24"). It was concluded that an 8" bed containing 8% ash and 4% carbon will expand at least threefold under gasification conditions in a 2" tube at 1 ft./sec. superficial velocity, and probably also at 0.5 ft./sec. It also explains why this melt cannot be evaluated in our existing equipment.

Two open-tube experiments were then performed with a melt containing 2% ash at the 4-inch and 8-inch levels in the 2" diameter reactor at 1740°F. In the experiment at 4-inch depth, introduction of 19 grams of coke with only 0.1 ft./sec. nitrogen flow caused the bed to go from 4" to 6", but with 0.9 ft./sec. steam flow the bed expanded to 9" maximum. Carbon was then removed by gasification. Addition of 19 grams of coke to the 4" bed with 0.1 ft./sec. N_2 and 0.9 ft./sec. steam produced an expansion to 20-21 inches in about a half minute which settled back to 10.5 inches before settling further as the carbon was depleted by gasification. A change to 0.5 ft./sec. total nitrogen and steam produced a 3-inch drop in bed height.

In the experiment at 8" depth with only 0.1 ft./sec. nitrogen flow, the addition of 38 grams of coke expanded the bed only 3 inches. When steam was then introduced at 0.9 ft./sec., the bed expanded to 17.5 inches total. Decrease in total velocity to 0.5 ft./sec. caused the bed to drop to 15.5 inches, a 2-inch change.

These experiments have established that introduction of coke into the melt with only nitrogen flowing produced much less initial expansion than in the steam-nitrogen atmosphere. This serves as a technique to overcome initial frothing, and will allow more diversity in testing in the small-diameter reactors. It was also established that bed height during gasification is also a function of ash content in the melt. A 2% ash melt expanded 2.25 times the quiescent bed height at 1 ft./sec. and 2 times at 0.5 ft./sec. velocity, while an 8% ash melt expanded at least three-fold. These expansion effects are a function of surface tension and viscosity of the melt. It is believed that tube diameter also is a factor, the effect being greater at smaller diameters.

These studies permitted the visual observation that the coke appears to be dispersed throughout the melt.

On the basis of the above experiments, it has been theorized that bed height showed an effect on reaction rate constant because expansion of part of the melt above the isothermal zone into a cooler zone of the reactor where rate is lower caused a decrease in the overall rate of reaction. Thus, it is believed that bed height may not have an effect on reaction rate constant. Accordingly, runs can now be made in the 2" diameter reactor to test this hypothesis.

B. Projections

Evaluation of bed height and diameter will be continued. A gasification run at 10 atmospheres pressure will be tried before other variables are studied at lower pressure.

IV. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

A. Accomplishments

The conceptual designs for producing pipeline gas from bituminous and subbituminous coals have been completed. Process flowsheets, material balances, and utilities summaries have been finished and are being checked and assembled for presentation. Capital cost estimating is in progress.

A series of studies has been initiated to evaluate the economic consequences of changes in design bases or assumptions. The first study considered the effect of quenching the synthesis gas and flue gas leaving the gasifier and combustor, respectively, to a lower temperature using a water spray. Two levels of quenching were considered: (1) to 1500°F in order to freeze any entrained melt droplets, and (2) to 400°F in order to condense any vaporized tars. Three cases were studied:

Case I. Quench both synthesis gas and flue gas to 1500°F.

Case II. Quench flue gas to 1500°F and synthesis gas to 400°F.

Case III. Quench both synthesis gas and flue gas to 400°F.

Such quenching would reduce the availability of heat in these gas streams and--even more significant--would affect the quantity of power that can be recovered by expanding the flue gas to atmospheric pressure.

The results of this study are summarized in Table I for the case of pipeline gas from subbituminous coal. Quenching both gas streams to 1500°F (Case I) helps the economics a bit because a larger quantity of flue gas is expanded, thus producing more power. Quenching the synthesis gas to 400°F (Case II) is detrimental because of the loss of steam generation that is ultimately converted into power. And quenching both streams to 400°F (Case III) has catastrophic results because none of the power needed for compressing combustion air can be recovered by expanding the flue gas.

TABLE I

EFFECT OF QUENCHING SYNTHESIS GAS AND FLUE GAS

ON COST OF PIPELINE GAS FROM SUBBITUMINOUS COAL

Basis: 250 MM SCFD of pipeline gas
Cost of Coal: $2 per ton
Value of by-product power: 4.5 mills/kwh
Maintenance and fixed charges at 11.2% per year
Synthesis gas leaves gasifier at 1830°F
Flue gas leaves combustor at 2200°F

	Increment Over Base Case (no quenching)		
	Case I	Case II	Case III
Investment, MM$	+12	+10	-5
Gas Manufacturing Cost, ¢/MSCF:			
Coal	+ 1.3	+ 1.7	+1.7
Fixed Charges	+ 1.5	+ 1.4	-0.7
Gross Change	+ 2.8	+ 3.1	+ 1.0
Power Credit	- 4.4	- 0.6	+16.5
Net Change	- 1.6	+ 2.5	+17.5

B. Projections

Preparation of process flowsheets, material balances, and utilities summaries will be completed. Capital cost estimating will be continued. The effect on pipeline gas cost of the following changes in design bases will be estimated:

1. Halving the equilibrium concentration of coal in the melt.

2. Halving the concentration of ash in the melt.

3. Halving or doubling the rate of gasification.

4. Changing superficial velocity in gasifier and combustor.

5. Doubling sodium losses.

V. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Environmental Testing of High-Temperature Materials

Oxidation Test #3 has continued in progress during this report period. The test samples were removed at the 500-hour mark with the following results noted:

a. Monofrax A (High-purity cast alumina) - This sample has been in the test the full 500 hours. The average overall corrosion rate on this sample was 0.03 in/year. The sample was still in excellent condition and was replaced in the reactor after examination.

b. Monofrax M (High-purity cast alumina with 1.1% SiO_2) - This sample has also been in the test 500 hours. The average overall corrosion rate was found to be 0.15 in/year. This sample was still in good condition and was replaced in the test reactor.

c. Corhart ZAK - 501 (49% Al_2O_3 - 34% ZrO_2 - 15% SiO_2) - This sample was in the test for 138 hours and was found in the bottom of the test vessel. It was in such poor condition that a corrosion rate could not be determined, and thus it was not returned to the test. A sample of Inconel 600 was inserted in its place.

d. Morganite Triangle RR (High-purity alumina) - This sample was in the reactor for 300 hours with an average corrosion rate of 0.0861 in/year. This sample still appears to be in excellent condition, and was placed back in the reactor for continued testing.

e. Industrial Sapphire (Single crystal) - This sample was in the test 415 hours. Although the sample had cracked, it only corroded at the rate of 0.06 in/year. This sample was found in the bottom of the reactor.

Monofrax A is thus confirmed to be an excellent choice for the intended use.

2. Gasification Rate Testing

The 4-1/4" ID reactor used previously for corrosion testing is now being used for gasification rate testing. The results of these tests have been reported by the Process Research Section as part of their work on gasification rate testing.

3. Mechanical Characteristics Testing

A new reactor of 5-3/4" ID by approximately six feet long has been proposed to allow testing of several important factors. These include such things as the effect of greater bed depth, melt expansion with various superficial velocities, properties of the melt, etc. This new reactor has been partially designed during this report period and its furnace placed on order.

B. Projections

1. Environmental Testing of High-Temperature Materials

Oxidation Test #3, currently in progress, will continue to 1000 hours.

Testing of at least the Monofrax A and Morganite Triangle RR to 1000 hours in the gasification atmosphere is currently in the planning stage, and will probably begin at the completion of Oxidation Test #3. This test would be under simulated gasification conditions with no solid carbon feed. A gas mixture would be fed to the unit to simulate actual commercial operation, although at atmospheric pressure.

2. Mechanical Characteristics Testing

Work will continue on the large-diameter reactor and its supports. Design work will continue on the accessory equipment required for this test setup.