GAS GENERATOR RESEARCH AND DEVELOPMENT

Progress Report No. 3
November 1971
(BCR Report L-441)

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Submitted to the

Office of Coal Research
Department of the Interior
Washington, D. C.

December 27, 1971

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December 1, 1971

Mr. Paul Towson, Engineer
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Office of Coal Research
U.S. Department of the Interior
Washington, D. C. 20240

SUBJECT: Monthly Progress Report No. 3
OCR Contract No. 14-32-0001-1207

Dear Mr. Towson:

Phase II studies on process and equipment development continue according to the new work schedule. Plans are being made to dismantle the 100 lb/hr Stage 2 PEDU in preparation of the area for the new PEDUs. A final summary report of the Stage 2 PEDU work is being prepared. Editing of the summary report on the coal composition and beneficiation studies continues and should be completed at an early date.

Equipment for the first phase of the cold flow model studies has been installed and some data have been obtained for feed nozzle orientation in an integrated gasifier.

In the bench-scale gas processing studies, to find a suitable methanation catalyst for use in the BI-GAS process, evaluation studies have shown that non-nickel catalysts have justified further work in this area. In bench-scale studies on char gasification, reactivity tests on the char received from Consolidation Coal Company continues.

Evaluation of the fluidized-bed methanation and gasification PEDU bid packages received from Koppers is in progress. Planning for procurement and erection of equipment for the two PEDUs continues.

Preparation of the bid package for the Homer City pilot plant continues with submission by Koppers planned for early December.

Yours very truly,

John W. Igoe

JWI:kag
8006

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF TABLES
(Continued)

LIST OF FIGURES

BITUMINOUS COAL RESEARCH, INC.
SPONSORED RESEARCH PROGRAM

GAS GENERATOR RESEARCH AND DEVELOPMENT

Progress Report No. 3

(BCR Report L-441)

I. INTRODUCTION

This report summarizes progress achieved during the ninety-fifth month of work on the general program, "Gas Generator Research and Development," being conducted by Bituminous Coal Research, Inc., for the Office of Coal Research. The program which was initiated under Contract No. 14-01-0001-324 December 20, 1963, was transferred to Contract No. 14-32-0001-1207 on August 19, 1971. Thus, this report represents the third report of progress under the new prime contract.

The overall objective of the program continues to be to develop processes for gasifying coal to produce fuel gas and high-Btu pipeline gas.

Laboratory-scale coal gasification experimentation is to be continued together with process and equipment development. With the aid of engineering subcontractor(s), a multipurpose research pilot plant facility is to be designed, constructed, and test operated.

A. Work Schedule

Work on the project is being conducted according to a schedule reflecting the program outlined under the new prime contract. This schedule was shown in Figure 1, page 2, Progress Report No. 1.

B. Monthly Progress Charts

Monthly progress charts reflecting proposed rate of effort and expenditures are shown in Appendixes A-1 and A-2.

II. PHASE II PROGRESS ACHIEVED DURING MONTH ENDING NOVEMBER 25, 1971

A. Laboratory-scale Process Studies

1. Coal Composition and Beneficiation Studies (R. G. Moses and R. D. Saltsman): The report summarizing work performed since September 20, 1970, on this phase of the work has been drafted and is being edited currently.

2. Laboratory Pyrolysis of Coal (J. E. Noll): Work performed on this phase of the project since September, 1970, is being summarized together with the work on coal composition. (See above.)

3. Fluidized-bed Gasification (E. K. Diehl and J. T. Stewart): Activity on the project continued during the past month, with most of the work centered on the laboratory investigations of char reactivity.

PEDU cost estimates were reviewed; further design study by Koppers has been delayed, pending completion of the Homer City pilot plant bid package.

a. Fluidized-bed PEDU: Following a review of the cost estimates submitted by Koppers in October, a formal request was made to OCR for their approval to proceed with the expenditure of funds to erect the unit. The request, submitted November 9, 1971, has not yet been acted upon by OCR.

During his visit to BCR on November 23, 1971, Paul Towson indicated that he had not yet had the opportunity to study the request in detail. However, he inferred that action would be forthcoming.

b. Laboratory Investigation: Reactivity studies were concluded for the reaction of carbon dioxide with a char from Consolidation Coal's Cresap plant (BCR Lot No. 2469). One hundred thirty-eight experimental runs were made at temperatures of 1000, 1080, and 1115 C, and at reacting gas concentrations of 15, 25, 50, 75, and 100 percent carbon dioxide in nitrogen. The complete rate equation for the reaction of this char sample with carbon dioxide may be expressed as:

$$(1-x) = \text{Ash} + (1 - \text{Ash})\, e^{-k\,(C_{CO_2})^{.50}t} \qquad (1)$$

$$\text{and } k = 1.75 \times 10^{6}\, e^{-\frac{1.92 \times 10^{4}}{T}} \qquad (2)$$

where x = fraction of char reacted
T = temperature in °K
C = concentration of reacting gas
t = time in minutes
k = apparent reactivity $\left(\frac{\text{lb. C reacted}}{\text{lb. C inventory - min}}\right)$
Ash = weight percent of ash in unreacted char

From Equation (2), we can find for this reaction an activation energy of 38 kcal/mole and a pre-exponential factor (Arrhenius constant) of 1.75×10^{6} min^{-1}. These values correspond to 48 kcal/mole and 3.96×10^{6} min^{-1} previously reported for the FMC char-carbon dioxide reaction. In both cases, the rate was found to be proportional to the square root of the carbon dioxide concentration. Figure 49 shows a typical plot of Equations (1) and (2) with the corresponding experimental data.

Table 41 is a comparison of the apparent reactivity k value from Equation (2) for the two chars. The Consol char is more reactive below 1200 C while the FMC char is more reactive at 1200 C and higher. This is also shown in the Arrhenius plot of Figure 50.

The reaction of Consol char with steam is presently being investigated.

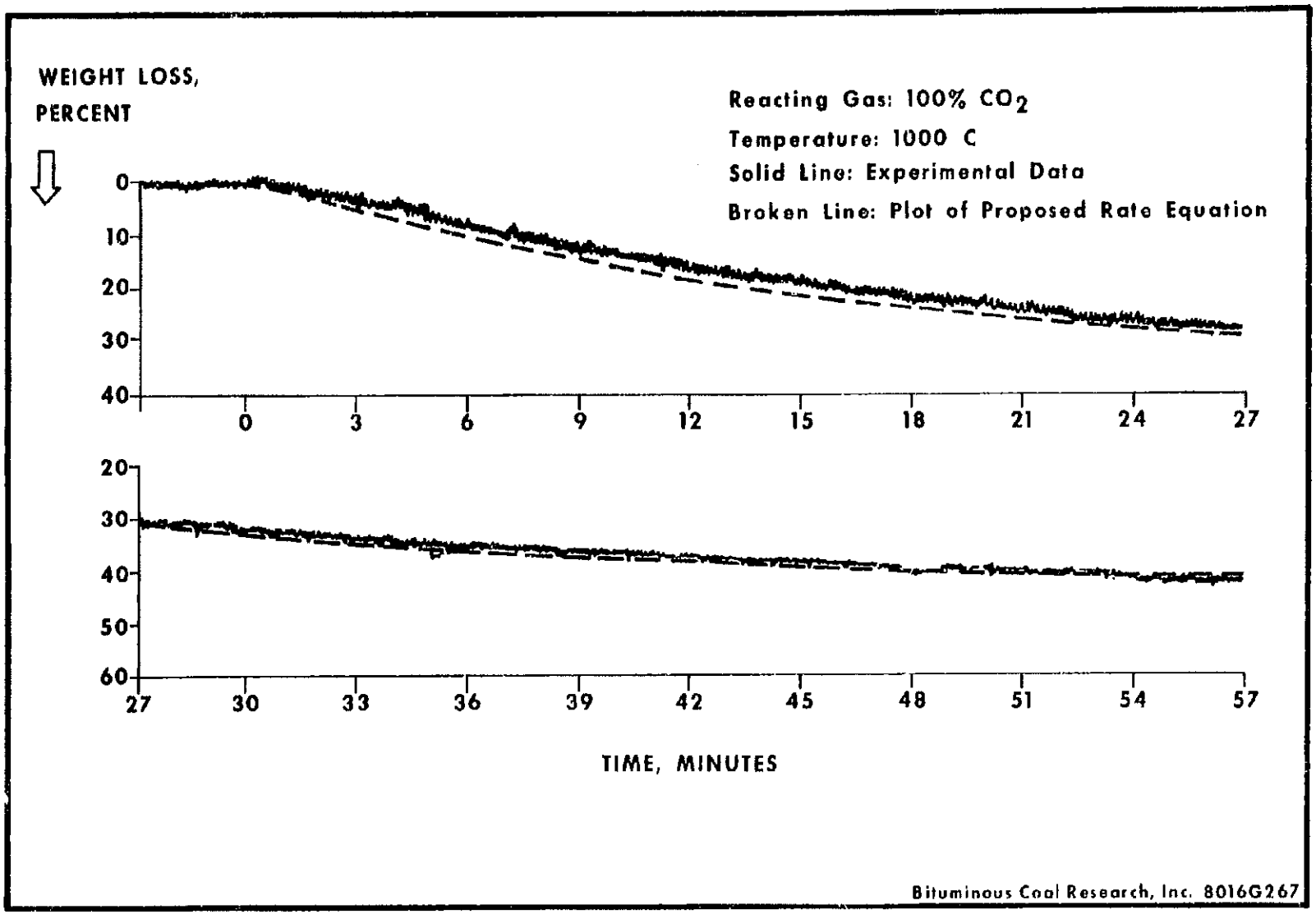

Figure 49. Correlation of Consol Char Reactivity Data

TABLE 41. APPARENT REACTIVITY VALUES FOR FMC AND CONSOL CHAR SAMPLES

		Temperature, C			
		900	1000	1100	1200
FMC Char (BCR Lot No. 2455)	$k = \frac{\text{lb C reacted}}{\text{lb C inventory - min}}$	.0072	.0352	.1358	.4361
Consol Char (BCR Lot No. 2469)	$k = \frac{\text{lb C reacted}}{\text{lb C inventory - min}}$	.0136	.0476	.1479	.3821

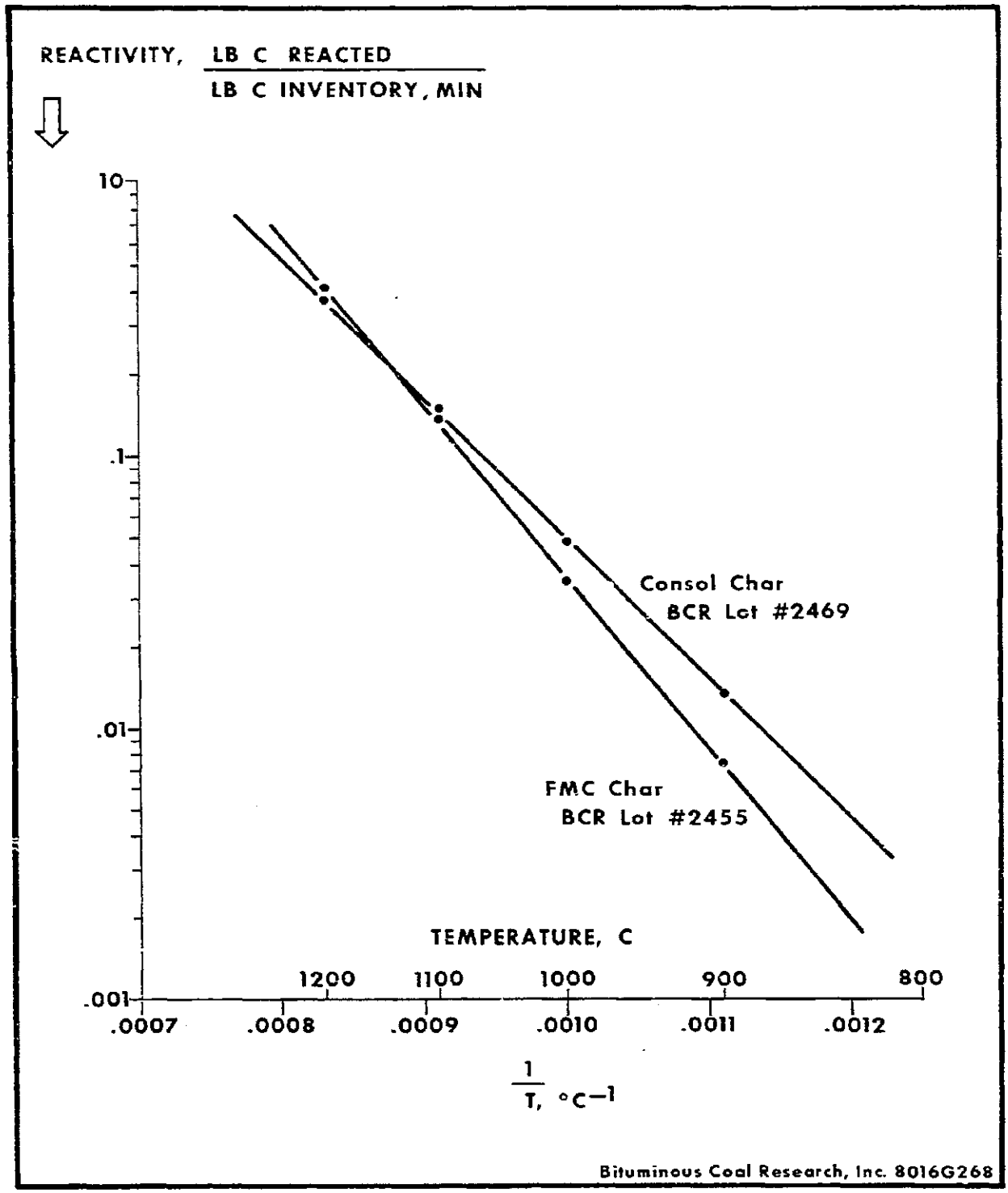

Figure 50. Char Reactivity as a Function of Temperature for the Char + Carbon Dioxide Reaction

c. Future Work: Upon receipt of approval from OCR, PEDU erection plans will be finalized. Detailed engineering by Koppers will be the first step, since that work will have to precede general procurement, especially that of certain specialty equipment items.

Char reactivity studies will continue. A summary report of the procedure and development of the reactivity equations is being drafted.

4. Gas Processing (M. S. Graboski): Work continued in the area of gas processing during the month of November in accordance with the time schedule shown in Figure 4, page 7 of Progress Report No. 1 (September 1971). Work reported here covers bench-scale studies and PEDU planning.

a. Bench-scale Studies: The purpose of the bench-scale program is to investigate methanation catalysts under conditions imposed by the BI-GAS process. During the month, three catalysts were screened in the BSM test unit. Life testing continued on Lot 2903 molybdenum catalyst.

(1) Data and Results for BSM Test 41: The purpose of BSM Test 41 was to determine if catalyst Lot 2904 would show any activity toward methanation. Catalyst 2904 is composed of chromic oxide on high-activity alumina and is prepared by Harshaw Chemical Company. Physical property data for Lot 2904 are given in Figure 51, "Size Distribution Data for Lot 2904 Catalyst."

Three grams of Catalyst 2904 were charged into the test unit. The temperature was increased under synthesis gas, and, at 730 F, there was visible evidence of methanation. The temperature was raised to 755 F and the rate of reaction was determined. Results for Test 41 are given in Table 42.

(2) Data and Results for BSM Tests 42 and 43: The purpose of Tests 42 and 43 was to determine if catalyst Lot 2906 would show any activity toward methanation. Catalyst 2906 is composed of iron oxide on high-activity alumina and is prepared by Harshaw Chemical Company. Data for Lot 2906 are given in Figure 52, "Size Distribution Data for Lot 2906 Catalyst."

Three grams of Catalyst 2906 were charged into the test unit. The temperature was increased under synthesis gas and, at 585 F in Test 42, evidence of methanation was present. Shortly thereafter, Test 42 was discontinued due to loss of cooling water. Reaction rates were measured at 720 and 800 F in Test 43. Results are summarized in Table 43.

(3) Data and Results for BSM Tests 44 and 45: The purpose of BSM Tests 44 and 45 was to determine the activity of BCR Lot 2915 towards the methanation reaction. Lot 2915 is a nickel-molybdenum catalyst supplied by Catalyst and Chemicals Inc. No physical property data are available for the catalyst. Three grams of catalyst were charged to the reactor in Test 44. The same material was used in Test 45. Temperature was increased under synthesis gas until reaction was initiated at slightly above 600 F. Rates were measured between 655 and 800 F. Data are summarized in Tables 44 and 45.

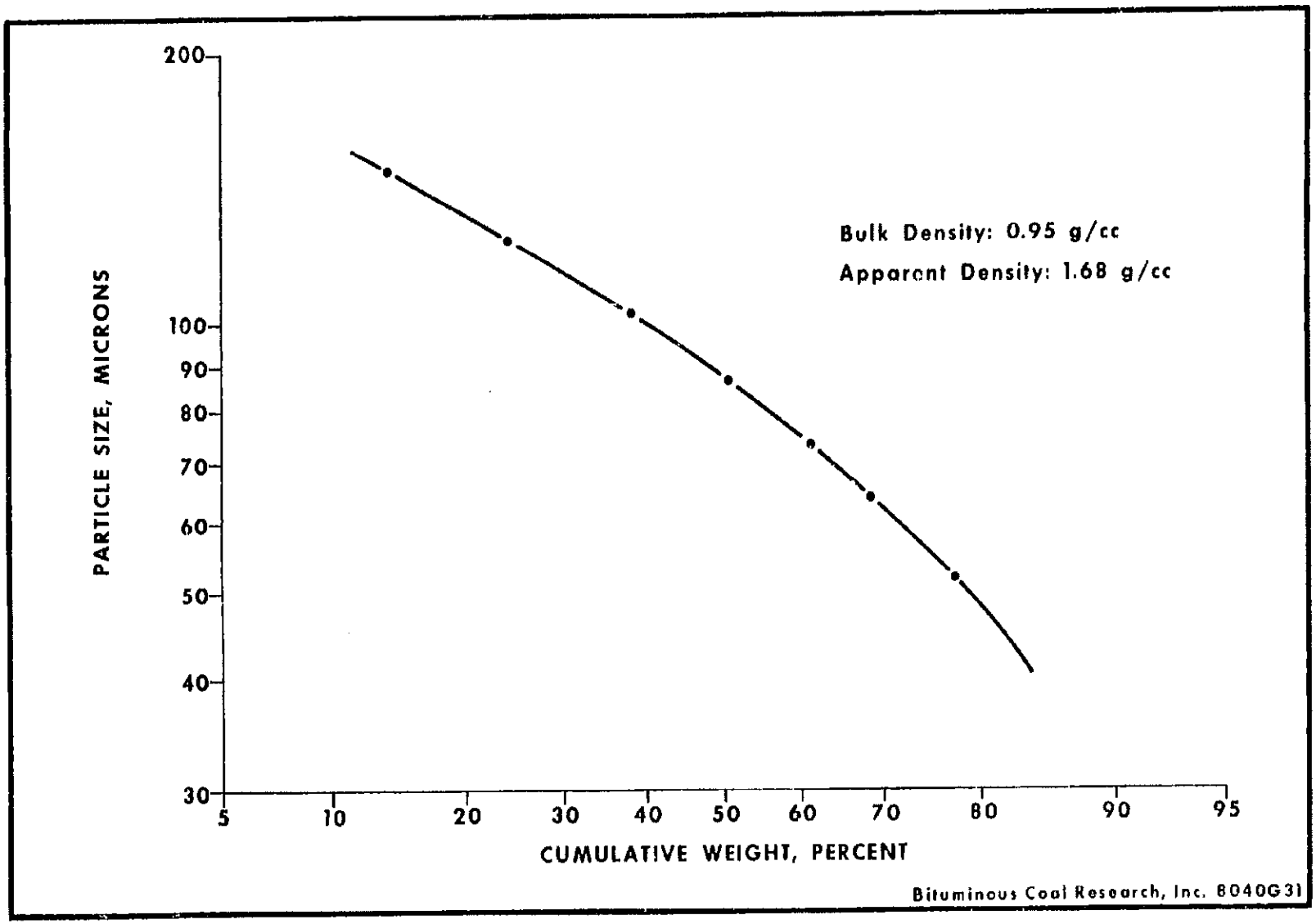

Figure 51. Size Distribution Data for Lot 2904 Catalyst

TABLE 42. TEST CONDITIONS AND RESULTS FOR BSM TEST 41

Test Conditions

Catalyst BCR Lot No. 2904
Mass, g 3.0
Size, mesh -50 +170
System Temperature, F
Period 1 755
Period 2 755

System Pressure, psia
Period 1 1040
Period 2 1040

Feed, percent

Hydrogen	59.57
Nitrogen	2.18
Carbon Monoxide	21.02
Carbon Dioxide	-
Methane	17.12
Ethane	0.01

Flow Rates	Period 1	Period 2
Feed, Orifice Meter, scfh	23.44	22.10
Product		
a. Dry meter, scfh	15.89	15.41
b. Water, g/hr	34.95	34.44

Results*

Material Balance	Period 1	Period 2
Total Mass In, g/hr	267.3	257.6
Total Mass Out, g/hr	268.8	260.5
Difference, percent	0.6	1.1
Total Nitrogen In, g moles/hr	0.57	0.55
Total Nitrogen Out, g moles/hr	0.60	0.59
Difference, percent	5.1	7.0
Total Carbon In, g moles/hr	9.79	9.57
Total Carbon Out, g moles/hr	9.79	9.57
Difference, percent	0.0	0.0

Conversions and Rates	Product, Mole Percent, Period		Conversions, g moles/hr, Period		Rates, g moles/hr/g Catalyst, Period	
	1	2	1	2	1	2
Carbon Monoxide	15.32	14.83	2.16	2.36	0.72	0.79
Hydrogen	49.81	48.77	5.50	5.34	1.83	1.78
Methane	30.73	32.08	1.77	1.97	0.59	0.66
Water	-	-	1.94	1.91	0.65	0.64
Nitrogen	2.92	3.05	-	-	-	-
Carbon Dioxide	0.56	0.58	0.12	0.12	0.04	0.04
Ethane	0.66	0.69	0.27	0.27	0.09	0.09

* Normalized Carbon Balance

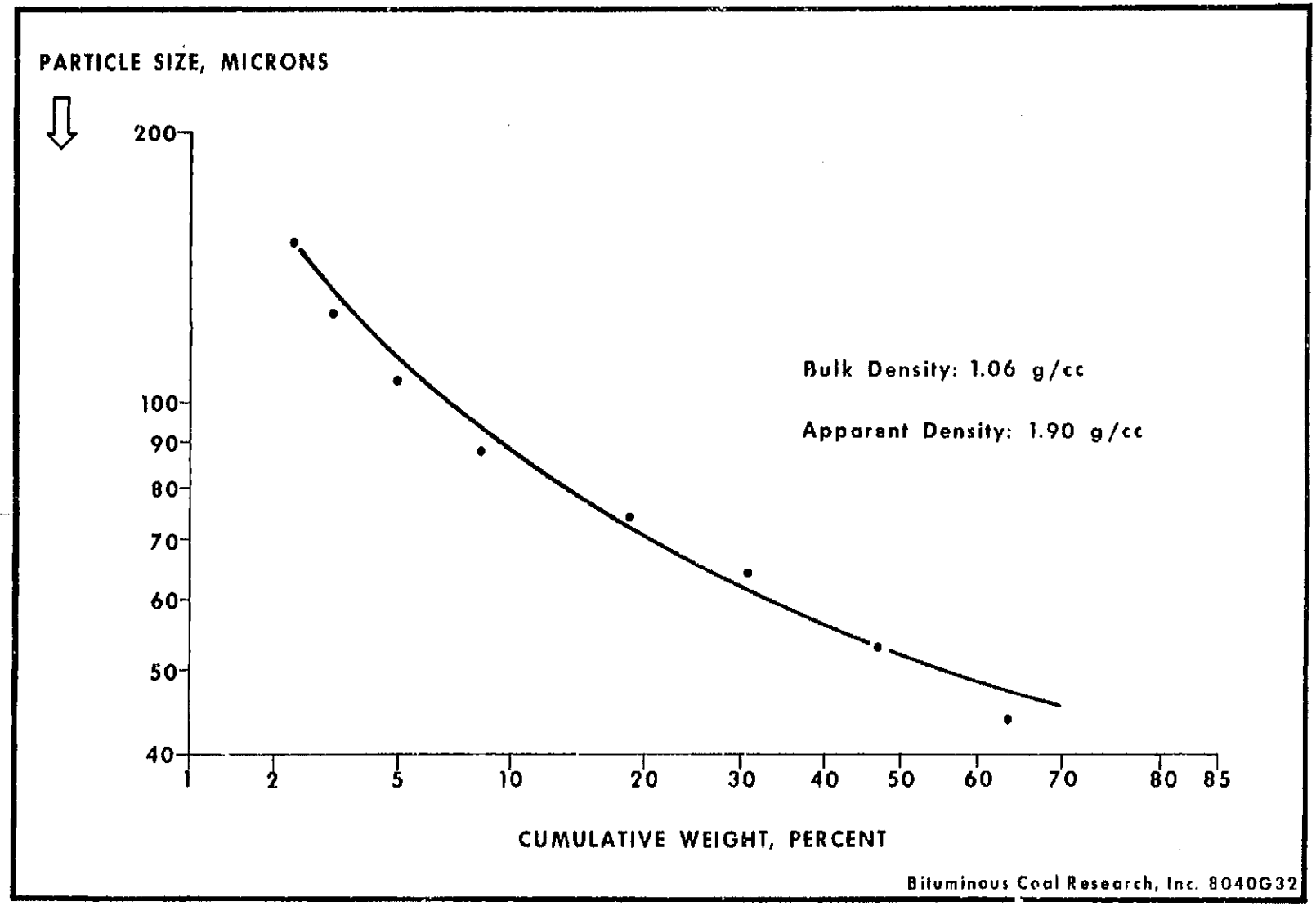

Figure 52. Size Distribution Data for Lot 2906 Catalyst

TABLE 43. TEST CONDITIONS AND RESULTS FOR BSM TEST 43

Test Conditions

Catalyst BCR Lot No.	2906
Mass, g	3.00
Size, mesh	-50 +170
System Temperature, F	
Period 1	725
Period 2	720
Period 3	800
System Pressure, psia	
Period 1	1000
Period 2	1000
Period 3	1020

Feed, percent	
Hydrogen	60.08
Nitrogen	2.02
Carbon Monoxide	21.22
Carbon Dioxide	---
Methane	16.65
Ethane	0.03

Flow Rates	Period 1	Period 2	Period 3
Feed, Orifice Meter, scfh	25.9	25.9	32.7
Product			
a. Dry meter, scfh	21.1	21.5	26.7
b. Water, g/hr	30.2	27.5	86.3

Material Balance	Results* Period 1	Period 2	Period 3
Total Mass In, g/hr	314.3	315.7	393.8
Total Mass Out, g/hr	315.8	317.8	403.2
Difference, percent	0.5	0.7	4.2
Total Nitrogen In, g moles/hr	0.62	0.62	0.77
Total Nitrogen Out, g moles/hr	0.63	0.63	0.79
Difference, percent	1.6	1.6	2.6
Total Carbon In, g moles/hr	11.47	11.53	14.38
Total Carbon Out, g moles/hr	11.47	11.53	14.38
Difference, percent	0.0	0.0	0.0

Conversions and Rates	Product, Mole Percent Period 1	Period 2	Period 3	Conversions, g moles/hr Period 1	Period 2	Period 3	Rates, g moles/hr/g Catalyst Period 1	Period 2	Period 3
Carbon Monoxide	17.60	18.01	12.52	1.86	1.72	4.91	0.62	0.57	1.64
Hydrogen	53.84	54.16	41.76	4.22	4.23	12.15	1.41	1.41	4.05
Methane	25.16	24.51	40.32	1.49	1.38	4.00	0.50	0.46	1.33
Water	---	---	---	1.68	1.52	7.78	0.56	0.51	1.60
Nitrogen	2.43	2.41	3.12	---	---	---	---	---	---
Carbon Dioxide	0.48	0.48	0.97	0.12	0.12	0.25	0.04	0.04	0.08
Ethane	0.49	0.43	1.31	0.24	0.24	0.66	0.08	0.08	0.22

* Normalized Carbon Balance

TABLE 44. TEST CONDITIONS AND RESULTS FOR BSM TEST 44

Test Conditions

Catalyst BCR Lot No.	2915
Mass, g	3.0
Size, mesh	-50 +170
System Temperature, F	
Period 1	765
Period 2	760
Period 3	703
System Pressure, psia	
Period 1	1090
Period 2	1097
Period 3	1022

Feed, percent	
Hydrogen	59.81
Nitrogen	1.96
Carbon Monoxide	21.44
Carbon Dioxide	0.00
Methane	16.77
Ethane	0.02

Flow Rates	Period 1	Period 2	Period 3
Feed, Orifice Meter, scfh	26.23	23.71	20.02
Product			
a. Dry meter, scfh	16.31	15.70	16.40
b. Water, g/hr	60.6	51.8	25.8

Results*

Material Balance	Period 1	Period 2	Period 3
Total Mass In, g/hr	312.9	295.9	249.2
Total Mass Out, g/hr	314.6	293.4	245.6
Difference, percent	0.5	0.5	1.0
Total Nitrogen In, g moles/hr	0.59	0.56	0.47
Total Nitrogen Out, g moles/hr	0.61	0.58	0.50
Difference, percent	3.4	3.5	6.2
Total Carbon In, g moles/hr	11.47	10.84	9.12
Total Carbon Out, g moles/hr	11.47	10.84	9.12
Difference, percent	0.0	0.0	0.00

Conversions and Rates	Product, Mole Percent			Conversions, g moles/hr			Rates, g moles/hr/g Catalyst		
	Period			Period			Period		
	1	2	3	1	2	3	1	2	3
Carbon Monoxide	12.38	12.82	17.00	3.88	3.55	1.78	1.29	1.18	0.59
Hydrogen	42.52	42.97	51.75	9.18	8.51	4.05	3.06	2.83	1.35
Methane	39.85	39.04	27.35	3.17	2.91	1.38	1.06	0.97	0.46
Water	---	---	---	3.37	2.89	1.43	1.13	0.97	0.47
Nitrogen	2.98	2.99	2.55	---	---	---	---	---	---
Carbon Dioxide	1.00	0.93	0.65	0.21	0.18	0.13	0.07	0.06	0.04
Ethane	1.27	1.25	0.70	0.50	0.46	0.14	0.17	0.15	0.05

* Normalized Carbon Balance

TABLE 45. TEST CONDITIONS AND RESULTS FOR BSM TEST 45

Test Conditions

Catalyst BCR Lot No.	2915
Mass, g	30
Size, mesh	-50 +170
System Temperature, F	
Period 1	710
Period 2	707
Period 3	655
System Pressure, psia	
Period 1	1074
Period 2	1104
Period 3	1060

Feed, percent	
Hydrogen	59.80
Nitrogen	1.98
Carbon Monoxide	21.41
Carbon Dioxide	---
Methane	16.79
Ethane	0.02

Flow Rates	Period 1	Period 2	Period 3
Feed, Orifice Meter, scfh	22.04	21.59	19.34
Product			
a. Dry meter, scfh	17.00	16.46	17.30
b. Water, g/hr	31.20	30.90	12.70

Material Balance	Results* Period 1	Period 2	Period 3
Total Mass In, g/hr	268.4	262.9	240.5
Total Mass Out, g/hr	269.2	263.6	240.1
Difference, percent	0.3	0.4	0.6
Total Nitrogen In, g moles/hr	0.50	0.51	0.46
Total Nitrogen Out, g moles/hr	0.55	0.53	0.46
Difference, percent	9.5	3.9	0.0
Total Carbon In, g moles/hr	9.80	9.62	8.82
Total Carbon Out, g moles/hr	9.80	9.62	8.82
Difference, percent	0.0	0.0	0.0

Conversions and Rates	Product, Mole Percent Period 1	Period 2	Period 3	Conversions, g moles/hr Period 1	Period 2	Period 3	Rates, g moles/hr/g Catalyst Period 1	Period 2	Period 3
Carbon Monoxide	16.21	16.48	---	2.09	2.04	0.99	0.70	0.68	0.33
Hydrogen	51.55	51.02	---	4.50	4.65	2.13	1.50	1.35	0.71
Methane	28.14	28.40	---	1.63	1.55	0.75	0.54	0.52	0.25
Water	---	---	---	1.74	1.71	0.71	0.58	0.57	0.24
Nitrogen	2.59	2.56	---	---	---	---	---	---	---
Carbon Dioxide	0.74	0.75	---	0.15	0.15	0.10	0.05	0.05	0.03
Ethane	0.77	0.79	---	0.30	0.30	0.15	0.10	0.10	0.05

* Normalized Carbon Balance

(4) Discussion of BSM Tests 41 to 45: During the month, three more methanation catalysts were screened. These included chrome, iron, and nickel-molybdenum. All showed good activity and selectivity under the synthesis conditions imposed.

Results for the chrome catalyst, Lot 2904, are summarized in Table 42. Reaction rates determined at 755 F are fairly high, and the second period results indicated that the rate was increasing slightly. Selectivity data for the chrome catalyst are given in Table 46. The major products in the gas phase were methane, ethane, and carbon dioxide. The relative amounts of these materials is the same as for other catalysts which have been found to promote both the shift and methanation reactions. The chrome catalyst is supplied in a fluidized bed form with a mean particle size of 88 microns, as shown in Figure 51. The promising results of Test 41 indicate that life testing of the chrome catalyst is worthwhile.

In Test 43, a fluidized iron catalyst was investigated. The data, as shown in Table 43, indicate high activity at the temperatures used. Iron has historically been used in the Fischer Tropsch synthesis to produce gasoline at lower temperatures and pressures. The Sasol operation, for example, uses synthesis temperatures of about 600 F and pressures of 350 psig; while in Test 43, reaction rates were determined at 720 to 800 F and above 1,000 psig. Selectivity data for the major products are given in Table 46. As was the case with the chrome catalyst, methane, ethane, and carbon dioxide were present in large quantities. The yield of ethane was slightly higher for iron than chrome, and a trace of propane was also present. Product water for iron, however, contained large amounts of organic materials, while the chrome catalyst product water was relatively pure. At the lower temperature, the iron catalyst product water was clear and had a sweet smell indicating the presence of low molecular weight alcohols, aldehydes, and other oxygenated organic materials. At the high temperature, the product water was cloudy and had a foul odor, possibly indicating the presence of organic acids. No quantitative analysis is available for the liquid effluent.

It is apparent from Test 43 that raising the temperature of the reaction system tends to increase the formation of light hydrocarbons from iron while almost completely suppressing the tendency to form gasoline and oil. Size distribution data for the fluidized iron catalyst are given in Figure 52. The mean particle size is 52 microns. Further testing of iron to determine catalyst life at high temperatures will be worthwhile, as indicated by results from Test 43 and past Fischer Tropsch experience.

Tests 44 and 45 were carried out using a nickel-molybdenum catalyst. Results are summerized in Tables 44 and 45. High activity was found for this catalyst and the product distribution data in Table 46 indicate that the catalyst promotes both methanation and the shift reaction. The same batch of catalyst was used in both tests with a system shutdown in between. The data for the two tests are plotted in Figure 53. No deactivation occurred over the test period as it did when this procedure was applied to plain nickel

TABLE 46. CONVERSION AND SELECTIVITY DATA FOR TESTS 41 TO 45

Catalyst Lot	2904	2904	2906	2906	2906
Test and Period	41-1	41-2	43-1	43-2	43-3
Temperature, F	755	755	725	720	800
Pressure, psia	1040	1040	1000	1000	1020
Carbon Monoxide Conversion, percent	40.8	44.8	29.0	26.7	60.9
Product Distribution					
Percent CO → CH_4	81.9	83.4	80.5	80.3	81.5
Percent CO → C_2H_6	12.5	11.5	13.0	13.8	13.5
Percent CO → CO_2	5.6	5.1	6.5	6.9	5.0

Catalyst Lot	2915	2915	2915	2915	2915	2915
Test and Period	44-1	44-2	44-3	45-1	45-2	45-3
Temperature, F	765	760	703	710	707	653
Pressure, psia	1090	1097	1022	1074	1104	1060
Carbon Monoxide Conversion, percent	60.5	58.5	34.8	38.2	37.9	20.0
Product Distribution						
Percent CO → CH_4	81.7	82.0	77.2	77.9	77.5	75.0
Percent CO → C_2H_6	12.9	13.0	15.5	14.4	15.0	15.0
Percent CO → CO_2	5.4	5.0	7.3	7.7	7.5	10.0

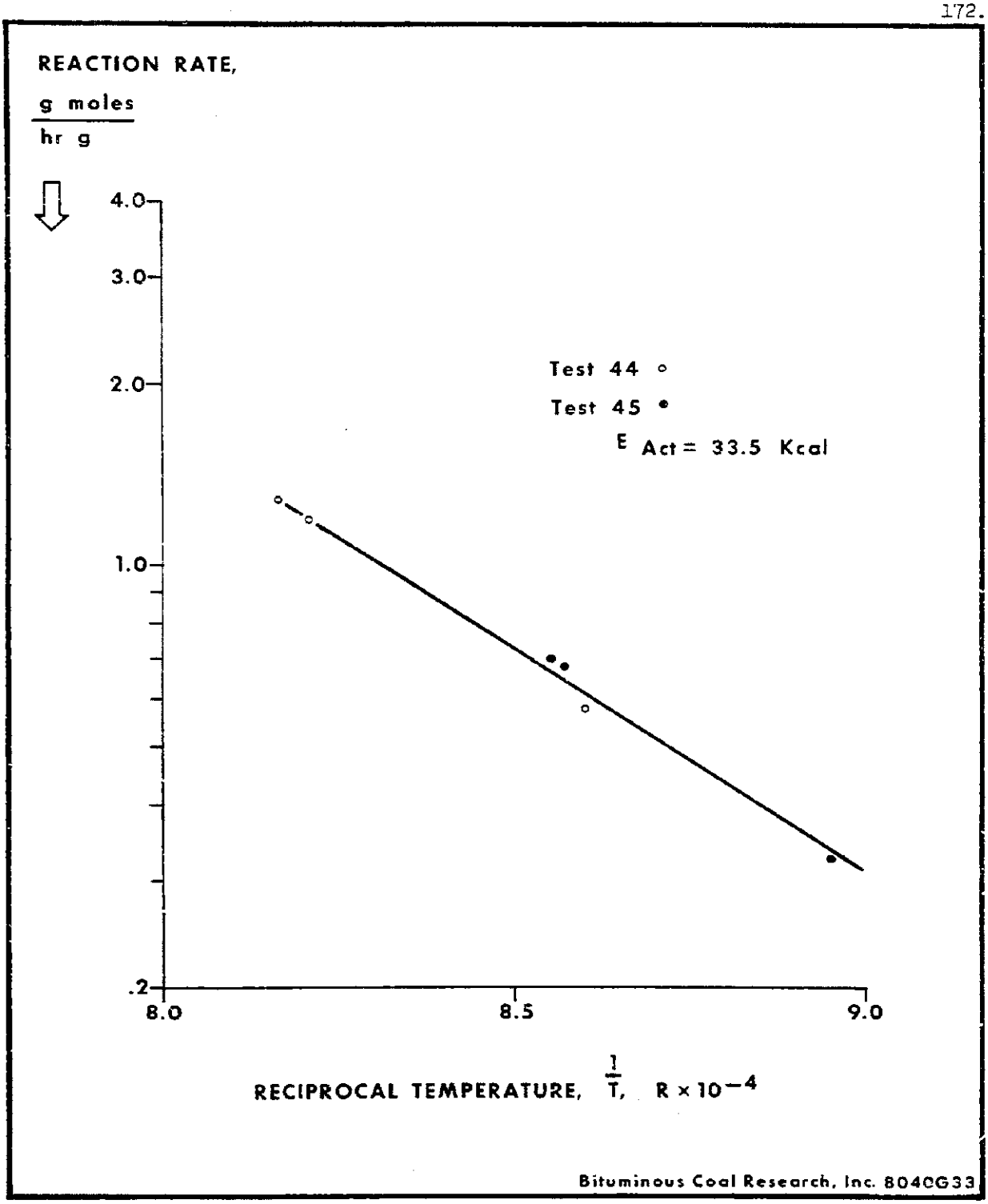

Figure 53. Effect of Temperature on the Methanation Reaction Rate Over a Nickel-Molybdenum Catalyst

catalysts. Results from the two tests, along with the encouraging results for the cobalt-molybdenum catalyst, which is the same type of catalyst, indicate further life testing of nickel-molybdenum is necessary.

The relative activities of the catalysts investigated this month are shown on Figure 54 along with several other selected catalysts. From Figure 54, several conclusions may be drawn. The qualitative effect of molybdenum on catalyst activity may be determined. The three molybdenum-containing catalysts all have about the same concentration of molybdenum. Addition of nickel enhances the catalyst activity while cobalt adversely affects the rate of reaction. Substitution of tungsten for molybdenum also reduces the activity. Chromium is found more active than molybdenum.

Summarizing the results to date:

(1) A wide variety of transition metals enhance the methanation synthesis including nickel, chromium, molybdenum, iron, and mixtures of nickel or cobalt with molybdenum and tungsten.

(2) Nickel and nickel-containing catalysts are among the most active methanation catalysts.

(3) The group VIB metals, chromium, molybdenum, and tungsten alone or compounded, enhance the activity in the same manner as they appear in the periodic table. Chromium has the greatest effect.

(5) Catalyst Life Test 2903: Data were reported last month for life testing of a molybdenum oxide catalyst to 420 hours. During this month, the test was extended well past the 1,000-hour level. The test outline as described on page 118, Progress Report No. 2, is still in Phase 1.

The effect of time on conversion is shown in Figure 55. At approximately 600 hours, the reduction process was completed and activity has, since then, remained stable. Product distribution data for the test period are shown in Figure 56.

Test data reported here show that the molybdenum catalyst is exhibiting good activity after 1100 hours of operation. The product distribution has remained relatively constant over this entire time period. The results on the molybdenum catalyst to date are very encouraging and it is felt that this material will be an adequate methanation catalyst.

b. PEDU Program: Work continued in the area of PEDU planning and design during the past month. As an important part of the PEDU program, the plastic cold model was test operated for debugging purposes and the actual test program outlined.

(1) PEDU Design Status: During the month, Dr. Zenz' comments were reviewed with respect to the PEDU, the panel board design was developed, and PEDU cost data supplied by Koppers were reviewed and transmitted to OCR.

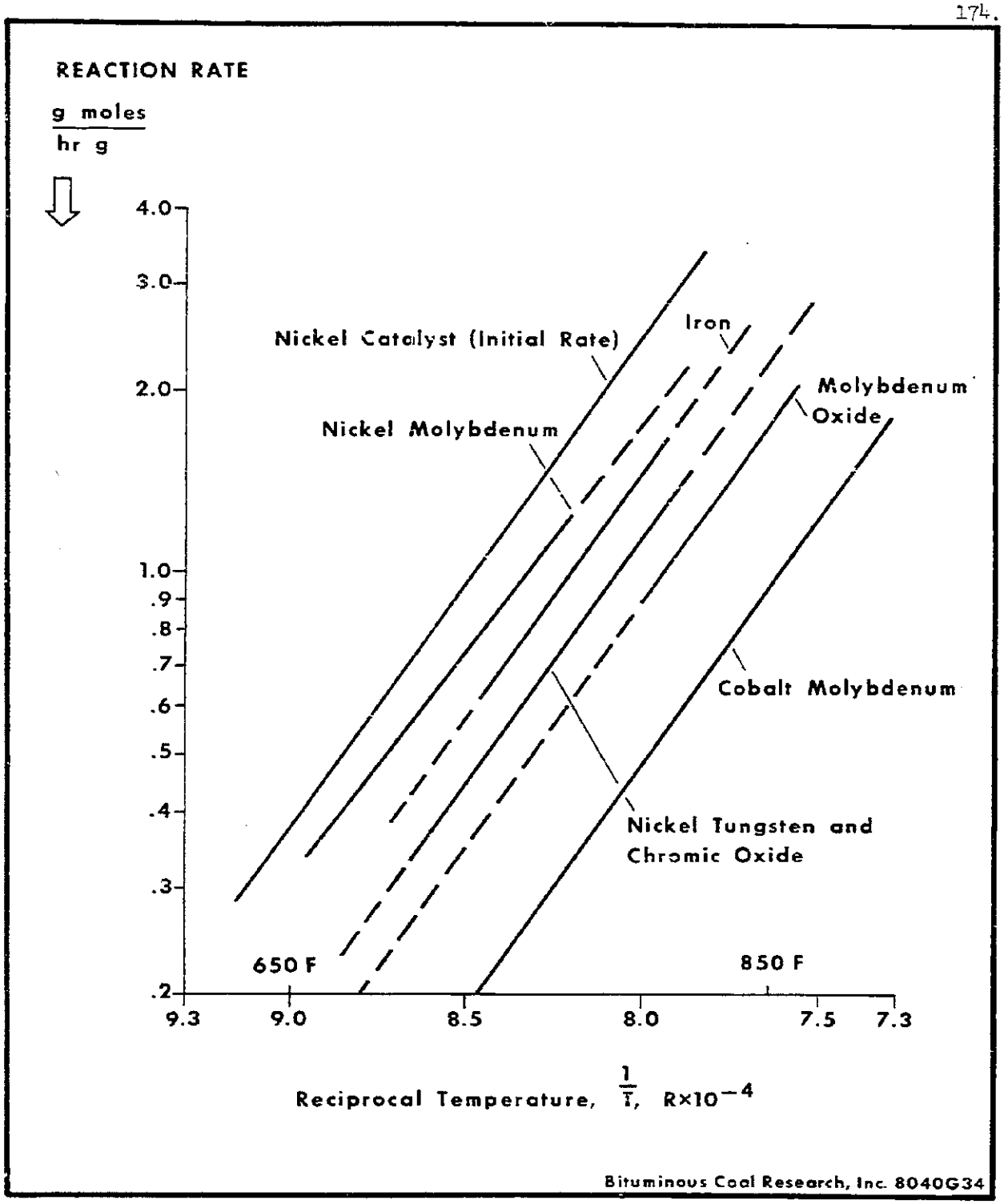

Figure 54. Relative Reaction Rates of Several Methanation Catalysts

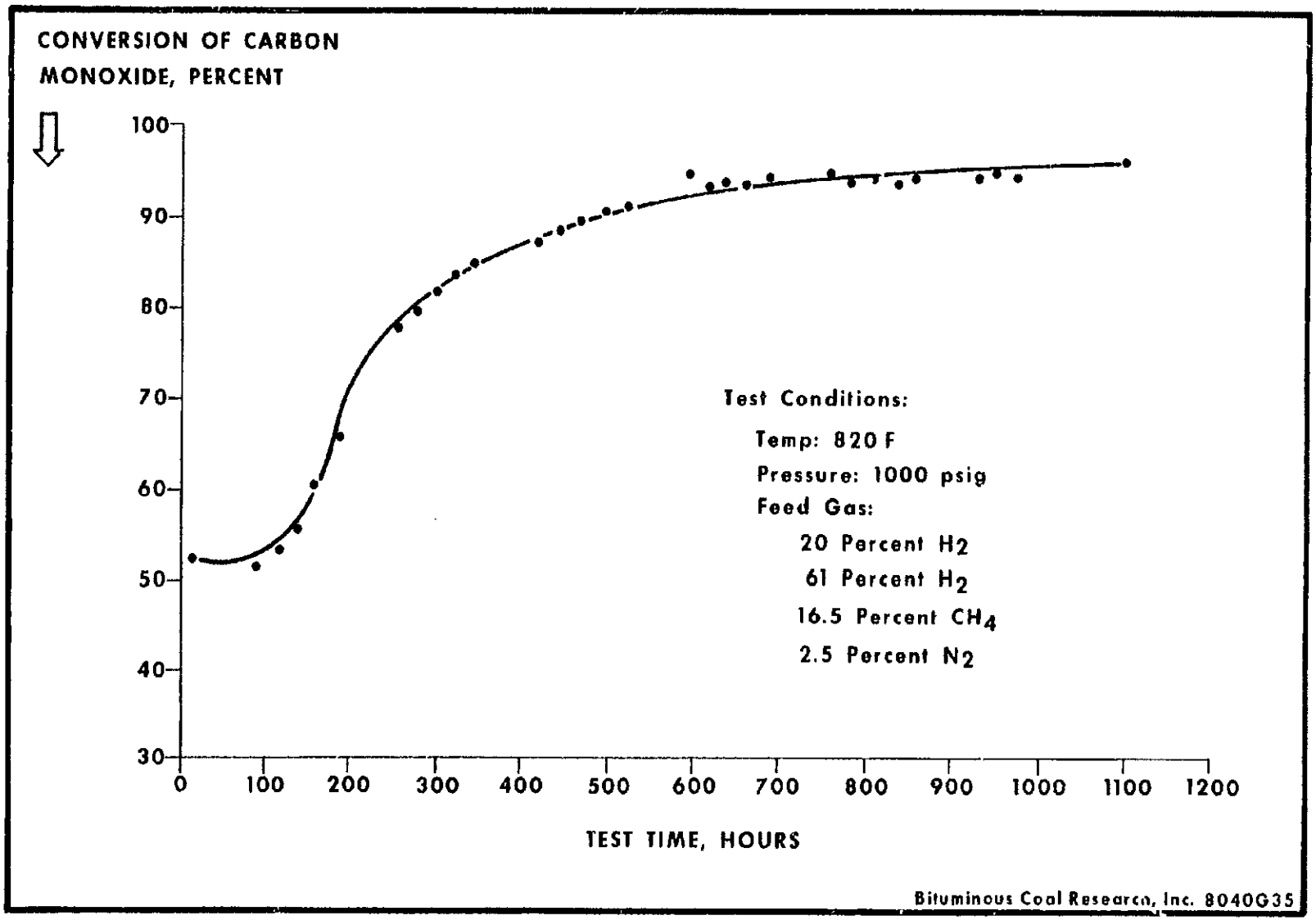

Figure 55. Carbon Monoxide Conversion Data for Life Test 2903

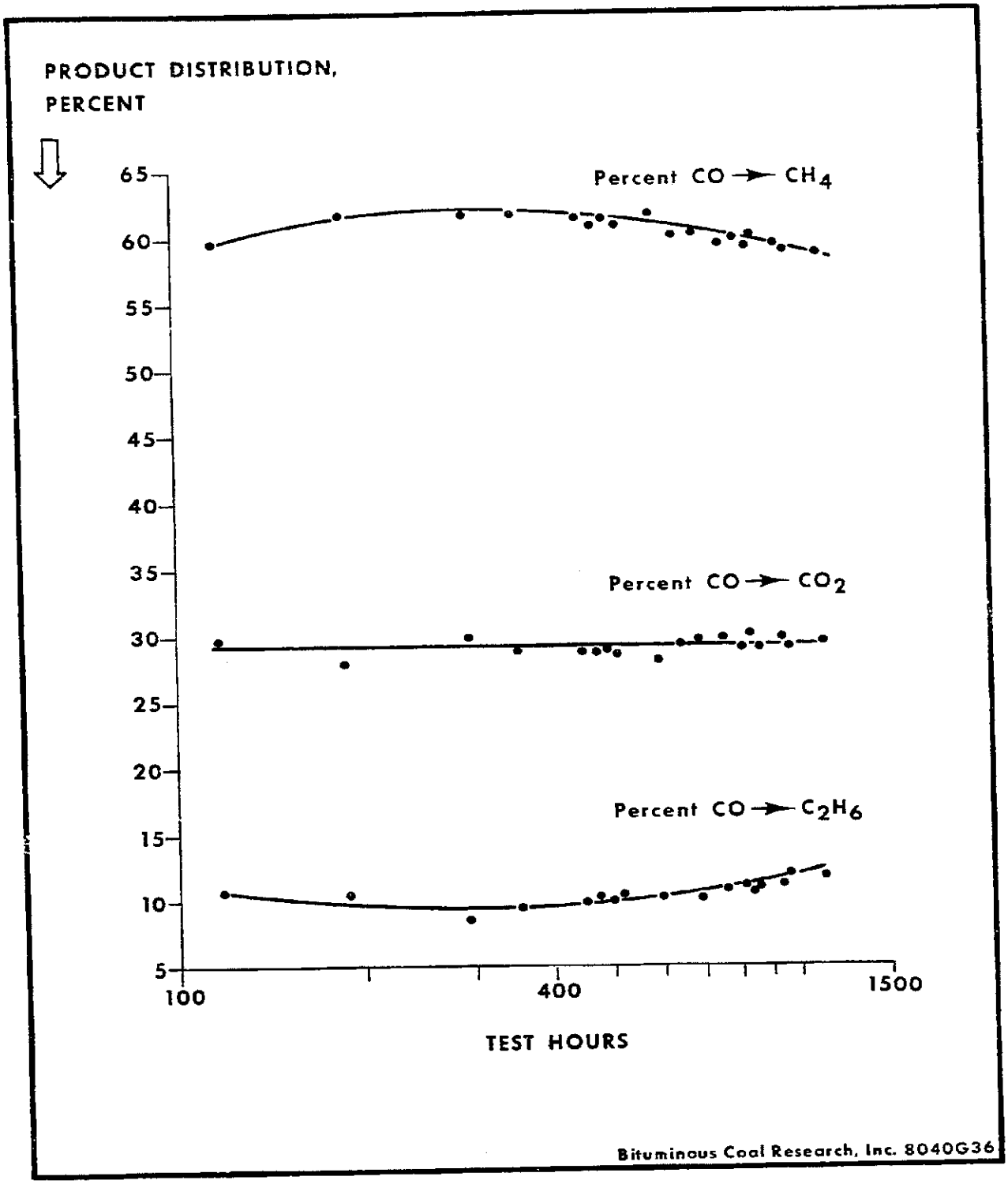

Figure 56. Selectivity Data for Life Test 2903 Catalyst

Dr. Zenz had several comments pertaining to the methanation PEDU. These were submitted as a report to BCR in a letter to R. A. Glenn dated October 22, 1971. Where Dr. Zenz' comments and criticisms were felt correct, design alterations were made.

During the month, a meeting with Koppers personnel was conducted to define the type of PEDU panel board BCR desired. The result of this meeting is described in Koppers' Conference Report 201.

Late in October, Koppers submitted a detailed cost estimate to BCR pertaining to the construction of the methanation PEDU. The summary of this meeting is outlined in Koppers' Conference Report 200. Detailed work sheets were supplied and BCR adjusted the dollar figures necessary to reflect reuse of existing equipment and use of BCR labor. On November 9, 1971, a letter was submitted to OCR with detailed cost figures, requesting approval to build the methanation PEDU. Paul Towson, as a result, visited BCR on November 23 to discuss the PEDU costs but to date no approval to build, based on that meeting, has been obtained.

(2) Cold Model Program: Preliminary tests with compressed air and sand have been carried out in the model. It has been found that bed expansion is in the neighborhood of 30 to 40 percent; therefore, before further tests are conducted, the length of the model will be increased from 6 to 10 feet. The test program has been developed.

In the development of the methanation program, synthesis will be conducted in a 6-inch PEDU fluidized bed. Before such a unit is constructed, the reactor vessel must be cold modeled to determine the operating characteristics of such a system.

In the cold model program, a number of variables will be investigated. The program is to include:

(a) Correlation of minimum fluidizing velocity

(b) Determination of minimum bubbling velocity

(c) Determination of slugging region (as a function of gas and solid properties and bed height)

(d) Effect of internals on slugging

(e) Effect of distributor on slugging

The most important factor to be determined is the slugging region. Slugging in a reactor, while not affecting heat transfer, results in increased conversion due to the plug flow nature of the reactor. Maximum bubble size calculations indicate that slugging may or may not occur depending on the correlation selected.

To determine the slugging region, tests will be made with sand and freon in a 6-inch plastic tube. In this system, similarity with respect to the particle to fluid density ratio will be maintained. Tests will be made both with and without internals. The conical distributor described for the PEDU (Progress Report No. 1) will be used but the plate configuration will be varied to adjust the jet penetration into the bed.

Later in the model program, tests will be conducted in a steel model unit (Figure 8, Progress Report No. 1) using actual catalyst and argon. The purpose of the tests in this case will be to directly simulate the particle Reynolds number found in the PEDU along with exact size distribution and shape of the particles. Data from the two models will be useful for future studies on the pilot plant methanator, since they will indicate the effect of gas viscosity and particle shape on the modeling process and should permit all further studies to be carried out in plastic tubes.

Limited data are available in the literature on slugging in high pressure systems. As the density ratio is decreased, slugging tends to become less favorable. Thus, while slugging has been observed in atmospheric beds of sand fluidized with air, the phenomena might not occur using a more dense gas. In the PEDU, the gas density will range from about 1 lb per cu ft to 1.5 lb per cu ft depending on the pressure and gas composition. The catalyst will have an apparent density of 115 lb per cu ft. To model this system, sand has been prepared to a size distribution similar to the catalyst and two gases, air and freon 12, have been selected for the fluidization medium. Table 47 compares the properties of the two systems, while Figure 57 shows the particle size distributions.

The initial testing will be carried out with air, no internals, and a 5-foot unexpanded bed. While the air tests are being conducted, photographic techniques will be investigated for the freon tests.

The sequence of freon 12 tests for each distributor plate will be the following:

(a) Adjust bed height to desired level

(b) Increase freon flow in stages until bed slugs

(c) Incorporate internals in the bed

(d) Repeat (a), (b) & (c).

If slugging does not occur without internals, then there is no reason to run further tests.

The sand has a larger mean particle size than the catalyst, for several reasons. First, if attrition of sand occurs, the mean particle will become smaller. Second, since slugging is a function of particle size, with slugging probability higher for coarse beds, it is conservative to use a slightly larger particle diameter for the studies.

TABLE 47. COMPARISON OF PHYSICAL PROPERTIES IN THE PEDU AND PLASTIC MODEL SYSTEMS

Property	PEDU	Model
1. Solids	Catalyst	Sand
a. Apparent Density	115 lb/ft^3	170 lb/ft^3
b. Size, mesh		
+ 100	3.79 percent	3.2
+ 120	4.85	11.7
+ 140	9.65	27.0
+ 170	21.57	39.1
+ 200	35.22	51.0
+ 230	44.54	66.0
+ 270	---	79.0
+ 325	76.14	87.0
- 325	100.00	100.0
c. Mean Diameter	62 Microns	74 Microns
2. Gas	Synthesis Gas	Air and Freon 12
a. Density	1-1.5 lb/ft^3	0.07 - 1.8 lb/ft^3
b. Approximate min. Fluidized Velocity	30 ft/hr	50 - 100 ft/hr
3. Reactor		
a. Diameter	6 inch	6 inch
b. Bed Height	0-8 feet	0-8 feet
c. Internals	(12) 1-inch Finned (1/4-inch)	(5) 1-inch Plain
d. Distributor	70° Cone - 2 in. drilled plate	70° Cone - 2 inch drilled plate
e. Density Ratio Ps/Pg	80 - 115	94 - 2500
f. Re @ min. Fluidization	0.20	0.03 - 1.80

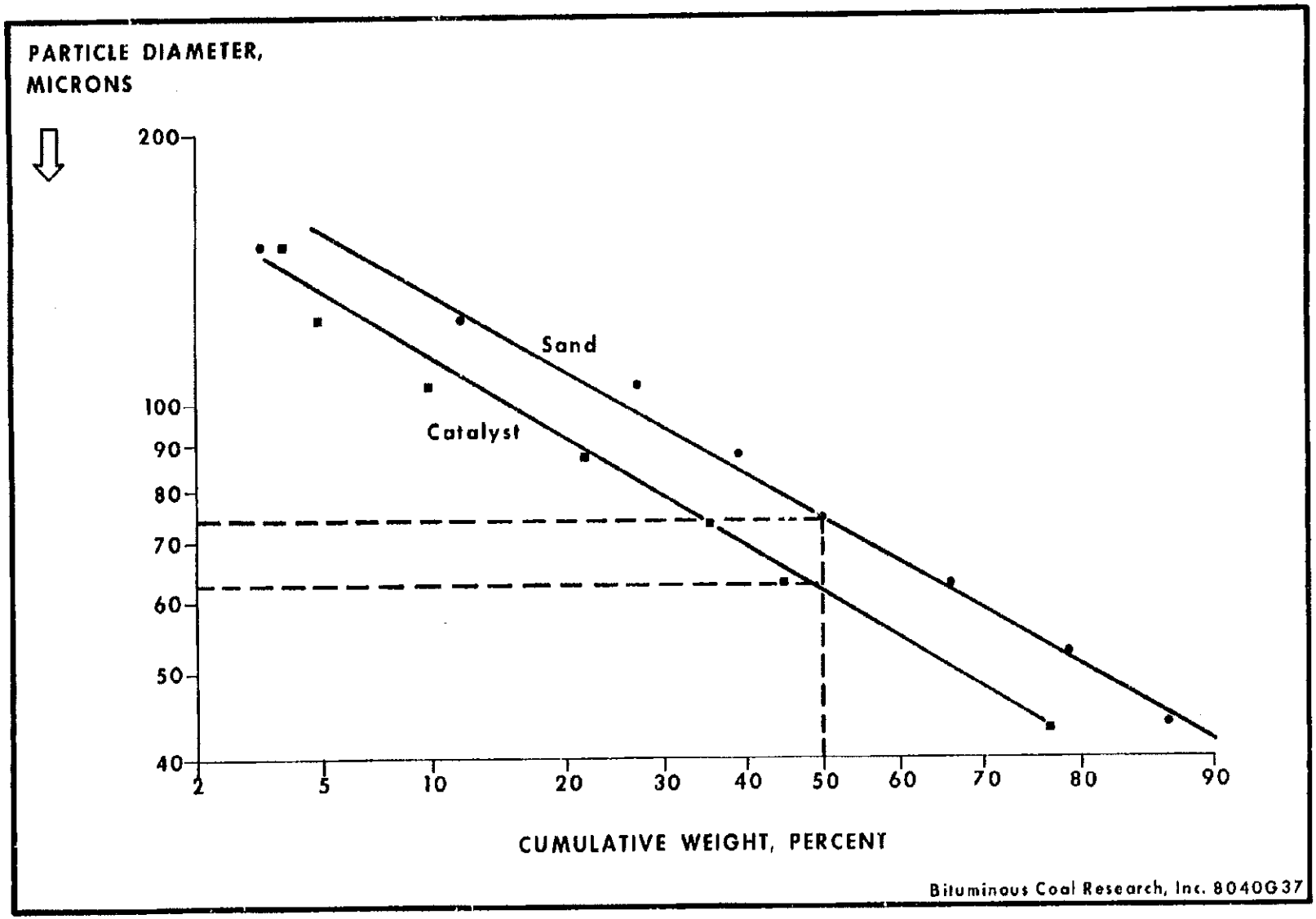

Figure 57. Comparison of Catalyst and Sand Size Distributions for Methanation Cold Model Studies

c. Future Work: Work will continue according to the gas processing schedule during the coming month.

At the bench-scale level, several catalysts will be screened in the BSM test unit. These include 2 percent nickel on refractory support, palladium, and copper chromite. Life testing of the molybdenum catalyst will continue. Phase 2 of the program will begin during the month; the space velocity will be reduced by one-half to determine the effect of space velocity on product distribution. Late in the month, the feed gas composition will be changed to reflect the shifted but unscrubbed synthesis gas. This gas will tend to suppress shift reaction and indicate product selectivity under conditions where carbon dioxide will not be formed.

Work on the PEDU will continue. Approval of funds to proceed with the detail design and construction are necessary if the gas processing time schedule is to be met. Further review and refinement of the PEDU design will be carried out. Final preparation for the model program should be completed and data collection on this portion of the program should begin.

5. Analytical Services (J. E. Noll): During the past month, 122 samples were analyzed. The number and type of analyses requested were as follows:

Type of Analysis Requested	Number of Samples Analyzed
Gas Chromatography	
Methanation Unit	38
Model Studies	84
TOTAL	122

6. Gas Chromatographic Procedures (J. E. Noll): No work was done on this project during the past month.

Future Work: Performing sample analyses is the only work planned.