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RESEARCH AND DEVELOPMENT DEPARTMENT\_ GG

## DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

Contract No. 14-01-0001-380

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Progress Report No. 6

**APPROVED:** 

Project Manager

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Director Chemical Engineering Development min Manager

Research and Development

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#### I. INTRODUCTION

Work was continued on process development. The evaluation of alternate methanation schemes was completed. The dual-fixed-bed, hotgas-recycle scheme appears to be the most economical as well as technically the soundest at the present time.

The gasification of anthracite at  $1700^{\circ}$ F follows the pseudo first . order rate expression log C/Co = -0.225(C) t.

With anthracite and bituminous ashes in molten sodium carbonate the viscosities equilibrate in 4 hours or less and the viscosities range from 300 to 8000 cps.

After about 100 hours of operation the materials of construction test samples were removed from the molten salt bath. Visual observations indicated severe to moderate corrosion.

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# PROCESS DEVELOPMENT

#### A. ACCOMPLISHMENTS

1. <u>Methane Synthesis</u>

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The evaluation of alternate methanation schemes has been completed. As was reported earlier, the four reactor types under consideration were:

- a. Transport reactor
- b. Dual-fixed-bed reactors, hot-gas-recycle system
- c. Fixed-fluidized-bed reactor
- d. Tube-wall reactor

The plant capacity chosen for this study was 90MM SCFD of pipeline gas because process designs for some of the schemes were already available from previous studies for this capacity. Since even the 90MM SCFD plant already consists of multiple trains of equipment, it is expected that the investment for a larger plant will be almost directly proportional to capacity and therefore the operating costs should be almost independent of plant size in this range.

In each of the cases considered the feed gas is a purified synthesis gas containing about 1.0 mole per cent  $CO_2$  and about 0.004 grains total sulfur/100 SCF. The remainder of the gas is essentially H<sub>2</sub> and CO in the ratio of 3 volumes H<sub>2</sub> to 1 volume CO. Operating pressure of the methanation step is approximately 320 psia.

#### a. <u>Transport Reactor</u>

In the transport reactor methanation system, preheated synthesis gas is fed to the reactor at about 465°F. Here the gas entrains a Raney nickel catalyst and carries it upward through the tubes of a heat exchanger designed to remove the exothermic heat of the reaction below

 $CO + 3H_2 \implies CH_4 + H_2O$ 

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by generating high-pressure steam. When reaction is completed, the products and the catalyst are separated, the catalyst being recycled and mixed with fresh synthesis gas, thus completing the catalyst circuit. Effluent gas from the reactor is cooled to condense water, resulting in a product gas containing about 95%  $CH_4$  and having a heating value of about 915 Btu per SCF.

Although there has been a considerable amount of research into the catalytic synthesis of methane performed recently in the United States and in England, no experimental work has been done on the transport reactor system as such. For this reason, the design of the reactor is based on data obtained for a similar reaction system -- namely, the work done at the Institute of Gas Technology on a fixed-fluidized-bed methanation reactor, and on Kellogg experience with the synthesis of liquid fuels in a transport reactor. A discussion of the results of the IGT experimental programs will be given later.

### b. Dual-Fixed-Bed Reactors, Hot-Gas-Recycle System

The hot-gas-recycle methanation scheme has been developed by the Bureau of Mines (1, 2). Basically, the system consists of two fixed-bed reactors in series; the first containing an iron catalyst in the form of lathe turnings, wherein the bulk of the methanation reaction occurs, followed by a second reactor containing Raney nickel catalyst wherein the reaction is completed. Heat of reaction is removed from the first-stage reactor partially by generating steam in cooling coils located between beds of packing and partially by externally cooling a recycle stream of reactor effluent. Heat is removed from the second-stage reactor by generating steam in external coolers between beds of the nickel catalyst. Product gas from this reactor scheme is essentially the same as for the transport reactor.

Unlike the transport reactor scheme, there has been a considerable amount of experimental work done by the Bureau on the hot-gasrecycle system. Both bench-scale and pilot-plant programs have been

2. Forney, A. J. et.al., Bureau of Mines Report of Inv. 61261 (1962)

<sup>1.</sup> Bienstock, D. et.al., Eureau of Mines Report of Inv. 5841 (1961)

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carried out; and these results have served as the basis for the present design and evaluation. The bench-scale methanation work was done with a 3" I. D. first-stage reactor and four 1" I. D. second-stage reactors (in parallel), while the pilot plant reactors were 12" I. D. and 3" I. D., respectively. Operating pressures in these experiments were of the order of 400 psig. In both programs the iron catalyst retained its activity for runs lasting as long as 2 to 3 months. Similarly, nickel catalyst lives of more than 1 month were demonstrated in both bench-scale and pilotplant operations. The Bureau now recommends catalyst lives of 6 and 3 months, respectively, for the iron and nickel catalysts. These latter figures have been used in the present evaluation.

#### c. Fixed-Fluidized-Bed Reactor

The fixed-fluidized-bed methanation reactor has been investigated at the institute of Gas Technology on both laboratory scale and pilotplant scale (3, 4). As the name implies, the reactor consists of a fixedfluidized bed of Raney nickel catalyst (as opposed to the moving fluidized bed of the transport reactor) through which the synthesis gas passes. The heat of reaction is removed by generating steam in bundles of tubes suspended vertically in the fluid bed. Product gas is essentially the same as that produced by the two previous schemes.

In the laboratory-scale methanator (1" I. D. ), catalyst lifetimes of about 2 months were observed at operating pressures of 75 to 150 psig. Methane production rates of about 20,000 SCF/lb. of catalyst were demonstrated in these small-scale tests. Attempts to reproduce the laboratory-scale results on a larger scale (6" I. D. reactor) were, in general, unsuccessful because of operating difficulties. However, even in the absence of these operating problems, methane yields based on catalyst were, at best, about one-third those obtained in the laboratory tests. It was finally concluded by IGT that the difference in results between the smalland large-scale methanators was due to differences in gas-solids contacting. For this reason, a methane production rate of 20,000 SCF/lb. is still recommended by IGT, and this is the number which has been used as a basis for catalyst consumption in the present evaluation.

4. Dirksen, H. A. et.al., Research Bull. #31, IGT (July '63).

<sup>3.</sup> Dirksen, H. A. et.al., "Production of Pipeline Gas by Methanation of Synthesis Gas over Raney Nickel Catalysts" presented at ACS, Atlantic City (Sept. 13, 1959).

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#### d. Tube-Wall Reactor

The tube-wall reactor is the most recent methanation scheme to be investigated by the Bureau of Mines (5). Basically, the reactor is envisioned to be a shell-and -tube heat exchanger with the outside of the tubes coated with a thin layer of nickel catalyst. Synthesis gas is fed into the baffled shell of the exchanger where it reacts at the tube surface. Heat of reaction is removed by generating steam in the tubes. The major advantage anticipated for this scheme is that of relatively easy temperature control.

Experiments to date have been made using a concentric-tube reactor. The first work was done with a 1 1/8" O. D. 12" long inner tube coated with catalyst and enclosed in a 1 1/2" I. D. pipe. With this apparatus, the synthesis gas is fed into the annulus where reaction occurs. Results of this work indicated that 900+ Btu/SCF product could be produced for more than 1000 hours at a space velocity of 7000 SCF/hr. -CF annular volume. More recent experiments have been made with a 1 1/4"O. D. x 36" tube coated with catalyst, and the results are substantially the same as those obtained in the smaller unit. We have therefore assumed a 1000-hour catalyst life and a space velocity consistent with that used in the experimental work for our evaluation.

#### e. Economics

A cost comparison of the four alternate methanation schemes discussed above is presented in Table 1. The transport reactor results in the lowest plant investment, but the dual-fixed-bed process affords the lowest operating cost of the four cases. The reason for this is that the catalyst cost for the transport reactor (assumed to be equal to that for the fluid-bed case) is much higher than is incurred in the fixed-bed scheme. The tube-wall reactor results in the highest operating cost of the four cases even though its investment is about the same as for the transport reactor. The reasons for this are a relatively high catalyst replacement cost and the cost associated with replacing the tubes in the reactors when the catalyst on them loses its activity.

<sup>5.</sup> Field, J. H. et.al., "Development of Catalysts and Reactor Systems for Methanation", presented at ACS, Philadelphia (April 5, 1964).

## TABLE 1

## COST COMPARISON OF METHANATION ALTERNATES

## PLANT CAPACITY - 90HH SCID OF PIPELINE GAS

## STREAM EFFICIENCY - 95%

| Reactor Type   | [ransport   | Hot-Gas-<br><u>Recycle</u>  | Fluidized-Bed  | <u>Tube-Wall</u>   |            |
|--|---|---|--|--|------------|
| Investment Summary:  |   |   |  |  |            |
| Erected Equipment Cost<br>Catalyst Inventory<br>Total Investment   | 2,200,000<br>300,000<br>2,500,000                             | \$14,2140,000<br><u>110,000</u><br>\$14,350,000                       | \$3,600,000<br>1,200,000<br>\$4,800,000                              | \$2,700,000<br>( <u>incl. Catalyst</u> )<br>(\$2,700,000)                    | E          |
| Utilities Summary:<br>Steam Generated, #/hr<br>Steam Consumed, #/hr.<br>Net Steam Generated, #/hr.   | 850,000<br>850,000  | 743,000<br><u>84,500</u><br>658,500                                   | 850,000<br>  | 850,000<br>850,000   |            |
| Power, kw<br>Cooling Water, GPM  | 10<br>8,300   | 60<br>25,750  | 65<br>8,200  | 10<br>3,320  |            |
| Principal Operating Costs, ¢/MSCF:   |   |   |  |  | 70         |
| Depreciation at 5% of Investment<br>Taxes & Insurance at 3% of Investment<br>Maintenance at 4% of Investment<br>Steam at 40¢/M//<br>Fower at 0.7¢/kwh<br>Cooling Water at 1.5¢/M Gal.<br>Operating Labor at \$3.20/Man-Hour<br>General Overhead at 100% of Operating Labor<br>Catalyst<br>Regeneration of Reactors | 0.40<br>0.24<br>0.32<br>-(9.06)<br>neg.<br>0.20<br>0.6<br>5.0 | 0.70<br>0.42<br>0.56<br>-(7.02)<br>0.01<br>0.77<br>0.6<br>0.6<br>0.71 | 0.77<br>0.46<br>0.62<br>-(9.06)<br>0.01<br>0.20<br>0.6<br>0.6<br>5.0 | 0.43<br>0.26<br>0.35<br>-(9.06)<br>neg.<br>0.20<br>0.6<br>0.6<br>2.57<br>6.4 | port No. 6 |
| TOTAL OPERATING COST, ¢/MSCF   | -(1,70)   | -(2.65)   | - (0,80)   | 2.35   |            |

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#### f. Discussion

Based on the above results, we have selected the dual-fixedbed, hot-gas-recycle methanation scheme for use in all future pipeline gas plant designs. In addition to the fact that this scheme appears to be the most economically attractive methanation system, it is also the one supported by the most conclusive experimental data, and is therefore technically the soundest at the present time.

The tube-wall reactor, although presently the least attractive, is potentially of considerable interest. If, for example, catalyst life could be extended from 1000 to 3000 hours at the same space velocity, its operating cost would be approximately the same as the hot-gas recycle system.

The transport reactor is potentially capable of yielding lower operating costs than the hot-gas-recycle scheme. In the absence of any experimental data, catalyst cost has been assumed to be the same as that demonstrated at IGT for a fixed-fluidized bed. This is probably a conservative assumption because the physical strength of the catalyst is very severely tested in the transport system. However, if a dual-reactor transport system were developed, using iron catalyst to do the bulk of the methanation and nickel catalyst for the finishing step, the advantages of efficient heat recovery and low catalyst cost might both be achieved.

Our selection of methanation process has thus been influenced considerably by the present state of technology.

#### 2. Gas Purification

The study of alternative gas purification processes was continued. Minor design changes were made in several processes so that all could be compared on the same basis; i.e., roughly the same number of parallel trains of equipment.

### 3. Hydrogen Production Costs

Estimated costs for producing hydrogen from bituminous coal, based on preliminary process designs, reasonably complete material balances, and very approximate estimates of capital investment, are presented in Table II.

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These cost figures are all predicated on a bituminous coal of the following composition at a cost of \$4 per ton:

| Proximate       |           | Ultimate | (dry basis) |
|-----------------|-----------|----------|-------------|
|                 | $W = F_0$ |          | Wt. %       |
| Moisture        | 2.5       | C        | 79.4        |
| Volatile matter | 39.0      | H        | 5.2         |
| Fixed carbon    | 53.4      | ່ວ       | 7.5         |
| Ash             | 5.1       | N        | 1.4         |
|                 | 100.0     | S        | 1.3         |
|                 |           | Ash      | 5.2         |
|                 |           |          | 100.0       |

Estimated investment is for the process units only, including coal storage and preparation, gasification, methane removal, water-gas shift, removal of CO<sub>2</sub> and sulfur compounds, and methanation. Investment for offsite facilities is not included, but utilities are charged at rates which include the necessary capital charges on utilities-generating facilities. It is assumed that coal ash is removed from the system by quenching gasifier melt with water and that 5% of the Na<sub>2</sub>CO<sub>3</sub> catalyst is lost in this operation.

Varying levels of product gas purity are indicated in Table II, depending on operating conditions and processing sequence chosen. Two levels of methane concentration in the raw gasifier effluent were assumed:

- 1. All hydrogen in the coal appears in the raw gas in methane.
- 2. Equilibrium is achieved for the following reaction at gasifier conditions.

 $CO \div 3H_2 \rightleftharpoons CH_4 \div H_2O$ 

Where methane removal is desired, it is accomplished by partial combustion (using oxygen) or by catalytic steam reforming. Hydrogen purity varies from about 88 to 99%, the major impurity being methane. Carbon oxides are reduced to less than 10 parts per million and sulfur compounds, to about 1 ppm. Product gas pressure is 350 psia, and the cost of compressing to any higher pressure desired is indicated by Figure 1.

## TABLE 11

#### HYDROGEN FROM BITUMINOUS COAL

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- Bases: 1. 250,000,000 SCFD of Product Gas
  2. 90% Stream Factor
  3. Helt Composition: 80% Ha<sub>2</sub>CO<sub>3</sub> 20% Coal Ash
  4. Hethod of Contacting: Sparging
  5. Hethod of Heat Supply: Fired-Tube Heater
  6. Product Hydrogen Pressure: 350 Psia

|                 | Ope   | <u>Casifler</u><br>rating_Condit | lons           |                                      |   |                    | <b>.</b> .                                    | <u>Pr</u>   | oduction Cost | . ¢/HSCF            | of Produc                  | t Gas             |                 |
|-----------------|-------|----------------------------------|----------------|--------------------------------------|---|--------------------|---|-------------|---------------|---------------------|----------------------------|-------------------|-----------------|
| <u>Cese No.</u> | Temp. | Pressure<br>(Pste)               | H20/C<br>(#/#) | CH <sub>4</sub> In<br><u>Rew Gas</u> | Hethod<br>of CH <sub>IL</sub><br><u>Removal</u> | investment<br>\$HH | Product<br>Purity<br><u>(% H<sub>2</sub>)</u> | Coal        | Utilities     | Na <sub>2</sub> CO3 | Labor<br>&<br><u>Ovh!d</u> | Charges<br>at 17% | <u>Total</u>    |
| 11-A            | 1800  | 400                              | 2.0            | ALL H2                               | Nons  | 37.0               | 87.7  | 6.6         | 1.3           | 0.4                 | 1.2                        | 7.6               | 17.1            |
| 11-B            | 1800  | 400                              | 2.0            | Equil.                               | None  | 38.3               | 94.5  | 6.3         | 1.5           | 0.3                 | 1.2                        | 7.9               | 17.2            |
| :1-C            | 1800  | 400                              | 2.0            | Att H2                               | Partial<br>Combustion                           | 35.9               | 99.0  | 6.2         | 6.0           | 0.3                 | 1.2                        | 7.4               | 21.1            |
| -0-7            | 1800  | 400                              | 2,0            | ATT H2                               | Reforming<br>(1)                                | 43.0               | 95.0  | 7 <b>.3</b> | 0.3           | . 0.3               | 1.5                        | 8.9               | 18.3            |
| 11-0-2          | 1800  | 400                              | 2.0            | ATT H2                               | Reforming<br>(2)                                | 43.0               | 95.0 <sup>°</sup>                             | 7.6         | 0.3           | 0.3                 | 1.7                        | 8.9               | 5. 18 <b>.8</b> |
| 11-E            | 1800  | 400                              | 3.0            | ATT H2                               | Reforming<br>(2)                                | 46,4               | 95.0  | 7.8         | 0.7           | 0.3                 | 1.7                        | 9.6               | 20.1            |
| <b>F</b>        | 1800  | 45                               | 3.0            | ATT H2                               | Reforming<br>(2)                                | 45.8               | 95.0  | 6.6         | 2.8           | 0.3                 | 1.7                        | 9.5               | 20.9            |
| 11-9            | ,1800 | 45                               | 3.0            | Equii.                               | Rone  | 41.0               | 99.0  | 5.9         | 4.6           | 0.3                 | 1.2                        | 8.5               | 20.5            |
| 11-H            | 1600  | 400                              | 3.0            | A11 H2                               | Reforming<br>(2)                                | 45.8               | 95.0  | 7.7         | 1.0           | 0.3                 | 1.7                        | 9 <b>.5</b>       | 20.2            |
| 11-J            | 16 00 | 400                              | 3.0            | Equit.                               | Reforming<br>(2)                                | 46.7               | 95.0  | 7.8         | 1.0           | 0.3                 | 1.7                        | 9.6               | 20.4            |

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(1) Reforming assuming a sulfur-resistant catalyst (2) Reforming assuming a standard catalyst preceded by sulfur removal

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Fixed charges are calculated as a percentage of investment and include 10% for depreciation, 4% for maintenance, and 3% for taxes and insurance. Although pipeline gas economics (Progress Report No. 3, page 4) were calculated using 5% depreciation (typical of a public utility), we felt that hydrogen production parallels more closely a chemical or refinery operation and have, therefore, used the higher rate. Calculated hydrogen costs presented in Table II are production costs and do not include any return on investment. To obtain a 10% return after income taxes, for example, would require that hydrogen selling price be about 9-12¢/MSCF higher than the production cost.

The utilities figures reported in Table II reflect a credit of steam production equal to about 2.5¢/MSCF of hydrogen. This is based on the assumption that heat generated in the hydrogen plant can be used elsewhere in the overall facility.

### 4. <u>Catalyst Losses</u>

Sodium carbonate catalyst may be lost from the gasification system by at least two means:

- a. Volatilization and/or entrainment in the effluent gas stream.
- b. Chemical combination or mechanical entrapment with ash components removed from the system.

Molten sodium carbonate is partially converted to the hydroxide in the gasifier according to the reaction below.

$$Na_2CO_3$$
 (1) + H<sub>2</sub>O (g)  $\pm 2NaOH$  (1) + CO<sub>2</sub> (g)

The fraction so converted depends on temperature and steam/carbon ratio used in gasification, but at  $1600^{\circ}$ F and

$$\frac{H_2O}{C} = 2$$

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about 1.5% of the sodium is preser as NaOH. A recent doctoral thesis (6) indicates that the boiling points of alkali metal hydroxides are much lower than previously reported. If true, this could lead to substantial losses of socium from the gasifier as NaOH vapor. Lower operating temperatures would reduce volatilization losses, but to go below about 1600 °F would require a catalyst with a lower melting point than pure Na<sub>2</sub>CO<sub>3</sub>. Additions of lithium carbonate and potassium carbonate for this purpose were investigated, and the results are presented in Table III. Column 7 shows total catalyst losses, expressed as cents per thousand standard cubic feet of pipeline gas product, by both mechanisms "a" and "b" and assuming that the recent boiling point determinations for NaOH, KOH, and LiOH are correct ( $\underline{0}$ ). On the other hand, if the older handbook data on vapor pressures of NaOH, KOH, and LiOH are correct, volatilization losses will be negligible and only ash removal losses need be considered. These costs are presented in columns 5 and 6, assuming, respectively, 95% recovery of catalyst in the ash removal system and 90% recovery. The following salt prices were used in calculating Table III.

|                                 | <u>¢/1b.</u> |
|---------------------------------|--------------|
| Na2CO3                          | 1.6          |
| K <sub>2</sub> CO3              | 8.5          |
| Li <sub>2</sub> CO <sub>3</sub> | 50.          |

There are two principal reasons why the use of potassium or lithium salts always leads to increased costs:

- a. At a given temperature the vapor pressure of KOH is about eight times that of NaOH.
- b. Although the vapor pressure of LiOH is lower than that of NaOH, the formation of LiOH at the conditions of operation appears to be much more favorable.

<sup>6.</sup> Spinar, L. H., University of Wisconsin, Ph. D., "Vaporization of Alkali Metal Hydroxides (1958).

|            |   |                      |   | TABLE III<br>CATALYST CO           | <u>.</u><br>DETE                                       |  | ,<br>,   | THE M. W. KE<br>Research &<br>Dep |
|------------|---|----------------------|---|------------------------------------|--|--|--|-----------------------------------|
| Column No. | . 1   | 2                    | 3   | 4                                  | 5  | 6                                      | 7  | artment                           |
| Case No.   | Melt Compo-<br>sition mol%  | Melling<br>Point<br> | Operating<br>Tempera -<br><u>ture <sup>o</sup>F</u> | % CO3<br>converted<br>to hydroxide | <u>Catalyst losse</u><br>Ash removal l<br>95% recovery | s,¢/MSCF of p<br>osses<br>90% recovery | ipeline gas<br>Ash removal<br>(95%) + volati-<br>lization losses | LOMPANY                           |
| I          | Pure Na <sub>2</sub> CO <sub>3</sub>  | 1560                 | -1600   | 1.5                                | 1.2  | 2.4                                    | 7.   |                                   |
| 11         | Purc Na <sub>2</sub> CO <sub>3</sub>  | 1560                 | 1700  | 4.5                                | 1.2 ·  | 2.4                                    | 34.  |                                   |
| III        | 6. 5% J.i2CO <sub>3</sub> )<br>93. 5% Na <sub>2</sub> CO <sub>3</sub> )   | 1500                 | 1600  | 94.<br>1.5                         | 3.6  | 7.2                                    | 200.   | KELLOGG                           |
| IV         | 5. 5% K <sub>2</sub> CO <sub>3</sub> )<br>94. 5% Na <sub>2</sub> CO <sub>3</sub> )  | 1500                 | 1600  | 2.1<br>1.5                         | 1.5  | 3.0                                    | 31.  |                                   |
| v          | 3% Li <sub>2</sub> CO <sub>3</sub> )<br>3% K <sub>2</sub> CO <sub>3</sub> )<br>94% Na <sub>2</sub> CO <sub>3</sub> )              | 1500                 | 1600  | 94.<br>2.1<br>1.5                  | 3.2  | 6.4                                    | 112.   |                                   |
| VI .       | 40% K <sub>2</sub> CO3) )<br>60% i4a <sub>2</sub> CO3)  | 1300                 | 1350  | 0.8<br>0.3                         | 3.3  | 6.7                                    | 19.  | Page N<br>Report                  |
| VII        | 37% Li <sub>2</sub> CO <sub>3</sub> )<br>63% Na <sub>2</sub> CO <sub>3</sub> )  | 1150                 | 1200  | 100.<br>0.3                        | 15.  | 30.                                    | 78.  |                                   |
| VIII       | -<br>13.3% Li <sub>2</sub> CO <sub>3</sub> )<br>43.5% K <sub>2</sub> CO <sub>3</sub> )<br>43.2% Na <sub>2</sub> CO <sub>3</sub> ) | 1150                 | 1200  | 100.<br>0.4<br>0.3                 | 7.7  | 15.5                                   | 31.  | 6                                 |

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Two conclusions have resulted from Table III:

- a. Catalyst costs cannot be reduced by adding potassium or lithium carbonate to lower the melting point.
- b. It is extremely important to ascertain the correct vapor pressure of molten NaOH.
   If the Spinar thesis is correct, drastic action must be taken to avoid excessive sodium carryover into downstream equipment.

## 5. Flowsheet Studies

Almost all process designs and economic studies to date have been based on bituminous coal. Investigations have been started to determine the effect on designs and costs of the other raw materials that must be considered - anthracite, sub-bituminous coal, and lignite. Initial efforts will be directed to the production of pipeline gas and hydrogen, but eventually the conversion of each of the four raw materials into each of four product gases will be considered.

### B. PROJECTIONS

1. Gas Purification

The evaluation of gas purification processes will continue. The effect of making product gases other than methane on the optimum purification sequence will be studied.

### 2. Flowsheet Studies

Investigations of the effects of raw materials other than bituminous coal and product gases other than methane on the design of the gasifica tion section will be continued. As optimum gas purification schemes are selected, complete conceptual designs - including flowsheets and cost estimates - for each product gas from each raw material will be prepared.

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#### III. PROCESS RESEARCH

#### A. ACCOMPLISHMENTS

Viscosity tests on anthracite ash/molten carbonate and bituminous ash/molten carbonate at 1650°F and 1800°F have been completed. With both ashes the viscosity equilibrates in  $\leq 4$  hours. The viscosities range from 300 to 8000 cps. The equilibrium values are given in the table below:

#### COAL ASH-Na2CO3 VISCOSITIES

| <u>Cozl Ash</u> | Wt. % in $Na_2CO_3$ | Temp. <sup>o</sup> F. | Viscosity, CPS |
|-----------------|---------------------|-----------------------|----------------|
| Anthracite      | 15                  | 1650                  | 1000           |
| Anthracite      | <u>з</u> о .        | 1650                  | 8000           |
| Anthracite      | 15                  | 1800                  | 300            |
| Anthracite      | . 30                | 1800                  | 7000           |
| Biraminous      | 15                  | 1650                  | 1000           |
| Dimminous       | 30                  | 1650                  | 4000           |
| Eitaminous      | 15                  | 1800                  | 800            |
| Biruminous      | 30                  | 1800                  | 3000           |

In several runs some evidence of ash settling was observed. An experiment incorporating melt mixing, just prior to viscosity measurement, will be performed in order to estimate the possible constribution of ash settling.

The complete test unit results for Run No. J-9655 indicate that at a constant inlet steam pressure the gasification of carbon is first order with respect to carbon in the melt to at least 85% of the carbon gasified. The percent carbon gasified was calculated by measuring the total reducing gas (CO+H<sub>2</sub>) produced at various times. This run gasified anthracite at 1700°F with an inlet steam pressure of 7. é psia, a superficial gas velocity of 0.08 ft/sec., and 4.6% coal in the inlet. The gasification rate at 7.6 psia steam (inlet) follows the expression -dc = 0.225(c), lbs. carbon gasified/hr. cu. ft. of melt.

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An attempt to increase the gasilication rate by operating at 13 psia steam, a superficial gas velocity of 0.3 ft./sec. and a molten salt bed height of 12 inches, failed due to melt turbulence and plugging of the outlet line. An  $\delta$  inch bed height is probably the maximum height for this apparatus.

## B. PROJECTIONS

Future work will include completion of viscosity tests using sub-bitumimous and lignite ashes. Efforts will be concentrated on the affect of bad height, steam pressure, and superficial gas velocity on the rate of gasification of coal.

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#### IV. MECHANICAL DEVELOPMENT

#### A. ACCOMPLISHMENTS

#### 1. <u>Environmental Testing of High-Temperature Materials</u>

The first corrosion test got started during this report period; the objective being a 250 hour endurance test. In the early stages of operation, some shut-downs were required to repair mechanical damages (fatigue killures) caused by the pneumatic vibrating device. Modifications to the supporting structure and revisions of some of the critical components removed this hazard from future operation.

Some difficulties were experienced with plugging of the gas outlet line and the solids feed inlet line. It appeared that at some periods of operation the bad splashed to the top of the reactor; and since this region is not in the furnace the salt bed froze, hence plugging the overhead lines. Minor revisions made to the overhead plumbing now allow for periodic clean-out.

During operation it was observed that some of the graphite fed . into the reactor was being carried out by the effluent gas. However, this amount of graphite lost to the reaction can be estimated and compensated for in the overhead feed rate.

After about 100 hours of running time, the temperature controller indicated an open thermocouple circuit. Further investigation revealed that the thermowell had corroded through and that the molten salt bad had destroyed the thermocouple. Since this condition could not be repaired without distrubing the corrosion samples, it was decided to end the test at this point. For future tests the thermowell wall thickness has been doubled and stainless steel-sheathed thermocouples will be used to avoid any recurrance of this malfunction.

The removed test camples showed visual indications of corrosion varying from severe to moderate. By agreement with The International Nickel Company, the samples were sent to their laboratory for their evaluation. To date, no results have been received from them.

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Figure 2 is a schematic flow diagram of the test process.

## E. PROFECTIONS

1. Environmental Testing of High-Temperature Materials

Preparations are underway to initiate Test #2. The objective of this test is to subject refractory samples to an endurance of 250 hours. The refractories selected for this test are:

Carborundum

Mullfrax H Mullfrax W Harbide Zircofrax O KT Silicon Carbide

Harbison-Walker

Chromex B Varnon BF Harklase Korundal XD

General Reiractories

Ritex CB



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### V. MANPOWER AND COST ESTIMATES

Figure 3 shows the projected manpower breakdown for Phase 1 for 1935 as well as the actual effort that was attained. It can be seen that a thirteen man effort was attained during January. This was principally due to the maintenance required to keep the corrosion test equipment operating.

Figure 4 shows the expenditures during January as well as the cost estimates for Phase 1 for 1965. For the month of January S21,210 was expended not including fee and G & A. The total expenditures through January were S97,376. This represents approximately 46% of Phase 1.

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