

GASIFICATION OF COAL UNDER CONDITIONS SIMULATING STAGE 2  
OF THE BCR TWO-STAGE SUPER-PRESSURE PROCESS

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INTRODUCTION

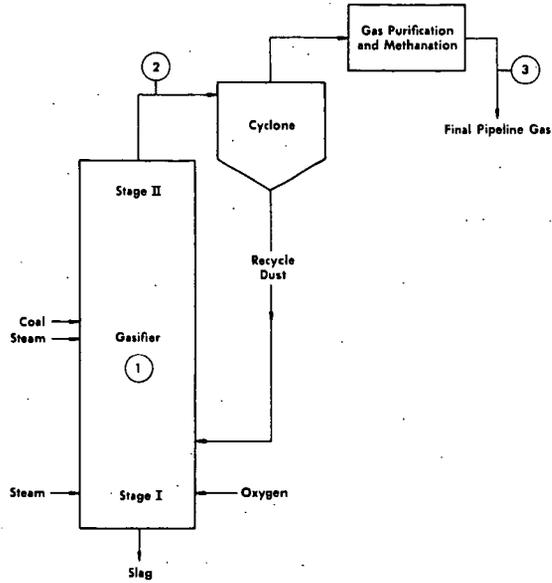
For the production of pipeline gas, coal gasification processes operating at elevated pressure and a low gas exit temperature produce a raw gas with a high methane content; this in turn leads to lower investment and operating costs than for processes that produce CO and H<sub>2</sub> as the principal products and do not form significant amounts of methane.(1, 2)\* An entrained coal gasification process using two reaction stages operating at 70 atm pressure offers promise for high yields of methane and the ability to process all types of coal regardless of caking properties or size consist.

To achieve the required rapid reaction in an entrained system, both a reactive fuel and a means for rapid heating are necessary. The volatile portion of bituminous coal or lignite is such a fuel and to utilize it properly for generation of gas of a high methane content, a two-stage super-pressure process has been devised. (See Figure 1.) In this process, heat and "Stage 1" or synthesis gas are generated in Stage 1 by gasifying recycle char under slagging conditions with oxygen and steam. In Stage 2 fresh coal and steam are introduced into the hot synthesis gas issuing from Stage 1. The fresh coal is thereby rapidly heated to reaction temperature of about 1750 F and partially converted into gas with a high methane content, mainly by pyrolysis of the volatile portion of the coal by reaction with steam and Stage 1 gas. For ultimate conversion into high Btu pipeline gas, the combined gases laden with unreacted char leave Stage 2 and pass successively through dust removal, shift reaction, acid gas removal and methanation steps.

As the process contains two stages, it has two types of problems that required further study: The first pertains to the slagging zone or Stage 1 of the process. The production of gas by slagging gasification of coal at atmospheric pressure has been done successfully on a commercial scale.(3) For slagging gasification at elevated pressure, processes have been developed on an experimental scale by various groups including the Bureau of Mines in the United States, and the Gas Council in England.(4) These investigations have shown that slagging coal gasification at elevated pressure is feasible and that development of a commercial process will, except for the control of metallic iron formation, be primarily a design problem. This previous work has also

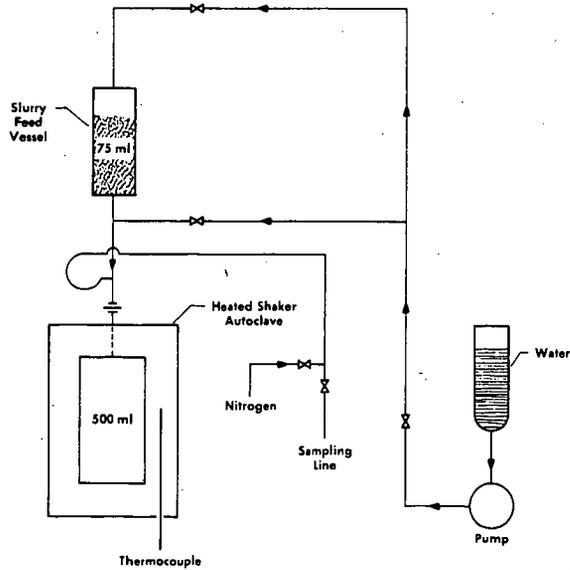
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\* Numbers in parenthesis refer to Literature References listed at end of paper.



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**Figure 1. Simplified Flow Diagram for BCR Two-stage Super-pressure Gasifier**



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**Figure 2. Flow Diagram of Batch Autoclave Reactor**

shown that meaningful results can only be obtained by experimentation on a scale that provides a minimum slag flow of 200 lb/hr, corresponding to a 1 ton/hr pilot plant using coal with 10 percent ash.

The second pertains to the "direct methanation" zone, or Stage 2 of the process. Although various processes have been devised for utilization of the volatile portion of coal for gas production, little information is available on the primary formation of methane directly from it.

This paper reports the results of laboratory-scale research which has been conducted to fill the gap in our knowledge concerning the rate of formation of methane under conditions prevailing in Stage 2 of this proposed two-stage super-pressure process.

### EXPERIMENTAL

In the experimental studies, tests have been made on the direct steam methanation of coal in two types of equipment. Batch tests have been conducted in small rocking-type high-pressure autoclaves. Continuous flow experiments have been made in a 1-inch reactor, 5 ft long, under Stage 2 conditions using simulated Stage 1 gas.

#### Tests in Batch Autoclaves

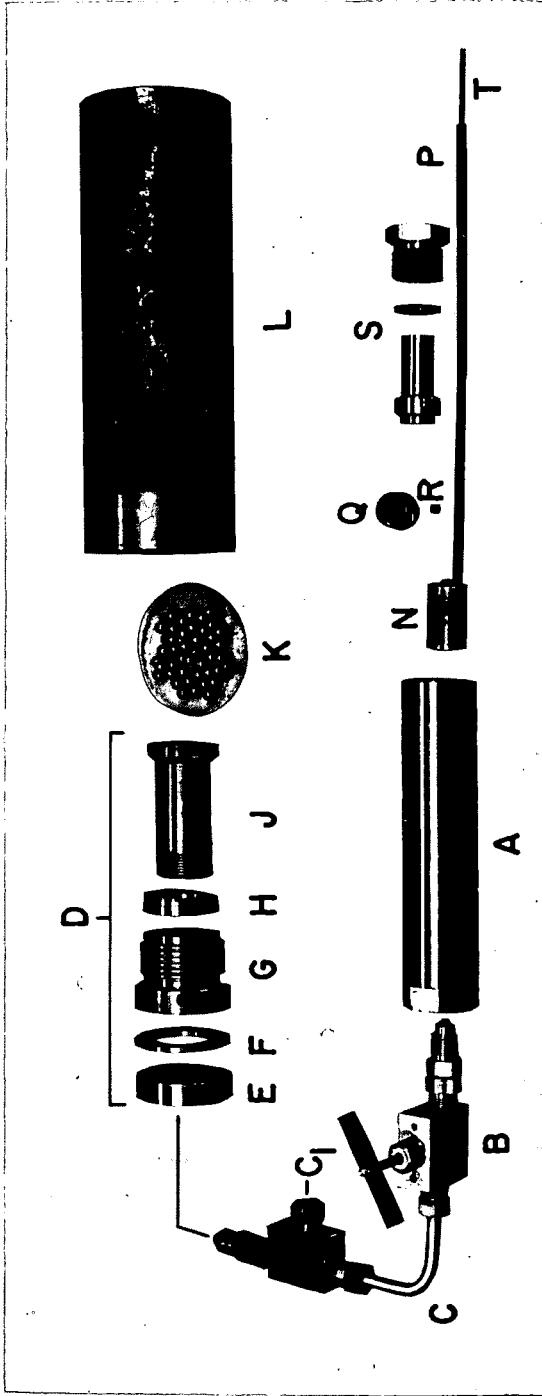
In the batch studies of the direct steam methanation of coal, duplicate autoclave systems were employed to obtain data as rapidly as possible without delay for cooling and reheating. One of the systems is shown diagrammatically in Figure 2. Both the feeder and reactor vessels are fabricated of super-strength alloys, 19-9 stainless steel DL alloy, to permit operation at temperatures up to 1500 F and pressures up to 10,000 psi. The specially designed 75 ml auxiliary feed vessel provides means for charging up to 30 g coal as a 40 weight percent slurry. A view of the overall reactor assembly is shown in Figure 3 together with an exploded view of the feed vessel fittings.

In a typical operation, a weighed charge of coal slurry, consisting of a mixture of 40 weight percent of minus 325 mesh coal and 60 weight percent water with or without added sodium carbonate catalyst, was injected rapidly by means of hydraulic pressure into the preheated, rocking autoclave containing a measured volume of nitrogen tracer gas. The water in the slurry flashed into steam and reacted with the coal forming methane and other gases.

The gaseous reaction products were sampled on a specified time schedule and analyzed by chromatography. After the system had cooled following the test, the residual gases were collected and the residues, consisting mainly of carbon and ash, were removed, weighed, and analyzed.

Tests were made under controlled, but widely varied, conditions. The time of reaction was varied from 2 to 120 minutes; the temperature from 730 C to 770 C; the pressure from 60 to 350 atmospheres. The experimental data and results are summarized in Tables 1 and 2.

In Table 1, the data and results are given for those tests in which gas samples were taken only at the end of the tests. In Table 2, the data and results are given for those tests in which gas samples were taken at stated



(8008P147)

**Slurry Feeder**

- A — Slurry Feeding Cylinder Without Fittings  
 B — Valve  
 C — Connections, Feeder to Reactor T  
 C<sub>1</sub> — Gas Outlet Connection

**Reactor**

- D — Cover  
 E — Locknut  
 F — Thrust Washer  
 G — Main Nut  
 H — Seal Ring  
 J — Main Body  
 K — 50 3/8" Diameter Stainless Steel Balls  
 L — Reactor Body

- N — Piston Attached to Placement Rod (P)  
 Q — Front View of Piston Showing Center Threaded Bleed Hole and Off-Center Threaded Hole for Rod  
 R — Allen Set Screw to Plug Center Bleed Hole  
 S — Cylinder Closure Fittings  
 T — Allen Wrench to Fit Allen Set Screw

**Figure 3. Exploded View of Components of Slurry Feeder and**

TABLE 1. RESULTS OF BATCH AUTOCLAVE EXPERIMENTS  
WITHOUT INTERMITTENT SAMPLING

|   | Test<br>12 | Test<br>13 | Test<br>14 | Test<br>16 | Test<br>18 | Test<br>19 | Test<br>20 | Test<br>22 |
|---|------------|------------|------------|------------|------------|------------|------------|------------|
| Temperature, C                          | 730        | 730        | 730        | 730        | 730        | 770        | 770        | 770        |
| Time, min                               | 120        | 120        | 120        | 120        | 12         | 120        | 120        | 12         |
| Coal Used, g daf                        | 8.71       | 9.26       | 10.50      | 10.40      | 10.42      | 10.84      | 8.45       | 10.14      |
| Catalyst, Wt % of Coal                  | 42.1       | 33.0       | 0          | 0          | 0          | 15.2       | 0          | 0          |
| Residue, g daf                          | 4.43       | 4.47       | 6.37       | 6.71       | 7.23       | 4.63       | 4.97       | 6.75       |
| Total Pressure Developed, atm           | 354        | 326        | 308        | 181        | 263        | 243        | 168        | 188        |
| Product Partial Pressures, atm          |            |            |            |            |            |            |            |            |
| H <sub>2</sub> O                        | 306        | 283        | 273        | 145        | 247        | 165        | 130        | 161        |
| CO <sub>2</sub>                         | 14.3       | 13.0       | 10.0       | 9.1        | 3.2        | 24.5       | 9.9        | 5.9        |
| CO                                      | 0          | 0.1        | 0.4        | 0.6        | 0.4        | 0.6        | 0.6        | 0.5        |
| H <sub>2</sub>                          | 15.3       | 13.6       | 9.3        | 9.3        | 2.9        | 26.4       | 11.4       | 6.3        |
| CH <sub>4</sub>                         | 18.1       | 16.8       | 16.2       | 17.4       | 7.8        | 24.6       | 14.3       | 12.9       |
| Gas Volume, scf/lb daf Coal             | 12.45      | 10.90      | 7.80       | 7.94       | 3.47       | 15.55      | 9.76       | 5.82       |
| Coal Converted, % daf                   | 49.1       | 51.8       | 39.4       | 35.6       | 30.6       | 57.3       | 41.2       | 33.4       |
| Btu in Gas, % Btu in Coal*              | 45.6       | 43.2       | 31.5       | 31.8       | 15.8       | 52.7       | 35.6       | 24.8       |
| Carbon in Gas, % C in Coal              | 31.1       | 27.8       | 21.4       | 21.7       | 9.6        | 37.6       | 20.4       | 16.0       |
| Carbon in CH <sub>4</sub> , % C in Coal | 17.4       | 15.7       | 13.2       | 14.3       | 6.5        | 18.5       | 11.7       | 10.6       |
| Preformed Methane, %                    | 83.0       | 83.2       | 87.0       | 87.7       | 90.9       | 78.5       | 82.8       | 88.5       |

\* Based on total carbon in products.

TABLE 2. RESULTS OF BATCH AUTOCLAVE EXPERIMENTS WITH INTERMITTENT SAMPLING

|   | Test 35 |       | Test 37 |       | Test 39 |       | Test 40 |       | Test 42 |       | Test 43 |       |       |
|---|---------|-------|---------|-------|---------|-------|---------|-------|---------|-------|---------|-------|-------|
|   | 35-2    | 35-60 | 37-4    | 37-60 | 39-8    | 39-60 | 40-2    | 40-60 | 42-8    | 42-13 | 42-60   | 43-4  | 43-60 |
| Temperature, C                          | 753     | 753   | 753     | 753   | 748     | 748   | 749     | 749   | 746     | 746   | 746     | 751   | 751   |
| Time, min                               | 2       | 60    | 4       | 60    | 8       | 60    | 2       | 60    | 8       | 13    | 60      | 4     | 60    |
| Coal Used, g daf                        | -       | 10.88 | -       | 10.37 | -       | 11.85 | -       | 9.29  | -       | -     | 12.21   | -     | 13.23 |
| Catalyst, wt % of Coal                  | 0       | 0     | 0       | 0     | 0       | 0     | 28      | 28    | 18.9    | 18.9  | 18.9    | 20.3  | 20.3  |
| Residue, g                              | -       | 7.20  | -       | 6.84  | -       | 7.61  | -       | 5.21  | -       | -     | 7.70    | -     | 7.13  |
| Total Pressure Developed, atm           | 191.4   | 188.7 | 211.8   | 183.2 | 271.4   | 241.0 | 203.3   | 184.8 | 242.4   | 209   | 135.5   | 227.1 | 222.5 |
| Product Partial Pressures, atm          |         |       |         |       |         |       |         |       |         |       |         |       |       |
| H <sub>2</sub> O                        | 177.9   | 152.6 | 190.3   | 141.0 | 242.6   | 188.7 | 183.0   | 135.3 | 214.1   | 182.0 | 95.8    | 206.0 | 166.1 |
| CO <sub>2</sub>                         | 0.42    | 6.23  | 1.60    | 9.65  | 2.98    | 11.23 | 2.50    | 10.77 | 4.48    | 4.76  | 9.06    | 3.04  | 13.9  |
| CO                                      | 0.56    | 0.45  | 1.04    | 0.73  | 0.89    | 0.82  | 0.06    | 1.03  | 0.20    | 0.14  | 0.47    | 0.04  | 0.74  |
| H <sub>2</sub>                          | 0.97    | 7.65  | 2.73    | 10.52 | 4.30    | 11.95 | 2.60    | 14.43 | 5.43    | 4.64  | 9.46    | 3.30  | 12.85 |
| CH <sub>4</sub>                         | 2.88    | 15.34 | 8.78    | 15.50 | 11.96   | 21.40 | 6.10    | 16.40 | 9.09    | 9.90  | 14.62   | 6.30  | 21.35 |
| C <sub>2</sub> H <sub>4</sub>           | 0.15    | -     | -       | 0.11  | 0.15    | -     | 0.20    | -     | -       | -     | -       | 0.11  | -     |
| C <sub>2</sub> H <sub>6</sub>           | 0.42    | 0.12  | 0.68    | -     | 0.84    | 0.09  | 0.90    | 0.09  | 1.00    | 0.64  | 0.17    | 0.90  | 0.25  |
| N <sub>2</sub>                          | 8.10    | 6.3   | 6.7     | 5.7   | 7.7     | 6.8   | 7.9     | 6.8   | 8.1     | 7.0   | 5.9     | 7.4   | 7.3   |
| Gas Volume, scf/lb daf                  |         |       |         |       |         |       |         |       |         |       |         |       |       |
| Coal                                    | 1.05    | 6.33  | 3.38    | 8.77  | 4.23    | 9.47  | 3.01    | 10.74 | 3.95    | 3.92  | 7.69    | 2.44  | 8.92  |
| Coal Converted, % daf                   | -       | 33.8  | -       | 34.0  | -       | 35.8  | -       | 43.9  | -       | -     | 36.9    | -     | 46.1  |
| Btu in Gas, % Btu in Coal*              | 10.3    | 28.5  | 17.1    | 33.4  | 21.8    | 38.5  | 16.1    | 41.2  | 18.3    | 20.6  | 31.4    | 13.0  | 38.1  |
| Carbon in Gas, % C in Coal              | 3.7     | 18.1  | 11.0    | 23.4  | 13.5    | 23.5  | 10.1    | 27.5  | 11.6    | 13.5  | 21.5    | 7.7   | 25.0  |
| Carbon in CH <sub>4</sub> , % C in Coal | 2.1     | 12.4  | 7.6     | 14.3  | 9.0     | 15.1  | 5.6     | 16.3  | 6.7     | 8.2   | 13.3    | 4.2   | 15.3  |
| Preformed Methane, %                    | 91.0    | 88.7  | 91.3    | 85.2  | 91.4    | 87.5  | 92.3    | 81.5  | 88.5    | 90.1  | 86.5    | 90.6  | 86.7  |

\* Based on total carbon in products, assuming same correction applied for intermittent samples as for final sample.

intervals during the test as well as at the end. By this latter procedure, additional information was obtained on the effects of time on the reactions.

#### Tests in Continuous Flow Reactor

In the flow experiments under Stage 2 conditions using simulated Stage 1 gas, a continuous flow reactor with a design capacity of 5 lb/hr, a maximum operating temperature of 1800 F (1000 C) and a maximum working pressure of 1500 psi (100 atm) was used. A schematic illustration of the total system using slurry feeding of coal is shown in Figure 4 and general view of the safety stall and control area is shown in Figure 5.

The 5-foot long reactor is fabricated from Haynes 25 alloy, and has a 3-inch outside diameter and a 1-inch inside diameter (Figure 6). Under operating conditions, the reactor volume of about 800 ml provides for a residence time of several seconds. The preheater furnace and each of the three sections of the reactor furnace are independently controlled by temperature-recorder controllers that regulate saturable core transformers. A metering piston-type pump is used to feed the slurry of coal in water. Pressurized Stage 1 gas, i.e., simulated product gas from Stage 1, is fed into the slurry stream at the discharge port of the pump to facilitate trouble-free flow of the slurry up the vertical lines into the preheater.

The Stage 1 gas-coal-superheated steam mixture is discharged from the preheater into the reactor at a temperature of about 600 F. Upon entering the reactor, the mixture is raised to operating temperature in the upper section, or Zone 1, is reacted in the middle section, or Zone 2, and is cooled back down to about 1000 F in the lower section, or Zone 3, before leaving the reactor.

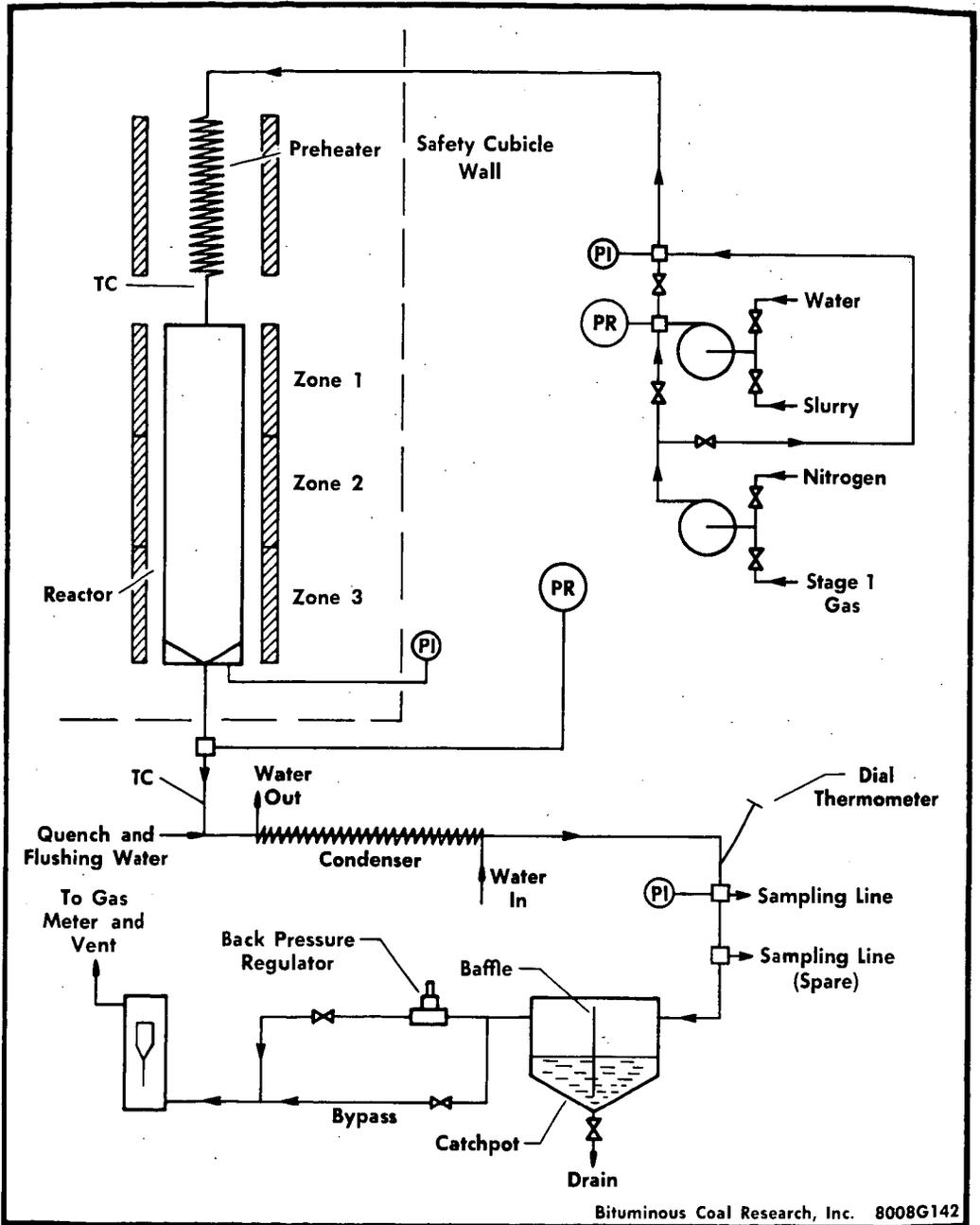
The product gases, containing the finely divided unreacted solids, are discharged from the reactor through a water-cooled condenser into a catchpot where the water condensate and solids are removed. From the catchpot the gases are fed through a pressure reducing valve to a wet test meter for measurement and then on to storage in a gas holder or venting to the atmosphere.

In the condenser, cooling of the gas and flushing of the solids is facilitated by injection of water at the inlet to the condenser at a controlled rate from an auxiliary high pressure metering pump.

Sampling valves are located at the downstream exit of the condenser ahead of the catchpot. Gas leaves in a small stream that is withdrawn continuously from the system and monitored for changes in composition by means of a thermal conductivity meter; during predetermined intervals samples are taken from this stream for chromatographic analysis.

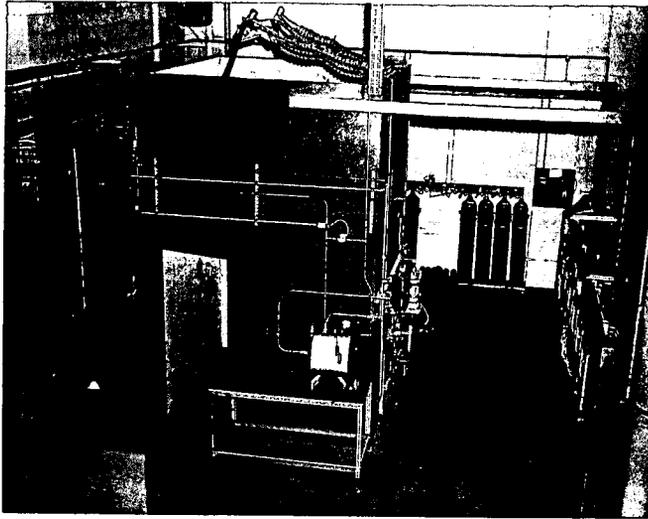
Argon, added to the Stage 1 gas as a tracer, is used to determine any changes in gas quantity that occur during the test. The approximate composition of the Stage 1 gas was as follows: hydrogen, 18 percent; argon, 10 percent; carbon monoxide, 55 percent; and carbon dioxide, 17 percent.

Material balances are established using the usual data obtained from weight, flow, temperature, and pressure measurements; these are verified by comparison with the argon tracer data.

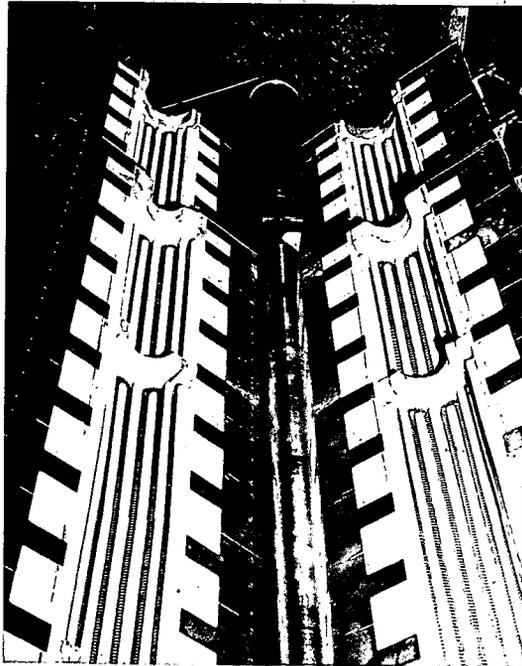


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**Figure 4. Flow Diagram for Continuous Flow Reactor Assembly Using Slurry Feeding**



**Figure 5. View of Continuous Flow Reactor Safety Cubicle and Control Area (8008P59)**



**Figure 6. View of Top Zones of Continuous Flow Reactor with Electric Furnace Open for Inspection (8008P54)**

To date, tests have been made in the flow reactor using both bituminous coal and lignite over a range of conditions approximating those which, at the moment, are considered optimum for Stage 2 operations.

Experiments with the Pittsburgh seam coal used in the autoclave test showed that it accumulated in the reactor. Even the results of very short operations were falsified by the char present in the reactor and resulted in too high apparent coal conversion. Mixing of the coal with silica of very small particle size (3 microns) remedied this problem and the reactor remained free of deposits in tests of 12-18 duration. However, the addition of silica lead to irregularly occurring and disappearing pressure buildups in the preheater coil and made a reduction of the coal content in the slurry necessary. This was especially the case when temperatures necessary to assure complete vaporization of the water in the slurry and to superheat the steam were used in the preheater. Nevertheless, satisfactory tests could be made. Concentrations of 20 percent lignite in slurry were used. After heating up the system and stabilizing the temperature, while feeding gas and water, tests approaching one hour of coal injection were made with lignite. This established that in runs of short duration reliable results are obtained. The reactor in all cases was practically free of deposits. There were some occasional irregularities caused by transient pressure buildups in the preheater or the condenser.

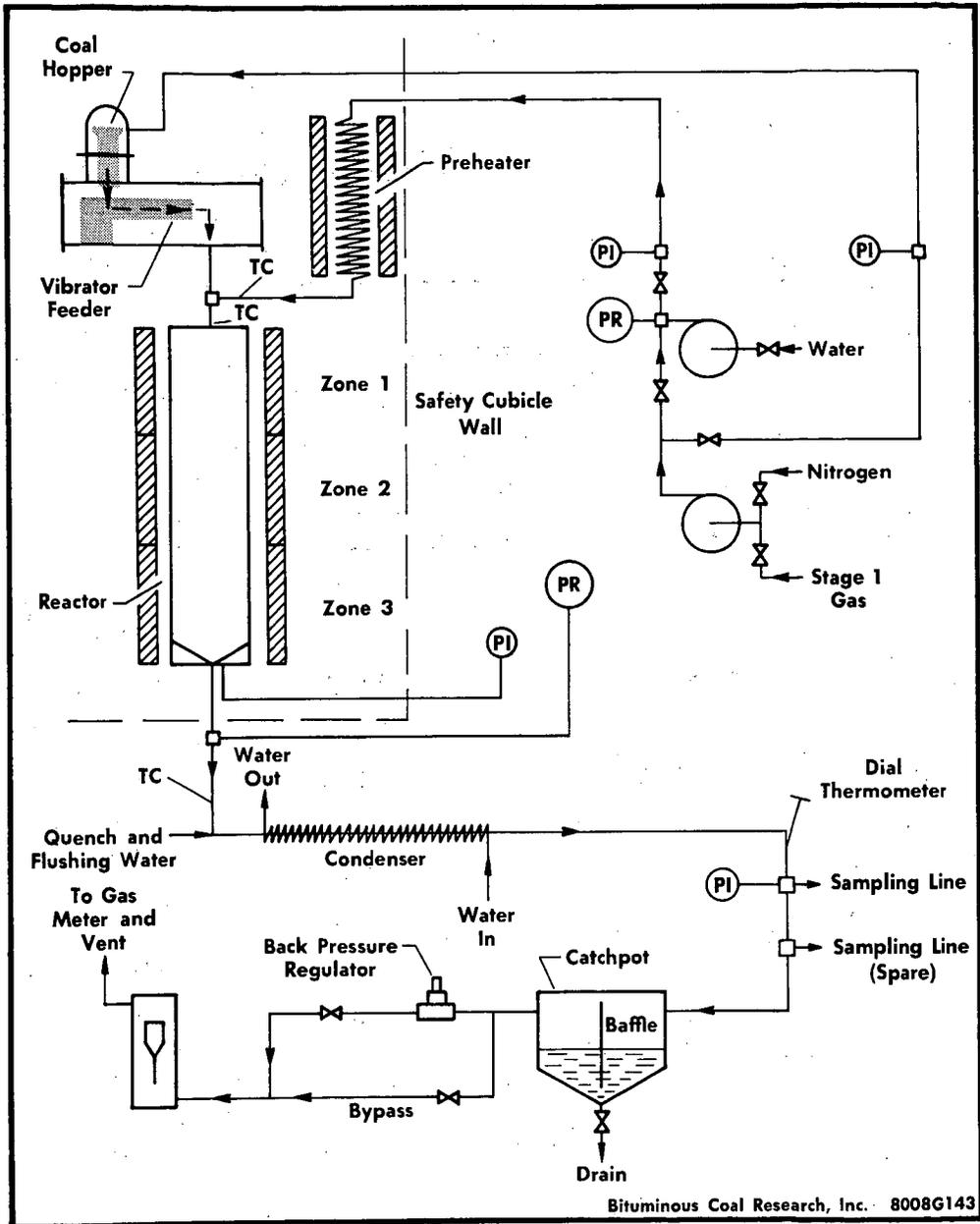
In the tests made using slurry feeding, the concentration of coal in relation to steam and Stage 1 gas was not as high as visualized for the commercial process. Thus, development of a dry coal feeder in which the coal feed rate is independent of the amount of water fed into the reactor represented a major improvement over the slurry feeding system. The flow diagram for the continuous flow reactor assembly as modified to use the dry coal feeder is shown in Figure 7.

Source and analytical data on the coals used are given in Table 3. The experimental data and results of tests in the continuous flow reactor over a wide range of conditions using both slurry feeding and dry coal feeding are summarized in Tables 4, 5, and 6. The data and results from tests with high volatile A bituminous coal are shown in Table 4. Table 5 presents data and results from tests with lignite fed as a slurry and Table 6, with lignite fed as a dry powder.

#### DISCUSSION

In the production of high Btu pipeline gas from coal, the objective is to convert the carbon in the coal into as much methane as possible in the initial gasification step, and if not into methane, then into carbon monoxide which in another step can be converted to methane by catalytic hydrogenation.

Thus, in the present study on the direct steam methanation of coal, either in batch autoclave tests or in continuous flow tests, the product gases of principal concern are methane, hydrogen, and carbon monoxide, and the greater the amount of methane in proportion to the amount of carbon monoxide and hydrogen, the smaller will be the final cost of the pipeline gas. As an index of this ratio of methane to carbon monoxide and hydrogen, the term "preformed methane" has been introduced, and, by definition, is the amount of methane in the initial product of gasification expressed as a percent of the total methane potentially available including that from conversion of the carbon monoxide and



**Figure 7: Flow Diagram for Continuous Flow Reactor Assembly Using Dry Feeding**

TABLE 3. SOURCE AND ANALYTICAL DATA ON TEST COALS

| <u>Source</u>                  | <u>Coal</u>                           |            |                |            |
|--------------------------------|---------------------------------------|------------|----------------|------------|
|                                | <u>High Volatile A<br/>Bituminous</u> |            | <u>Lignite</u> |            |
| State                          | Pennsylvania                          |            | North Dakota   |            |
| County                         | Allegheny                             |            | Mercer         |            |
| Seam                           | Pittsburgh                            |            | --             |            |
| <u>Proximate Analysis, %</u>   | <u>As Used</u>                        | <u>Daf</u> | <u>As Used</u> | <u>Daf</u> |
| Mositure                       | 1.02                                  | -          | 19.4           | -          |
| Ash                            | 4.74                                  | -          | 10.8           | -          |
| Volatile Matter                | 37.60                                 | 39.80      | 27.8           | 40.0       |
| Fixed Carbon                   | 56.64                                 | 60.20      | 42.0           | 60.0       |
| <u>Calorific Value, Btu/lb</u> | 14,100                                | 14,970     | 8,540          | 12,270     |
| <u>Ultimate Analysis, %</u>    |                                       |            |                |            |
| C                              | 79.19                                 | 83.90      | 51.80          | 74.27      |
| H                              | 5.48                                  | 5.71       | 5.54           | 4.85       |
| N                              | 1.52                                  | 1.62       | 0.64           | 0.91       |
| S                              | 1.35                                  | 1.43       | 1.08           | 1.55       |
| O (by diff)                    | 7.73                                  | 7.34       | 30.14          | 18.42      |
| Ash                            | 4.73                                  | -          | 10.80          | -          |

TABLE 4. OPERATING DATA AND RESULTS FOR TESTS IN CONTINUOUS FLOW REACTOR USING HIGH-VOLATILE BITUMINOUS COAL

|  | Test Number |       |       |
|--|-------------|-------|-------|
|  | CFR-4       | CFR-7 | CFR-8 |
| <u>Operating Conditions</u>                        |             |       |       |
| Temperature, F                                     | 1730        | 1690  | 1720  |
| Pressure, atm                                      | 70          | 70    | 70    |
| Reactor Volume, cc*                                | 320         | 280   | 180   |
| Residence Time, sec                                | 6.5         | 5     | 3.0   |
| <u>Input</u>                                       |             |       |       |
| Water, g/min                                       | 24          | 30    | 32    |
| Partial Pressures of Materials in Feed Stream, atm |             |       |       |
| H <sub>2</sub> O                                   | 35.7        | 38.0  | 41.5  |
| H <sub>2</sub>                                     | 6.2         | 5.5   | 5.4   |
| CO   | 18.8        | 16.0  | 15.6  |
| CO <sub>2</sub>                                    | 5.6         | 5.0   | 4.8   |
| C in Coal, g/min                                   | 0.78**      | 2.68  | 2.37  |
| Heat in Coal, kcal/min                             | 7.75        | 26.6  | 23.5  |
| <u>Output</u>                                      |             |       |       |
| Product Gas, N liters/min                          | 33.0        | 33.0  | 32.5  |
| Product Water, N liters/min                        | 27.2        | 35.9  | 39.8  |
| Partial Pressures of Materials in Product Gas, atm |             |       |       |
| H <sub>2</sub> O                                   | 31.6        | 36.5  | 38.5  |
| H <sub>2</sub>                                     | 11.4        | 8.6   | 6.4   |
| CO   | 15.2        | 16.0  | 16.0  |
| CO <sub>2</sub>                                    | 8.3         | 5.0   | 5.7   |
| CH <sub>4</sub>                                    | 0.2         | 0.7   | 0.86  |
| Heat in CH <sub>4</sub> , kcal/min                 | 1.7         | 6.7   | 8.5   |
| Heat in (CO + H <sub>2</sub> ), kcal/min           | 5.5         | 6.5   | 8.6   |
| Heat in Total Gas, kcal/min                        | 7.2         | 13.2  | 17.1  |
| C in Coal Gasified, g/min                          | 0.1         | 0.71  | 1.9   |
| Preformed Methane, %                               | 27          | 60    | 56    |
| <u>Yields, Percent C in Coal</u>                   |             |       |       |
| C in CH <sub>4</sub>                               | 12          | 16    | 20    |
| C in (CO + CO <sub>2</sub> )                       | 3           | -     | -     |
| C in Total Gas                                     | 15          | -     | -     |
| <u>Yields, Percent Btu in Coal</u>                 |             |       |       |
| Btu in CH <sub>4</sub>                             | 21          | 29    | 36    |
| Btu in (CO + H <sub>2</sub> )                      | 71          | 24    | 37    |
| Btu in Total Gas                                   | 92          | 53    | 73    |

\* Within 40 F of maximum temperature.

\*\* Coal without silica in this test.

TABLE 5. OPERATING DATA AND AVERAGE RESULTS FOR TESTS USING  
LIGNITE IN CONTINUOUS FLOW REACTOR WITH SLURRY FEEDING

|   | CFR Test No. |      |      |      |      |
|---|--------------|------|------|------|------|
|   | 29A          | 29B  | 30   | 31   | 32   |
| <u>Operating Conditions</u>                           |              |      |      |      |      |
| Temperature, F  | 1740         | 1740 | 1740 | 1740 | 1740 |
| Pressure, atm   | 70.0         | 70.0 | 72.0 | 84.0 | 72.0 |
| Reactor Volume, cc*                                   | 274          | 274  | 283  | 300  | 202  |
| Residence Time, sec                                   | 3.0          | 3.9  | 3.2  | 3.9  | 3.4  |
| <u>Input</u>  |              |      |      |      |      |
| Water, g/min  | 39.1         | 37.1 | 39.6 | 43.5 | 37.2 |
| Partial Pressures of Materials<br>in Feed Stream, atm |              |      |      |      |      |
| H <sub>2</sub> O                                      | 39.1         | 49.3 | 40.5 | 51.0 | 52.6 |
| H <sub>2</sub>  | 6.1          | 4.1  | 6.2  | 7.2  | 3.5  |
| CO  | 16.8         | 11.2 | 17.1 | 17.3 | 10.7 |
| CO <sub>2</sub>                                       | 5.1          | 3.4  | 5.2  | 5.4  | 3.1  |
| C in Lignite, g/min                                   | 4.70         | 4.60 | 4.48 | 5.05 | 7.60 |
| Heat in Lignite, kcal/min                             | 43.0         | 42.0 | 40.8 | 46.5 | 70.0 |
| <u>Output</u>   |              |      |      |      |      |
| Product Gas, N liters/min                             | 53.5         | 31.0 | 55.1 | 48.4 | 24.8 |
| Product Water, N liters/min                           | 40.2         | 41.1 | 40.6 | 44.9 | 42.5 |
| Partial Pressures of Materials<br>in Product Gas, atm |              |      |      |      |      |
| H <sub>2</sub> O                                      | 30.0         | 39.8 | 30.6 | 40.4 | 45.5 |
| H <sub>2</sub>  | 15.4         | 11.8 | 15.3 | 17.6 | 12.0 |
| CO  | 8.3          | 9.3  | 8.2  | 7.3  | 3.5  |
| CO <sub>2</sub>                                       | 12.1         | 10.0 | 13.9 | 13.8 | 7.6  |
| CH <sub>4</sub>                                       | 1.06         | 1.19 | 1.13 | 1.64 | 1.96 |
| Heat in CH <sub>4</sub> , kcal/min                    | 13.4         | 11.4 | 13.9 | 17.2 | 20.1 |
| Heat in (CO + H <sub>2</sub> ), kcal/min              | 10.0         | 6.9  | 9.1  | 2.7  | 13.3 |
| Heat in Total Gas, kcal/min                           | 23.4         | 18.3 | 23.0 | 19.9 | 33.4 |
| C in Lignite Gasified, g/min                          | 1.11         | 1.30 | 2.40 | 1.46 | 1.27 |
| Preformed Methane, %                                  | 63.0         | 68.0 | 66.0 | 88.0 | 66.0 |
| <u>Yields, Percent C in Lignite</u>                   |              |      |      |      |      |
| C in CH <sub>4</sub>                                  | 16.3         | 14.4 | 17.9 | 19.5 | 14.5 |
| C in (CO + CO <sub>2</sub> )                          | 7.2          | 14.1 | 35.0 | 9.5  | 2.2  |
| C in Total Gas  | 23.5         | 28.5 | 52.9 | 29.0 | 16.7 |
| <u>Yields, Percent Btu in Lignite</u>                 |              |      |      |      |      |
| Btu in CH <sub>4</sub>                                | 31.2         | 27.2 | 34.0 | 37.0 | 28.9 |
| Btu in (CO + H <sub>2</sub> )                         | 23.1         | 16.5 | 22.3 | 6.0  | 19.0 |
| Btu in Total Gas                                      | 54.3         | 43.7 | 56.3 | 43.0 | 47.9 |

\* Within 40 F maximum temperature.

TABLE 6. OPERATING DATA AND AVERAGE RESULTS FOR TESTS USING  
LIGNITE IN CONTINUOUS FLOW REACTOR WITH DRY FEEDING

|   | CFR Test No. |       |       |      |       |
|---|--------------|-------|-------|------|-------|
|   | 33           | 34    | 35    | 36   | 38    |
| <u>Operating Conditions</u>                           |              |       |       |      |       |
| Temperature, F  | 1720         | 1750  | 1725  | 1780 | 1770  |
| Pressure, atm   | 72.0         | 72.0  | 70.0  | 70.0 | 81.5  |
| Reactor Volume, cc*                                   | 242          | 250   | 210   | 452  | 445   |
| Residence Time, sec                                   | 3.4          | 2.4   | 4.2   | 10.4 | 8.5   |
| <u>Input</u>  |              |       |       |      |       |
| Water, g/min  | 34.0         | 55.1  | 6.0   | 12.4 | 16.9  |
| Partial Pressures of Materials<br>in Feed Stream, atm |              |       |       |      |       |
| H <sub>2</sub> O                                      | 43.3         | 51.1  | 11.7  | 24.8 | 34.0  |
| H <sub>2</sub>  | 5.2          | 3.8   | 10.7  | 8.3  | 8.6   |
| CO  | 15.6         | 11.6  | 32.5  | 25.3 | 26.4  |
| CO <sub>2</sub>                                       | 4.6          | 3.4   | 9.5   | 7.4  | 8.0   |
| C in Lignite, g/min                                   | 9.70         | 14.80 | 17.20 | 5.90 | 18.80 |
| Heat in Lignite, kcal/min                             | 90.0         | 137.5 | 154.0 | 53.5 | 174.0 |
| <u>Output</u>   |              |       |       |      |       |
| Product Gas, N liters/min                             | 41.2         | 60.2  | 45.3  | 37.5 | 49.2  |
| Product Water, N liters/min                           | 36.9         | 63.4  | 5.8   | 7.4  | 11.6  |
| Partial Pressures of Materials<br>in Product Gas, atm |              |       |       |      |       |
| H <sub>2</sub> O                                      | 34.1         | 33.0  | 6.9   | 11.5 | 15.5  |
| H <sub>2</sub>  | 13.4         | 14.8  | 13.1  | 16.9 | 18.0  |
| CO  | 7.5          | 6.5   | 24.9  | 18.5 | 19.0  |
| CO <sub>2</sub>                                       | 12.6         | 12.2  | 14.3  | 16.0 | 18.0  |
| CH <sub>4</sub>                                       | 2.3          | 2.66  | 5.6   | 2.98 | 7.24  |
| Heat in CH <sub>4</sub> , kcal/min                    | 28.3         | 43.9  | 39.4  | 18.1 | 51.1  |
| Heat in (CO + H <sub>2</sub> ), kcal/min              | 6.3          | 33.7  | 4.6   | 5.6  | 17.6  |
| Heat in Total Gas, kcal/min                           | 34.6         | 77.6  | 44.0  | 23.7 | 68.7  |
| C in Lignite Gasified, g/min                          | 3.0          | 5.90  | 3.94  | 2.83 | 6.76  |
| Preformed Methane, %                                  | 85.0         | 60.5  | 92.0  | 81.0 | 79.0  |
| <u>Yields, Percent C in Lignite</u>                   |              |       |       |      |       |
| C in CH <sub>4</sub>                                  | 15.4         | 16.8  | 12.4  | 17.5 | 15.5  |
| C in (CO + CO <sub>2</sub> )                          | 13.9         | 35.8  | 10.0  | 30.5 | 20.9  |
| C in Total Gas  | 29.3         | 52.6  | 22.4  | 48.0 | 36.4  |
| <u>Yields, Percent Btu in Lignite</u>                 |              |       |       |      |       |
| Btu in CH <sub>4</sub>                                | 29.7         | 31.9  | 24.6  | 33.9 | 29.4  |
| Btu in (CO + H <sub>2</sub> )                         | 6.6          | 26.9  | 2.9   | 10.5 | 10.1  |
| Btu in Total Gas                                      | 36.3         | 58.8  | 27.5  | 44.4 | 39.5  |

\* Within 40 F of maximum temperature.

hydrogen to methane by catalysis. The amount of "preformed methane" is calculated according to the following equation:

$$\% \text{CH}_4^* = \frac{\% \text{CH}_4 \times 100}{\% \text{CH}_4 + 1/4 (\% \text{CO} + \% \text{H}_2)}$$

where

$\% \text{CH}_4$ ,  $\% \text{CO}$ ,  $\% \text{H}_2$  = percent  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{H}_2$  in product gas by analysis

$\% \text{CH}_4^*$  = percent preformed methane

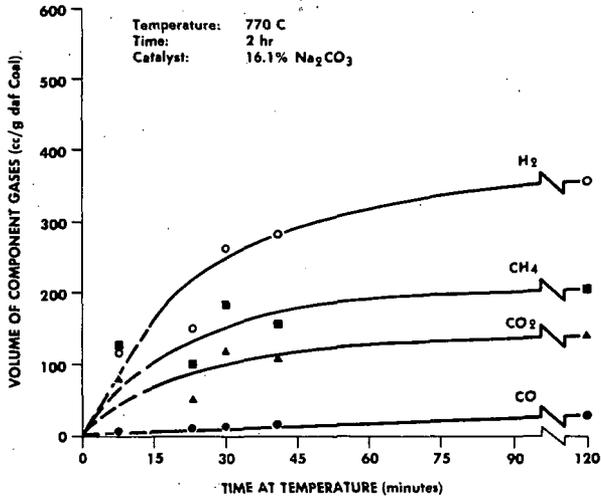
On a volume basis, hydrogen is the main component of the product gas from the direct reaction of steam with coal in the autoclave tests. This is illustrated in Figure 8 which presents data from an experiment at 770 C with a total reaction time of 2 hours.

Over the range of temperature studied, an increase in conversion with an increase in temperature is observed in experiments at both 12 and 120 minutes; and an increase in conversion is observed with an increase in time at the same temperature. This is shown in Figure 9 in which the gas yield, expressed as a function of the Btu content of the coal charged, is plotted versus temperature at the different reaction times. An increase in residence time from 12 to 120 minutes results in an increase in gas yield of about 15 percent of the coal heating value. A similar increase is caused by the addition of sodium carbonate to the coal; however, additional data are needed to establish the full significance of using catalysts.

Over the entire range of experimental conditions covered by these experiments, that is, pressure, 60 to 350 atmospheres; temperature, 730 to 770 C; and, reaction time, 2 to 120 minutes, methane is the main product on a heating value basis. It constitutes more than 90 percent of the total Btu in the gas at the 10 percent conversion level, and it still is more than 70 percent of the total Btu in the gas formed even at 60 percent conversion level. All the data from batch autoclave tests are compared in Figure 10 on the basis of conversion of coal to gas and formation of "preformed methane."

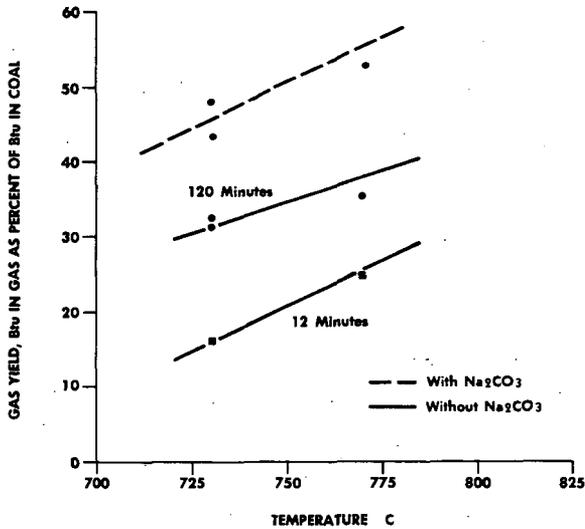
Methane is formed in good yield as well as in high concentration under the conditions of the autoclave tests. However, to attain the same high yields at short residence time as required in a commercial gasifier, the temperatures must be much higher than those explored in the autoclaves. Therefore, the continuous flow reactor was used next to determine the rate of methane formation and to establish the feasibility of using coal entrainment in Stage 2 of the two-stage process.

Data on the quality of the product gas obtained in the continuous flow reactor using both Pittsburgh seam coal and lignite are summarized in Figure 11; in this graph the yield of preformed methane is plotted against conversion expressed on a Btu basis. In addition, the curve for the correlation of the batch autoclave data and the yields used for cost estimating purposes are shown for comparison. On the lower right, a correlation of the results obtained with Pittsburgh seam coal in the presence of silica is given. Lower methane concentrations are indicated than in the autoclave tests.



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Figure 8. Effect of Time at Temperature on Gas Composition in Batch Autoclave Test at 770 C



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Figure 9. Effect of Temperature on Gas Yield without Catalyst in Batch Autoclave Test

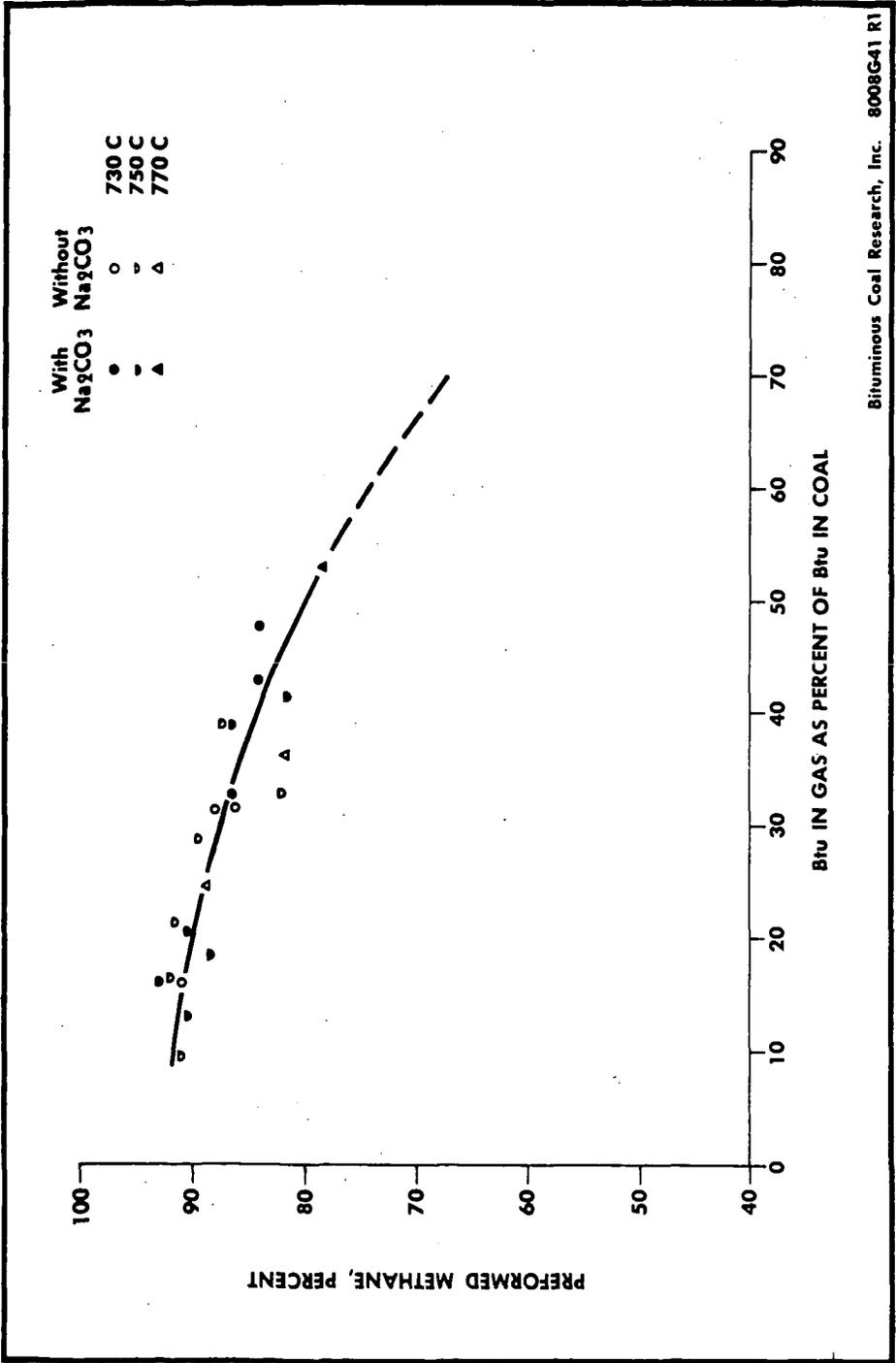


Figure 10. Yields of Gas and Performed Methane in Batch Autoclave Tests

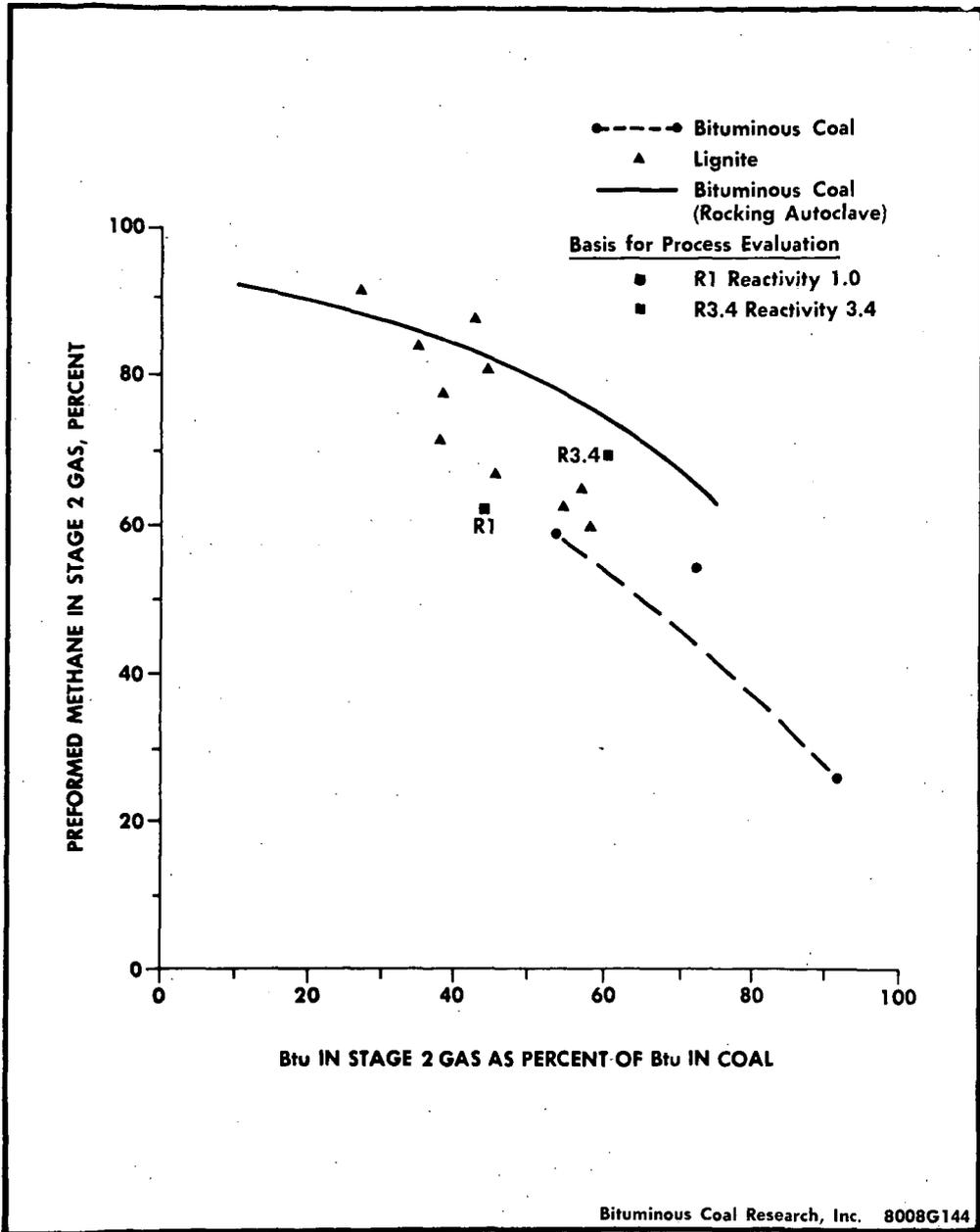


Figure 11. Correlation of Total Gas Yield and Preformed Methane in Continuous Flow Reactor Tests.

Methane concentrations are especially low in those tests in which the preheating of the coal slurry did not lead to complete vaporization of the water. In tests with thermocouples inside the reactor, it was found that the temperature inside the reactor drops considerably below that of the reactor walls under such conditions, and thus would easily cause these low conversions. In later tests with lignite, methane concentrations and conversions were obtained equivalent to those observed in the autoclave tests with bituminous coal.

Experimental results on only the yield of methane in tests in the continuous flow unit are shown in Figure 12; this is a plot of the methane yield, expressed as percent of the calorific value of the coal converted into methane, versus the percent of the Btu in coal converted into gas. The methane concentrations obtained in the flow unit are, as stated above, lower than those in the autoclave tests; consequently, the points in this graph for the continuous flow experiments also lie below the autoclave correlation curve at all levels of conversion. However, the points for the methane yield on a Btu basis are close to those assumed for the cost calculations in the overall engineering evaluation of the process projected to commercial-scale operation.(2)

The wide scatter of points on the Figures 11 and 12 are a reflection of the wide variation in conditions used in the tests, and examination of them reveals certain correlations that merit further consideration and study. For this, the experiments using lignite may be categorized as follows according to the conditions used:

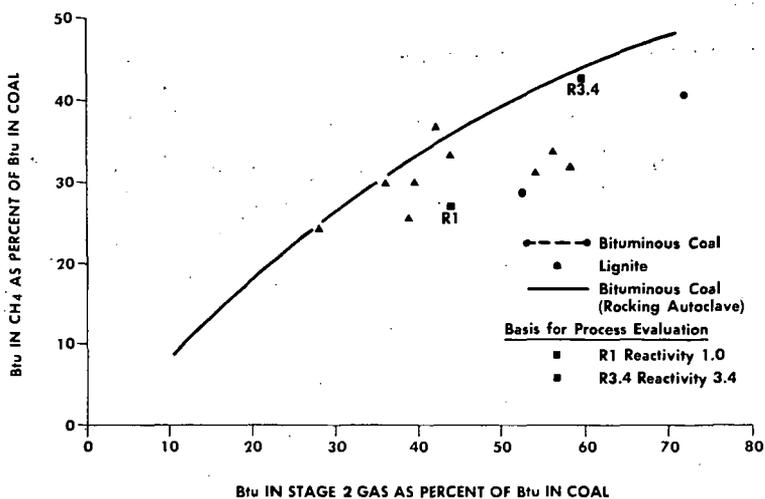
- (a) Less than 3.5 seconds residence at 70 atm and either below or above a peak reaction temperature of 1760 F.
- (b) Same as (a), but more than 3.5 seconds residence time.
- (c) Same as (a), but at 81 atm.
- (d) Same as (a), but more than 3.5 seconds residence time and at 81 atm.

In Figure 13, the rate of formation of methane is shown as a straight line function of the rate of feeding the lignite, and thus as a first approximation independent of other reaction conditions. However, closer examination of the operating conditions for each point on the graph shows that high hydrogen partial pressure (above 15 atm) at the reactor outlet, high total pressure (81 versus 70 atm), and high peak reactor temperature (above 1760 F versus below 1760 F) result in methane formation rates higher than those indicated by the line on the graph. Also data points below the curves are for tests made with hydrogen partial pressures below 13 atm at the reactor outlet.

The effect of hydrogen partial pressure at the reactor outlet ( $p_{H_2}$ ) on the yield of methane is shown in Figure 14. Except for two points, the correlation is good, showing that increased  $p_{H_2}$  results in increased yields of methane.

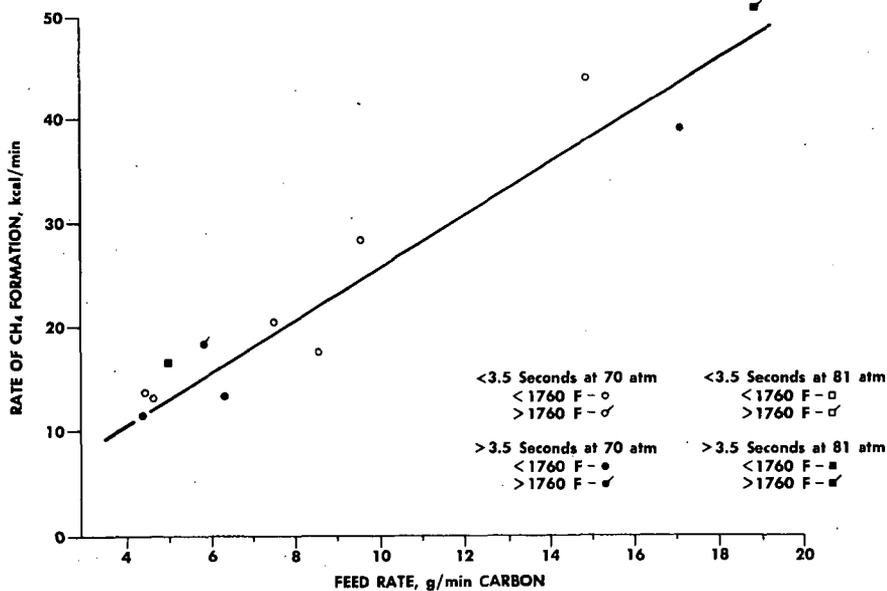
This indicated dependence of methane yield on  $p_{H_2}$  leads to a consideration of the factors that affect the hydrogen partial pressure at the reactor outlet. The material balances for the various tests show that the shift reaction is a major source of hydrogen in the product gas. The amount of hydrogen attributable to this source can be calculated from the equation:

$$K = \frac{(H_2 + X)(CO_2 + X)}{(CO - X)(H_2O - X)}$$



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Figure 12. Correlation of Total Gas Yield and Methane Formation in Continuous Flow Reactor Tests



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Figure 13. Effect of Feed Rate on Methane Formation in Continuous Flow Reactor Tests Using Lignite

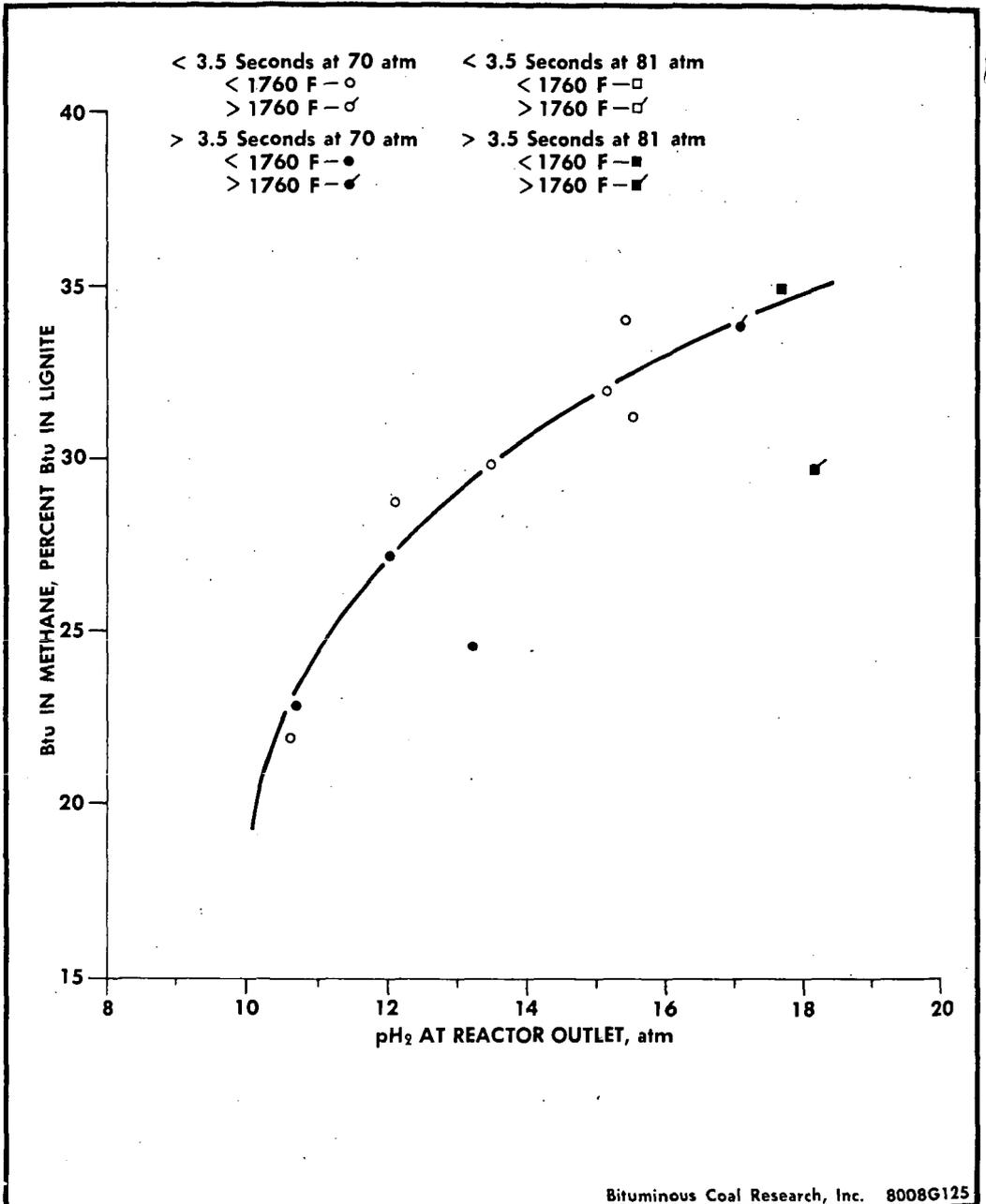


Figure 14. Effect of Hydrogen Partial Pressure at Reactor Outlet on Methane Formation in Continuous Flow Reactor Tests Using Lignite

where  $H_2$ , CO,  $CO_2$ ,  $H_2O$  are the partial pressures of these gases in the feed stream entering the reactor--where X is the fractional increase or decrease in the partial pressure of these gases due to reaction--and, where K is the equilibrium constant. Solving this equation for X to obtain the amount of  $H_2$  produced by the shift reaction leads to a cumbersome quadratic expression.

For use in evaluating experimental results, this complex quadratic expression may be simplified to  $1/2 \sqrt{(CO)(H_2)}$ ; the total expression for the feed stream composition (E) then becomes:

$$E = H_2 + 1/2 \sqrt{(CO)(H_2)}$$

and is found to correlate well with hydrogen partial pressure at the reactor outlet ( $pH_2$ ).

The correlation of the yield of methane with E (Figure 15) is not as good as with  $pH_2$  (Figure 14); however, this correlation should prove useful in the evaluation of data from future experiments. Present indications are that inclusion of a term in the expression E reflecting the Stage 1 gas/coal ratio will improve the correlation significantly.

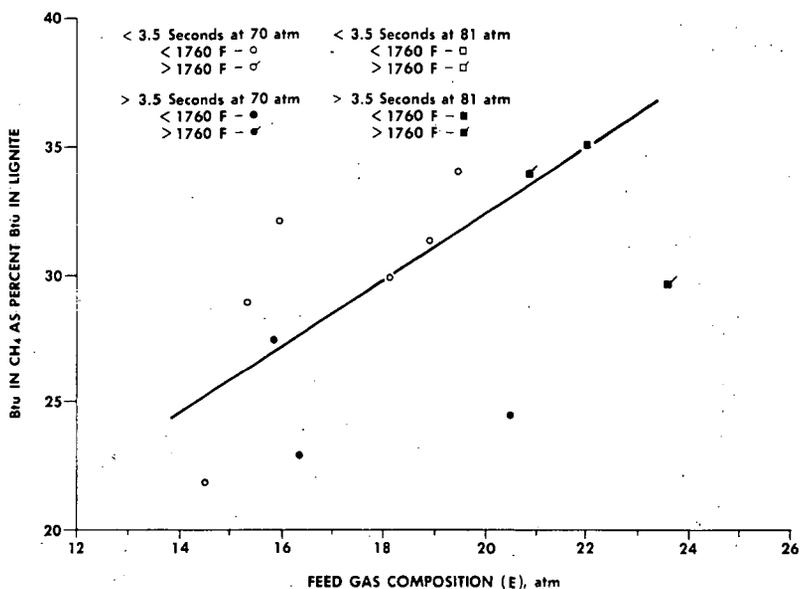
While hydrogen concentration affects mostly the methane yield the concentration of the steam/lignite ratio is most pronounced on the yield of  $(CO + H_2)$ ; this is shown in Figure 16. In spite of the scatter, it is apparent that high steam/lignite ratio favor increased yields of  $(CO + H_2)$ .

In carbon gasification processes, changes in gasification rate with increased carbon "burn-off" are often observed. The quantity of "Btu in gas as percent of the Btu in lignite" increases with "burn-off"; it is plotted in Figure 17 versus the gasification rate expressed as kcal/hr/kcal inventory. This indicates that experimental conditions that lead to high conversion lead also to high lignite reactivity as expressed by the gasification rate referred to lignite inventory. The points obtained in tests with residence time between 2.3 and 4.2 seconds fall close to the curve; however, to the left of the curve, showing a lower gasification rate, are points for two tests with residence time of 8.5 and 10.4 seconds.

#### SUMMARY AND CONCLUSION

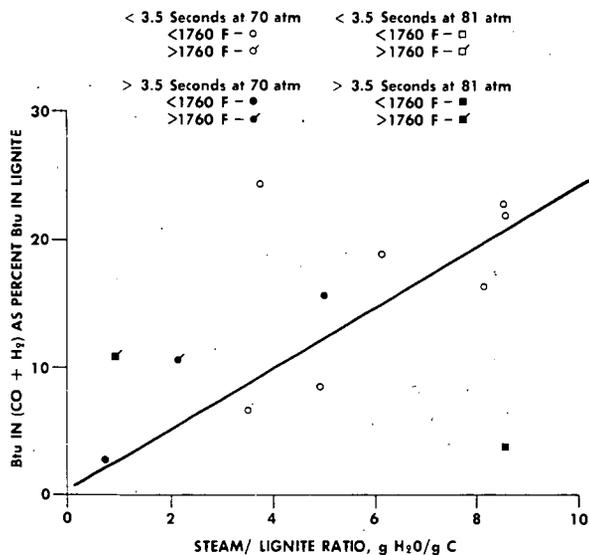
In summary, it can be stated that the experiments in bench-scale equipment have shown that methane is formed from high volatile coals at 70 atm pressure at a rate and in a yield consistent with previous assumptions for the second stage of a conceptual process for gasifying coal.

A more definitive study of the process variables is being planned by operation of a 100 lb/hr internally-heated process and equipment development unit. Shock heating by means of hot Stage 1 gas will produce a well defined Stage 2 reactor volume and a temperature gradient similar to that expected in a commercial plant. A previous economic evaluation of such a two-stage coal gasification process led to a pipeline gas manufacturing cost of about 50¢/M scf.



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Figure 15. Effect of Feed Stream Composition on Yield of Methane in Continuous Flow Reactor Tests Using Lignite



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Figure 16. Effect of Steam/Lignite Ratio on (CO + H<sub>2</sub>) Formation in Continuous Flow Reactor Tests

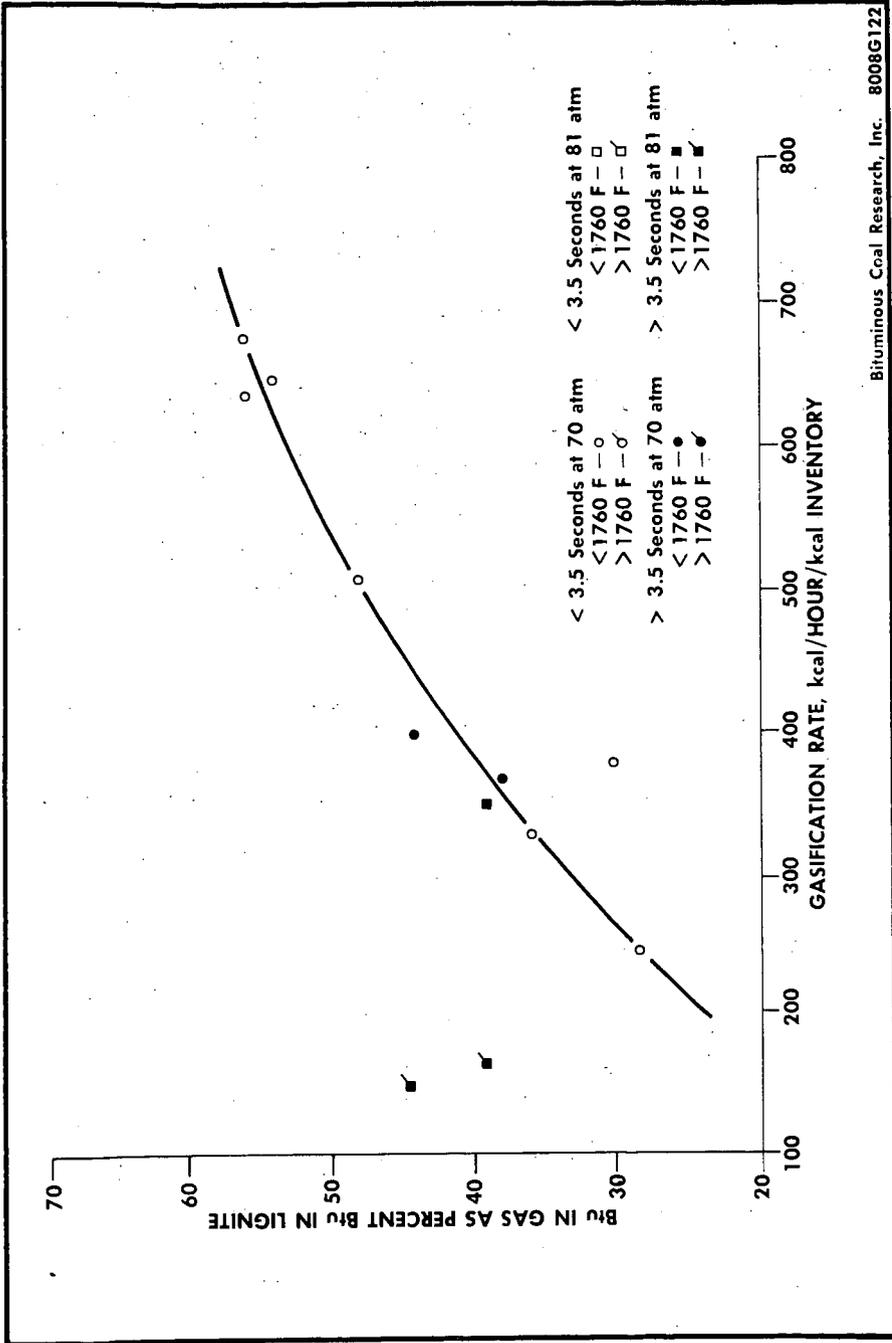


Figure 17. Effect of Conversion on Gasification Rate in Continuous Flow Reactor Tests Using Lignite

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