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DEPT OF THE INTERIOR

DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

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Progress Report No. 13

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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:



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 AND PROJECTIONS

This monthly summary is the thirteenth since the awarding of the contract. It is concerned with the first phase of the contract and outlines the progress that has been made in the three main areas that are now being studied: process research, chemical engineering studies and mechanical development.

The experimental program on the combustion of coal in the melt was continued. In the proposed flowsheet coal is burned in the melt to produce the heat required in the gasification step. A total of ten runs have been made and these have shown that combustion rates comparable to those projected in estimating gas costs have been achieved. On the other hand, the data are not yet sufficient to elucidate the effect of all the process variables on combustion rate, and the combustion test program will be continued.

It is of interest, however, that addition of ash to the molten salt yielded a significant increase in combustion rate and an important decrease in sodium volatility. These results will, of course, exert major influence on the choice of ash concentration at which to operate the gasification system.

In last month's discussion of ash removal, it was reported that sodium carbonate losses during bicarbonate precipitation were somewhat higher than anticipated but incremental gas costs due to this factor were found to be quite small. Further analytical work on samples from these experiments has shown that the sodium bicarbonate precipitate which is to be returned to the gasifier for sodium recovery includes some 25-28% of the silica in the quenched melt. This essentially confirms the assumption of 20% return of SiO_2 that was used in the estimated economics presented last month.

Up to this time viscosity measurements had been made with mixtures of ash and melt. This month experiments were made with mixtures of coke, ash and melt. The results indicated that coke addition to the melt increases the viscosity as much as ash addition. Furthermore, it



was found that the viscosity of salt-ash-coal mixtures decreased markedly when the system is subjected to shear. This will help to ease the problems of designing molten salt transfer lines and of mixing the melt in the gasifier.

Process designs for pipeline gas from bituminous and sub-bituminous coal were continued. The objectives are to produce process flowsheets for complete plants incorporating recent experimental data, to provide overall material and energy balances, and to estimate investment and operating costs more precisely. Operating conditions based on the most recent laboratory work are being employed so that a firm base case can be established. When this has been completed, the effects of operating parameters will be explored.

Of prime importance to the overall program is the search for materials of construction that will contain the very corrosive mixture of molten sodium carbonate, coal and ash. Test specimens from corrosion test No. 3 of the high-temperature materials have been examined. This test was concluded after 200 hours at about 1800 F in an environment that closely resembles the commercial plant conditions. Zirconia Y-1027 and Monofrax A (99.3% alumina) were unaffected and are considered as acceptable for commercial application. All three alloys -- RA 446 (25 Cr - 73 Fe), Thermalloy 28 (29 Cr - 0.5 Ni), Thermalloy 38 (28 Cr - 11 Ni) -- were found unsatisfactory for commercial application. The following refractories were found unacceptable -- Monofrax K-3, Chromex B and Ritex CB. The last two were satisfactory in test No. 2 but failed in test No. 3 at more-severe conditions. The Zirconia spray coat on the RD 600 alloy was gone. Test No. 4 is now in progress. Several alloys -- Inconel 600 and Incoloy 800 with three concentrations of aluminum, three metals -- molybdenum, tungsten, and platinum; and three refractories are to be subjected to test conditions for 500 hours.



III. PROCESS RESEARCH

A. Accomplishments

1. Combustion Studies

Eight combustion runs were made with Coke III, a bituminous coal (Island Creek #27) coked at 950°C., in which temperature, molten salt bed height, ash content, particle size, and concentration of coke in the melt were studied. The conditions and results of these runs are presented in Table I. Coke was employed because it simulates what may be present in the molten salt gasifier before passing into the combustion zone. After adding the coke, a 5-minute devolatilization period followed with a 2 l/min of nitrogen flow. Analyses of the composite gases for the 5-minute period showed 2-10% H₂, 10-29% CO, 5-13% CO₂, a trace of CH₄, and the remainder N₂. For convenience, the assumption was made that only the fixed carbon of the coke remained in the melt when air was introduced.

Although the results were calculated in the manner used for gasification runs, i.e. the percent of carbon combusted was determined and a first order plot made, the data points did not follow the simple first-order kinetics. Practically all of the runs gave a curve of increasing rate, indicating a dependence on oxygen concentration. As time permits and more data becomes available, further effort will be made to arrive at the proper kinetics for this system. As an expediency for purposes of comparison, the time at 50% carbon disappearance was used to calculate the specific combustion rate constant shown in the table. Thus this value has the same numerical significance as the gasification rate constant used in previous reports. The CO₂ and O₂ content of the product gas is given for three time intervals and at the end of the run. Unless noted, the carbon monoxide content was a trace or zero.

The effect of temperature, 1840°F versus 1940°F, can be obtained from the first two runs, J-9823 and 9824, where the rate constant was 44% higher for the higher temperature. Product gas composition verifies the improvement.



TABLE I

COMBUSTION OF BITUMINOUS COKE III IN MOLTEN Na_2CO_3 /1/

Run No. -J-	9823	9824	9825	9826	9827	9828	9829	9830
Date - 1965	8/3	8/5	8/10	8/12	8/16	8/18	8/23	8/25
Feed	-----Coke III-----							
% Fixed Carbon	92.2							
% Vol. Matter	2.0							
% Ash	5.8							
gms. Charge	24	24	49.5	24	24	49.5	23	24
mesh size	-----12/20-----			40/60	-----12/20-----			-200
Na_2CO_3 - gms.	414	414	414	414	828	828	414	414
- bed ht.-inches	4	4	4	4	8	8	4	4
Ash - % in melt /2/	-	-	-	-	-	-	10	-
Conditions								
Temperature - °F	1845	1935	1840	1840	1835	1840	1840	1840
% C in melt at start	5	5	10	5	2.6	5.2	4.4	5
% O ₂ in Dry Air	-----21-----							
Air Rate - cc/min	-----4230-----							
Run Time - min.	135	115	145	105	125	175	95	85
Results								
Product Gas								
% CO ₂ - 5 min.	13.5	18.0	19.5	14.0	13.5	14.0	18.0	17.0
-35 min.	10.5	15.5	20.0	11.0	8.5	14.0	10.0	11.5
-65 min.	10.0	2.5	18.5	8.0	8.5	12.5	1.5	2.0
-end	0.3	0.5	0.5	0.5	1.5	1.0	0.0	0.3
% O ₂ - 5 min.	6.5	3.5	2.0	5.5	9.5	8.0	tr	3.5
-35 min.	10.0	5.5	2.5	9.5	13.0	8.0	13.0	10.0
-65 min.	10.5	17.5	4.0	11.0	13.0	7.5	18.0	17.0
-end	18.5	20.0	21.0	19.0	17.5	19.0	20.0	18.0
Minutes to 50% C left	42	29	47	40	46	74	21	(27)
Comb. Rate Const. /3/	0.43	0.62	0.38	0.45	0.39	0.24	0.86	(0.67)
Total % consumed	101	89	103	92	103	85	101	69
Notes			/4/				/5/	/6/

- /1/ Atmospheric pressure, 0.5 ft/sec superficial air velocity, a 5-minute devolatilization in 2 l/min of N₂ precedes air injection.
- /2/ Bituminous coal ash from Island Creek #27 before coke addition.
- /3/ Same kinetic basis as used for gasification runs.
- /4/ About 0.5% CO present in product gas for the 1st 45 minutes, decreased to 0% in the next 40 minutes.
- /5/ Temperature increased 30°F when air added; 2.5% CO in the product sample gas at 5 minute; only trace of O₂ in the 25-minute sample.
- /6/ Some carbon blown over; values for "min. to 50% C left" and "rate constant" based on output.



An increase in the concentration of carbon in the melt at 1840° F from 5 to 10% at the start of combustion had no effect upon the rate constant. This is evident from the first and third runs, J-9823 and 9825. Product gas compositions show that about twice as much carbon was oxidized for the 10% carbon-in-melt run, but the rate constant was about the same.

Particle size of the coke, 12/20 mesh versus 40/60 mesh (U. S. Std. Sieve Series), had no effect on the combustion rate constant, 0.43 and 0.45 respectively, in runs J-9823 and 9826. However in run J-9830, -200 mesh coke was fed and although considerable loss of coke was noted (31%) the rate constant of 0.7 on an output basis is believed to be real and represents an improvement due to the fine particle size.

Two levels of molten salt bed height were studied, the standard 4-inch and an 8-inch quiescent bed height in runs J-9827 and 9828 at 2.6 and 5.2% initial carbon level, respectively. The high-bed run at 2.6% carbon gave the same rate as the low-bed run, J-9823, at 5% initial carbon level. Based upon the previous conclusion that carbon concentration had no effect on the rate constant, it is concluded that bed height had no effect on rate. However, run J-9828 at the high bed height and 5.2% carbon concentration gave poorer results, about 56% of the standard run J-9823. Explanation of this run must await further experimentation.

Run J-9829 with 10% ash from bituminous coal in the molten salt, was the most outstanding. Just as in the gasification run with ash in the melt, a strong catalytic effect can be attributed to the presence of ash. The rate constant was doubled, going from 0.43 to 0.86 when 10% ash was added to the salt. From the product gas, the complete consumption of oxygen in the first 25 minutes as well as breakthrough of carbon monoxide indicates that possibly the rate could be even higher under excess oxygen conditions. In this run, a significant increase in temperature for the first time was noted as the air was cut in.

In addition to the above favorable effects one other very notable observation must be mentioned in connection with the presence of ash. Direct recovery of salt from the transfer line and receiver section of the unit average 17.5 grams \pm 3.5 grams for all the combustion runs except the one with ash present. The latter gave only 2.3 grams of solid carryover, a very significant and desirable drop in solid evaporation from the melt. It thus appears that ash ties up most of the volatile sodium oxide or hydroxide which is normally volatilized under combustion conditions.



2. Additional Viscosity Determinations of Coke-Ash-Sodium Carbonate Melts

Two additional experiments measured the effect of addition of -60 mesh Coke III to a sodium carbonate melt containing ash from bituminous coal (Island Creek #27) at 1700°F. In the initial experiment at 10-20 rpm on the Brookfield viscometer the following results were obtained. Ash was mixed into the melt using carbon dioxide and coke was added in small increments with nitrogen as the mixing gas. No frothing

<u>% Coke III in Na₂CO₃ Melt with 10% Ash</u>	<u>Viscosity - cps</u>
0	200
5	450
10	800

occurred. Viscosities were measured under non-agitated conditions. An indication of changing viscosity with shear speed of the Brookfield was noted.

The second experiment is shown in the following tabulation.

<u>Na₂CO₃ Melt with % Ash</u>	<u>% Coke III</u>	<u>Viscosity - cps at</u>		
		<u>10 RPM</u>	<u>20 RPM</u>	<u>50 RPM</u>
10	0	-	150	70
15	0	600	500	400
20	0	1050	1050	700
10	5	-	400	400
10	10	-	800	650

The above effect of decreasing viscosity with increasing shear is characteristic of a pseudo-plastic material. Many emulsions show this effect. The above results show that coke addition increases the viscosity of 10% ash-melt almost as much as ash addition (values range from 76 to 100% and average 87%).



Measurements of viscosity at this temperature and with the long spindle leave much to be desired, consequently these results must only be considered as approximate and relative. When gas is bubbled through the ash-coke-melt at 0.25-0.5 ft/sec superficial gas velocity, the viscosity reading approaches zero.

3. Sodium Recovery Studies

Experiments have been performed to determine the loss of sodium in residues obtained from extraction of solid mixes resulting from quenching 5 and 10% coke in 10% ash-sodium carbonate melts and with a wash water to residue ratio of 3/1. Chemical analyses are currently underway.

Silica analyses on some of the previously prepared samples, in which mixtures of ash and molten salt (no coke added) were used, have been received. Results indicate that about 25-28% of the silica in the quenched melt shows up in residue number 2, the sodium bicarbonate solid which is circulated back to the gasifier. Some 67 to 70% of the silica occurred in residue number 1, which is discarded. The R_2O_3 oxides (alumina, iron oxide, etc.) appear to remain in residue 1. About 84 to 95% of the total was determined as being present there. Analytical accuracy, lack of homogeneity, and sample size do not allow a reliable decision on the distribution of the missing oxide material.

B. Projections

1. Combustion Studies

Further combustion runs will continue to investigate the effect of ash, aging of the coke, and the effect of variables using other feedstocks.



IV. CHEMICAL ENGINEERING STUDIES AND DEVELOPMENT

A. Accomplishments

1. Ash Removal and Sodium Recovery

Further experimental work in ash removal and sodium recovery by bicarbonate precipitation was recommended to extend the range of several variables into areas that recent process studies indicate to be more attractive for a commercial design. Data are needed in the following areas:

- a. The effect of lower ash concentration, e.g. 5%, in the melt.
- b. The effect of ungasified coal in the melt.
- c. The effect of using less water to wash the ash-coal residue remaining after dissolution of Na_2CO_3 . Three weights of wash water per weight of residue will be satisfactory.

2. Process Flowsheets

Process designs for making pipeline gas from bituminous coal and from sub-bituminous coal were continued. The objectives of this work are:

- a. To produce process flowsheets for the complete plant, from raw material to final product.
- b. To incorporate recent experimental data and guide future experimental work into critical areas.
- c. To provide overall material and energy balances.
- d. To estimate investment and operating costs more precisely.

The following bases have been chosen for these designs:

- a. Product: 250 MM SCFD of pipeline gas



b. Gasifier operating conditions:

Temperature	1830°F
Pressure	400 psig
Ash in melt	8%
Coal in melt	4%
Gasification rate	3 lb/hr/lb coal in melt
Steam/carbon	2 lb/lb

c. Method of supplying heat: direct combustion of coal in melt at gasifier pressure.

d. Combustor operating conditions:

Temperature	1900°F
Pressure	400 psig
Combustion rate	3 lb/hr/lb coal in melt
Excess air	30%
Combustion product	CO ₂

e. Method of ash removal and sodium recovery: quench with water, filter and precipitate NaHCO₃.

f. Gas purification sequence: Fluor Solvent CO₂ Removal Process, iron oxide, and activated carbon.

g. Methanation process: Bureau of Mines dual-reactor, hot-gas-recycle.

B. Projections

Process design studies for making pipeline gas will be continued. When a firm base case has been established on the basis enumerated above, the effect of the following parameters will be explored:

1. Operating temperature, including its effects on melt viscosity and rates of gasification and combustion.
2. Higher gasification rates, which are expected to be attained at 400 psig but have not yet been demonstrated.



3. Ash content of melt, including its effect on viscosity and sodium losses.
4. Coal concentration in melt.
5. Steam/carbon ratio in gasifier (steam utilization).
6. Excess air in combustor.



V. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Environmental Testing of High Temperature Materials

The test specimens of completed Test #3 have been examined and evaluated for corrosion resistance. The results are as follows:

RA 446 (25 Cr - 73 Fe)

All three specimens were recovered but severely corroded. This alloy is unsatisfactory for commercial application in this process.

Thermalloy 28 (29 Cr - 0.5 Ni)

Thermalloy 38 (28 Cr - 11 Ni)

None of the samples (6) of these two materials were recovered and, consequently, assumed disintegrated. These specimens were cut from centrifugally cast tubing and, therefore, the microstructure of the test specimens may be a contributing factor in their poor performance.

RA 600 with .040"/.050" Thick Zirconia Spray Coat

All three of these specimens were recovered with the zirconia coating gone. The RA 600 base metal, however, appeared to be in very good condition, showing only minor corrosion effects.

Zirconia Y-1027

All three samples of this material were recovered and appeared to be unaffected by the test environment. This was predicted on the basis of the performance of zirconia (Zircorfrax 0) in Test #2.



Zircofrax 0

Although this refractory showed up well in Test #2, none of the samples were recovered after Test #3. This poor showing is attributed to the poor structural make up of the test specimens rather than the material (zirconia). (This refractory is produced by Carborundum on a developmental basis.)

Monofrax A (99.3% Alumina)

The three samples of this material also came out of Test #3 relatively unaffected. Since this material is considerably cheaper than zirconia, further testing of it is contemplated to establish it as an acceptable alternate to zirconia.

Monofrax K-3 (60.4% Al₂O₃; 27.3% Cr₂O₃)

None of the samples of this refractory was recovered.

Chromex B

None of the samples of this refractory was recovered. The performance of this material appeared acceptable in Test #2 but the greater severity of Test #3 (1800°F vs. 1650°F) proved the material to be unsatisfactory.

Ritex CB

Of the three specimens of this material only one (in the total submerged position) was recovered. However, from handling, the recovered specimen crumbled easily. As in the case of the Chromex B, this material appeared acceptable in Test #2 but the greater severity of Test #3 proved it unsatisfactory.

Test #4 was initiated at the latter part of this report period and is currently in progress. The equipment and process used in Test #3 are used in this test, but it is planned to extend the duration to 500 hours. The materials included in this test are as follows:

Metal Alloys

- 60 Cr - 40 Ni
- Inconel 600
- Incoloy 800 with 1.50 Al
- Incoloy 800 with 2.40 Al
- Incoloy 800 with 3.60 Al



Refractories

Zirconia Y-1027
Zirconia RMF-5F
Zirconia 60D (Castable)
Monofrax A
Silicon Nitride (Carborundum)

Metals

Molybdenum
Tungsten
Platinum (wire)

2. Coal Feeding Studies

The coal feeding device (described previously) for the bench-scale, high-pressure reactor has been completed and assembled. As of the end of this report period, the facilities for testing the feeder are being set up.

B. Projections

1. Environmental Testing of High Temperature Materials

At the completion of Test #4, the metal alloy samples will be sent to the INCO laboratory where corrosion rates will be determined. The refractory samples will be examined for corrosion effects and evaluated for this service.

The feasibility of testing a small reciprocating pump (1" dia. bore) made of zirconia is being studied. If the pump can be manufactured at a reasonable cost, plans for the project will be initiated.

2. Coal Feeding Studies

As soon as the test facilities are complete, testing will begin on the coal feeding device. These tests are designed to check the pressure integrity of the feeder and also to check the delivery rates attainable at various rotational speeds. Once these tests have been satisfactorily completed, the feeder will be incorporated into the bench-scale high-pressure unit system.