

MWK-MPK-8

THE M. W. KELLOGG COMPANY
Research & Development
Department



OFFICE OF COAL RESEARCH
RECEIVED

1965 APR 27 PM 1 16

DEPT OF THE INTERIOR

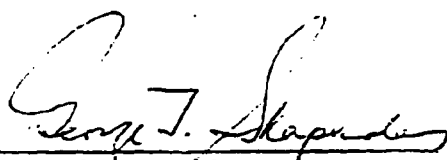
DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS


Contract No. 14-01-0001-380

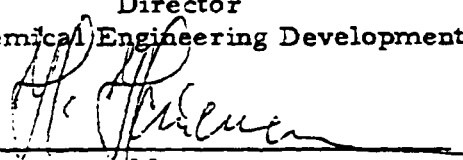
March 31, 1965

Progress Report No. 8

APPROVED:


Project Manager


Director
Chemical Engineering Development


Manager
Research and Development



CONTENTS

	<u>Page No.</u>
I. INTRODUCTION	1
II. PROCESS DEVELOPMENT	2
III. PROCESS RESEARCH	8
IV. MECHANICAL DEVELOPMENT	13
V. MANPOWER AND COST ESTIMATES (To be transmitted with invoices)	



I. INTRODUCTION

The objectives of the development program were reviewed in the light of recent experimental findings specifically the severe corrosion experienced by all metals tested and the lower than anticipated gasification rates obtained. It was found that production of pipeline gas from bituminous coal at a cost of 50¢/MSCF is still a reasonable goal.

Six coke gasification runs in molten sodium carbonate at 1700°F have been completed. Preimpregnation of coke with 10% Na₂CO₃ prior to charging to the reactor appears to increase the rate of gasification at least 100%. The hydrogen to oxygen ratio in the exit dry gas is variable and indicates significant amount of oxidation (by CO₂ and/or steam) or reduction (by H₂, CO and/or carbon) of the Inconel reactor. The best calculation of the rate data, therefore, is probably based on the use of total oxides of carbon evolved as the criterion of percent carbon gasified.

Measurements of ash/molten carbonate viscosities were completed. The particle size of the ash has very little effect on the equilibrated ash/melt viscosity.

Initial results of sodium leachability in the demonstration of a proposed sodium recovery scheme indicate about 90% sodium recovery.

The test of refractory materials was concluded when the test reactor corroded through. Several samples were recovered. Data on the metal alloys indicate high corrosion rates on all metals tested. The lowest rate was Inconel 600 with 1.6 inches per year (metal unaffected by corrosion).



II. PROCESS DEVELOPMENT

A. ACCOMPLISHMENTS

The objectives of the development program were reviewed in the light of recent experimental findings, specifically (1) the relatively severe corrosion experienced by all metals tested in contact with the molten salt, and (2) the lower-than-anticipated gasification rates obtained. The effect of these findings on projected process economics was explored, specifically the economics of producing pipeline gas from bituminous coal. A number of the cases considered are outlined in Table 1, along with the estimated plant investment and product gas cost.

Case 1 is virtually identical to a case presented in an earlier Progress Report (1), assuming a specific carbon gasification rate of 4 pounds per hour per pound of carbon present in the melt and that a satisfactory metal is found for construction of a fired-tube melt heater. Total plant investment is about 90 million dollars and gas production cost is 43 cents per thousand cubic feet (¢/MSCF).

Case 3 illustrates the effect of a specific gasification rate only one-twelfth as large, i. e. 0.32 lb C/hr/lb C, which is in the range of rates being obtained experimentally. Gas production cost is increased by only about 3¢/MSCF. This relatively small increase may be traced to 3 factors:

1. Gasifier cost in case 1 represented only a moderate portion of total investment.
2. Gasifier cost did not increase directly with increase in volume.
3. Maintenance and fixed charges are computed at only 12% of investment per year.

(1) Progress Report No. 3, October 31, 1964, p. 9.



Any further significant reduction in gasification rate below 0.32 lb. C/hr/lb C will, however, have a much greater effect on gas cost.

The remainder of Table 1 explores other methods of supplying heat to the gasifier, assuming that a fired-tube melt heater is not technically feasible. These alternate methods have been discussed in previous reports (1, 2). Cases 6 through 9 are based on supplying heat by direct combustion of coal in the melt at low pressure (say 30 psig). This method raises two severe technical problems:

1. A pump must be developed for circulating melt between combustor (30 psig) and gasifier (400 psia).
2. The combustion must, if at all possible, produce CO₂, not CO, as the primary product. This may be difficult if, in order to achieve acceptable gasification rates, the circulating melt contains more carbon than must be burned to satisfy the energy balance. Any CO produced will appear in the flue gas and will represent a significant energy loss unless it can be used elsewhere in the plant.

If heat is supplied by direct combustion at low pressure and if combustion produces CO₂ even in the presence of excess carbon, then gas production cost will be about 50¢/MSCF (Case 6). The increase over case 3 is due largely to the cost of power for circulating melt and compressing combustion air.

If CO is produced instead of CO₂ and if this energy cannot be utilized, a severe cost penalty is introduced, as shown by case 7 with a gas production cost of 71¢/MSCF. Assuming arbitrarily that 70% of the CO heating value can be utilized reduces gas cost by 6¢/MSCF (Case 9). Case 9A assumes that the rate of combustion is no greater than the rate of gasification and, further, that 100% excess air must be used to obtain this rate.

The possibility of forming CO in the combustor could be avoided if there were no excess carbon present, i. e. if only that quantity of carbon that must be burned to satisfy the energy balance is brought

(2) Progress Report No. 1, August 31, 1964, p. 10.



into the combustor. This requires that carbon concentration in melt be only about 0.3%, which leads to very poor gasification rates and enormous gasifiers. Very approximate estimates of investment and gas cost show that this alternative (Case 8) deserves no further consideration.

In Cases 11 through 14 heat is supplied by direct combustion in the melt at gasifier pressure (400 psia). A melt pump is no longer necessary, but a new technical problem is raised: air for combustion must be compressed to 400 psia and flue gas must be expanded to provide most of the energy needed for compression. A method must be developed for reducing entrained melt and ungasified carbon in the hot flue gas to a level that can be tolerated by the expander. Burning to CO_2 in the presence of excess carbon is also a necessity in these cases if substantial penalties are to be avoided.

This work has led to the following conclusions:

1. The production of pipeline gas from bituminous coal at a cost of 50¢/MSCF (not including any return on invested capital) is still a reasonable goal.
2. Studies of materials of construction should be given the following priority:
 - a. A satisfactory material for lining vessels and pipe containing the melt. This is absolutely vital to the process regardless of ultimate gasifier design.
 - b. A material for fabricating valves in contact with the melt. Such valves are needed to control the flow of melt between gasifier and ash removal system.
 - c. A material for fabricating a melt pump, which will be needed if the melt is to be circulated against a high head, but is not vital to all designs.



- d. A material (probably a metal) for furnace tubes that can operate continuously at a temperature above 1800°F in contact with a flowing melt. These are required only for the fired-tube melt heater case.
3. The lower-than-anticipated gasification rates have not had serious economic consequences, for the reasons enumerated previously. However, any further reduction in rate would have a much greater effect. The gasification rate used in the calculations is typical of those being obtained experimentally at atmospheric pressure; the rate is expected to improve significantly at the high gasification pressures that must be used for other reasons.
4. Experiments designed to study combustion of coal in the melt should be directed to finding designs and conditions under which CO₂ is the primary combustion product even with a large excess of carbon present. The effect of combustor configuration and efficiency of gas-melt contacting on flue gas composition should be investigated.
5. Gasification and combustion experimental work should be pursued at high pressure (400 psig) as soon as the necessary equipment can be installed.
6. Process flowsheets for the complete plant should be assembled as soon as possible to permit a more thorough study of waste heat utilization. Plant thermal efficiency may be quite dependent on the effectiveness with which low level heat is used, and the dependence will probably vary appreciably with the raw materials and end products that must be considered.

Case No.	1	3	6	7	9	9A	8	11	12	13	14	
Variables												
Specific gasification rate, k, #c/hr. #c present	4	0.32	→									
Carbon in melt, %	10	→					0.3	10	→			
Gasification rate, #c/hr. ft ³ melt	50	4	→				0.12	4	→			
Method of Heat Supply	Fired-tube heater		Direct combustion in melt at low pressure (30 psig)				Direct combustion in melt at gasifier pressure (400 psia)					
Rate of combustion in melt, #c/hr. ft ²	-	-	10	20	→		4	10	20	→		4
Equilibrium achieved for C + CO ₂ ⇌ 2CO in direct melt combustion	-	-	No; assume burning to CO ₂	Yes	Yes	→ (13)		No excess carbon; burn to CO ₂	No; assume burning to CO ₂	Yes	→ (13)	
Disposition of CO heating value in flue gas	-	-	-	Wasted	→		70% utilized	-	-	→		70% utilized
Total Plant Investment, MM\$	90	112	101	115	115	145	800	104	134	162	212	
Gas production cost, ¢/MSCF	43	46	50	71	65	74	150	46	60	64	70	
Gas selling price to provide 7% return after income taxes, ¢/MSCF	57	63	66	89	83	97	280	62	81	89	103	

TABLE I - EFFECT OF SELECTED PROCESS VARIABLES ON PIPELINE GAS ECONOMICS

BASES & ASSUMPTIONS:

- | | | |
|---|--|--|
| 1. 250 MM SCFD of pipeline gas. | 6. %C feed to gasifier = 2H/H. | 10. Ash removed by water quench-bicarbonate precipitation; Na ₂ CO ₃ loss = 5% per pass. For 10% loss per pass, add 2¢/MSCF. |
| 2. Bituminous coal at \$4/ton. | 7. % coal gasified = 97.5; for 90% coal gasified, add 4¢/MSCF. | 11. Maintenance & fixed charges at 12% of investment per year. |
| 3. Gasification temp. = 1700°F. | 8. Specific gasification rate assumed to be valid all the way to 97.5% gasified. | 12. No by-product credits. |
| 4. Gasification pressure = 400 psia. | 9. Ash level in melt = 20%. | 13. Combustion with 20% excess air, except Cases 9A and 14, which have 100% excess. |
| 5. Assumed gasification rates at 1700 F, 400 psia | | |



B. PROJECTIONS

Evaluations of gas purification schemes and secondary product recovery, which have been suspended during the review of program objectives, will be resumed. Preparation of process flow-sheets for the complete pipeline gas plant will be started so that overall thermal efficiency can be studied.

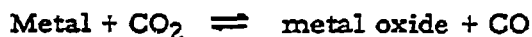


III. PROCESS RESEARCH

A. ACCOMPLISHMENTS

1. Gasification Kinetics

A summary of the results of coke gasification in the 2 inch I. D. bench scale reactor are given in Table 2. Examination of hydrogen to oxygen atomic ratios in the water-free exit gases yielded widely varying ratios for the runs listed. The ratio increases slightly over the course of a particular run, suggesting increasing oxidation of the Inconel reactor with the production of excess reducing gas (CO and/or H₂).



Several runs yielded lower than 2/1 ratio indicating the reversal of the above oxidation-reduction reactions.

Previously reported rate data on coal gasification are therefore in error and must be corrected, although the correction will probably be small. The effect of pre-impregnation (with sodium carbonate) on the rate of gasification was studied. Experiments J-9659 and J-9661 were performed using portions of the same preimpregnated Mexican coke. Run J-9662 was made with non-impregnated coke. The data indicate a 7 to 12 fold increase in rate due to impregnation. A second batch of preimpregnated coke, however, yielded a value only twice the rate of the control. The particular details of preimpregnation may be important and will be investigated. The effect of preimpregnation on the rate on bituminous coke gasification is also given in the Table 2. The basis for calculation is total oxides of carbon evolved and not the reducing power of the gas as was previously used. Preimpregnation appears to double the rate of bituminous coke gasification.

TABLE 2 - GASIFICATION OF COKE IN MOLTEN Na_2CO_3 (11)

Run No.	GMS. Carbon in Melt	Coke (1)	Preimpregnation	Run Time Mins.	% Input Carbon Gasified		Hydrogen Oxygen Ratio in Outlet Dry Gas	Specific Gasifi- cation Rate Constant k, hr ¹ (6)
					Basis Carbon Oxides Out	Basis 1/2 (CO+H ₂)Out		
J-9659(7)	16.4	21.9 g. Dry Mexican Coke (4)	2.4 g. Na_2CO_3 (9)	90	120	63.4	0.9	1.8
J-9661(7)	16.2	21.6 g. Dry Mexican Coke (4)	2.4 g. Na_2CO_3 (9)	115	97.4	62.5	1.2	1.1
J-9662(8)	18.0	24 g. Dry Mexican Coke (4)	None	160	68.4	79.8	2.4	0.15
J-9776(7)	15.8	21.0 g. Dry Mexican Coke (4)	2.3 g. Na_2CO_3 (10)	185	88.4	105.4	2.4	0.33
J-9777(8)	35.0	38.6 g. Dry Coke (5)	None	365	90.6	129	3.0	0.17
J-9778(7)	31.1	34.3 g. Dry Coke (5)	3.8 g. Na_2CO_3	290	100.2	70.6	1.35	0.30

- (1) All 12/20 mesh.
 (2) Balance of inlet pressures is N_2 (total pressure = 14.7 psia)
 (3) $\text{N}_2 + \text{H}_2\text{O}$ feed (moles/hr) x 0.044
 (4) 25% ash
 (5) Bituminous coke, 90.7% carbon (Island Creek #27 coal)
 (6) For first order decomposition of carbon, $\log \frac{C}{\text{CO}} = -k t$, basis oxides of carbon evolved
 (7) Fresh Na_2CO_3 charge
 (8) Melt from previous run was charged
 (9) Preimpregnation Preparation #1
 (10) Preimpregnation Preparation #2
 (11) Na_2CO_3 charge gas: 414; temperature, °F: 1700-1770; partial pressure of steam(2): 13.3-13.6; Sup. Gas Velocity(3)ft/sec : 0.51; Olescent Bed Height, in.: 4





2. Physical Property Data

The viscosity versus time relationships for Elkol sub-bituminous coal ash - Na_2CO_3 mixtures were obtained. This completes the present studies on the effect of ash from different types of coals.

A study has been made aimed at gaining knowledge of the effect of ash particle size on viscosity. Each type of ash used in main viscosity studies was quite finely divided (mostly -60 mesh). To study the effect of coarser particle size, batches of bituminous coal ash and lignite ash were fused in a muffle furnace at 2300°F . The solidified ash was then ground in a mortar to minus 12 mesh using a technique which minimized the production of fines. The fused ash was then used for viscosity studies. In each case the coarser material was slightly slower equilibrating and gave a slightly lower final viscosity.

3. Sodium Carbonate Recovery

Preliminary studies on extracting Na_2CO_3 from ash-carbonate mixtures were carried out using water for extraction. Studies of various recovery schemes have shown that an attractive scheme would involve extraction with NaHCO_3 solution, conversion of the recovered Na_2CO_3 to NaHCO_3 using CO_2 and finally precipitating NaHCO_3 by cooling. Forty grains of melt, containing 15% bituminous coal ash and 85% Na_2CO_3 previously held for 5 hours at 1800°F , was ground to minus 12 mesh and boiled for 10 minutes in 250 ml of 10% NaHCO_3 solution, the mixture was then filtered. More than stoichiometric CO_2 was then bubbled thru the hot filtrate to convert the recovered Na_2CO_3 to NaHCO_3 . The solution was then cooled to 71°F and filtered. The residue contained the recovered sodium as NaHCO_3 contaminated to a small extent by minerals dissolved from the ash.



Duplicate tests gave sodium recoveries of 89.4% and 91.1%.

4. Coal Analyses

Proximate and ultimate analyses of six coals being studied are shown in Table 3.

B. PROJECTIONS

Gasification work will continue with emphasis on bituminous coal and ash. Experimentation on sodium recovery scheme continues.



IV. MECHANICAL DEVELOPMENT

A. ACCOMPLISHMENTS

1. Environmental Testing of High Temperature Materials

During the first day of this report period, the test reactor corroded through necessitating shut-down of the test. The tests will be resumed when a new test reactor is designed and built. In addition to the corrosion failure of the vessel, the sample rack corroded and fell to the bottom of the reactor. Because of this latter mishap the test samples had to be recovered from the solidified salt bed by dissolving the salt away with hot water. After completely washing away the salt, four samples were recovered. The condition of these samples varied as follows:

#1 Sample retained its original shape and seemed generally sound in structure although minute surface cracks appeared.

#2 Sample was removed from the reactor with the bottom 1/4 missing. The recovered portion seemed very sound and had no apparent surface cracks.

#3 Sample retained its original shape but seemed weakened in structure and showed minute surface cracks.

#4 Sample was removed from the reactor in two parts. The structure seemed weakened.

All four samples were placed in boiling water for 6 hours and after removal, samples 1 and 2 seemed unaffected. Samples 3 and 4 broke after removal from the boiling water and the pieces from sample 4 could be crumbled by hand. Because of its shape, sample 2 was recognized as a carborundum product



and was subsequently identified by carborundum as Zircofrax O (94% ZrO_2). Positive identifications have not yet been made on the remaining samples but preliminary analyses indicate samples 1 and 3 to be chrome-magnesite compositions (Chromex B and Ritex CB).

Corrosion rate data on the metal alloys from Test 1 have been received from the International Nickel Company and are recorded in the table below. Note that two bases for evaluation have been made. The first, "Minimum Thickness of Metal Remaining", is determined by a change in thickness of the test sample as indicated by micro-meter measurement before and after test. The second, "Metal Unaffected by Corrosion", is determined and accounts for intergranular corrosion into the metal surface remaining. This second criterion is more significant for construction materials since such penetration may greatly reduce the structural value of the altered layer.

CORROSION DATA - TEST #1

<u>Alloy</u>	<u>Minimum Thickness of Metal Remaining</u>	<u>Metal Unaffected by Corrosion</u>
Incoloy 800	1.401	3.510
Incoloy 804	.895	1.850
Inconel 600	.140	1.589
Inconel 702	1.612	1.812
50 Cr. -50 Ni	.984	1.990
AISI Type 310	1.121	3.880
RA 333	.772	2.260



B. PROJECTIONS

1. Environmental Testing of High Temperature Materials

Plans are underway for the design and construction of a new test reactor. It is planned to make this new reactor of a single tube rather than the double tube configuration used in Tests 1 and 2. Evidence in these two tests indicated that the corrosion rates on the test samples depended considerably on the elevation positions relative to the liquid level of the bed. Test samples (also the internals and the reactor) showed the greatest corrosion just above the gas interface. Because of this position factor a comparison of the corrosion resistance of the samples may be deceptive. To eliminate this variable from the results of future tests, it is planned to put all test coupons of each material at three different elevations; submerged within the bath, at the interface, and above the interface. The new reactor will be constructed from a centrifugally cast tube of 25% Cr - 20% Ni alloy, large enough in diameter (about 4" ID) to accommodate 10 samples at one elevation and thick enough (about 1/2") to assure adequate life.