GAS GENERATOR RESEARCH AND DEVELOPMENT

Progress Report No. 2
October 1971
(BCR Report L 434)

Prepared by

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Submitted to the

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

November 15, 1971

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November 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. 2
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. The final two tests of the 100 lb/hr Stage 2 PEDU have been evaluated. Plans are being made to dismantle this unit in preparation of the area for the new PEDUs. A final summary report of the Stage 2 PEDU work is being prepared. Erection of equipment for cold flow model studies is underway in order to obtain data for feed nozzle orientation in an integrated gasifier. Editing of the summary report on the coal composition and beneficiation studies continues and should be completed at an early date.

In the bench-scale gas processing studies, to find a suitable catalyst for use in the BI-GAS process, evaluation of methanation catalysts has shown that non-nickel catalysts should be studied. Work in this area is being planned. In bench-scale studies on char gasification, reactivity studies of a new char received from Consolidation Coal Company have begun.

Evaluation of the fluidized-bed methanation and gasification PEDU bid packages received from Koppers is in progress. A private consultant, Dr. F. A. Zenz, was engaged to aid in this evaluation. Planning for procurement and erection of equipment for the two PEDUs continues.

In the planning for Phase III, the preparation of the engineering bid package by Koppers for the Homer City pilot plant continues to remain on schedule.

Yours very truly,

John W. Igoe

JWI:mmw

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BITUMINOUS COAL RESEARCH, INC.
SPONSORED RESEARCH PROGRAM

GAS GENERATOR RESEARCH AND DEVELOPMENT

Progress Report No. 2

(BCR Report L-434)

I. INTRODUCTION

This report summarizes progress achieved during the ninety-fourth 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 second 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, Progress Report No. 1, page 2.

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 OCTOBER 25, 1971

A. Laboratory-scale Process Studies

1. Coal Composition and Beneficiation Studies (R. G. Moses and R. D. Saltsman): The summary report on this phase of the work now being written, summarizing work performed since September 20, 1970, is expected to be completed next month.

2. Laboratory Pyrolysis of Coal (J. E. Noll): No work was done on this project during the past month, pending evaluation of previous results. A report summarizing work performed on this phase of the project since September, 1970, will be completed next month.

3. Fluidized-bed Gasification (E. K. Diehl and J. T. Stewart): Work on the 100 lb/hr fluidized-bed PEDU design is continuing, with emphasis on establishing final cost estimates and freezing design in anticipation of beginning detail design work.

Char reactivity studies, using other chars, are continuing.

a. Fluidized-bed PEDU: Activity during the month consisted primarily of a detailed review of the specification manual submitted by Koppers on October 1, 1971.

On October 19 and 20, the PEDU design and proposed experimental program were discussed with Dr. F. A. Zenz, consultant, who was retained by BCR to review the fluidization aspects of the methanation and gasification programs. Dr. Zenz had only minor comments concerning the fluidized-bed gasifier. He supported our selection of PEDU size, and indicated that we have provided for sufficient flexibility in operation to develop optimum conditions for gasifying char. He suggested a minor change in the grid hole diameters to assure the desired pressure drop through the grid at the lower superficial gas velocities that we may attain under some experimental operation. Dr. Zenz agreed that the overall design is sound for the type of experiments we plan.

Further work during the month involved a detailed cost analysis, based on updated information from Koppers.

b. Laboratory Investigations: Reactivity studies were initiated on char from Consolidation Coal's Cresap plant. As yet, insufficient data have been developed. It is anticipated that data will be available for next month's report.

c. Future Work: Decisions regarding final design of the PEDU should be completed within the next report period, as well as final cost estimates.

Char reactivity studies will continue. Plans will be made to obtain a sample of char from IGT.

4. Gas Processing (M. S. Graboski): Work continued in the area of gas processing during the month of October in accordance with the time schedule shown in Figure 4, page 7 of Progress Report No. 1 under the new prime contract. Work reported 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, four catalysts were screened in the BSM test unit. In addition, the life test program centered about the test outline given in Progress Report No. 1 for Lot 2684 nickel catalyst and a new program was initiated on Lot 2903 catalyst.

(1) Data and Results for BSM Test 37: The purpose of BSM Test 37 was to screen BCR Lot 2731 catalyst for activity and stability at high carbon monoxide partial pressures. Lot 2731 is a prototype nickel catalyst developed by the Harshaw Chemical Company.

In Test 37, 2.5 grams of Lot 2731 catalyst were charged and reduced in the BSM unit. The catalyst was then tested at 645 F and 1,000 psig for activity.

Initial conversion was high but the catalyst showed a rapid decline in activity. Composition data for the test are given in Table 23. Figure 34 shows the rate of water production during BSM Test 37.

(2) Data and Results for BSM Test 38: The purpose of BSM Test 38 was to screen BCR Lot 2691 catalyst for activity and stability at high carbon monoxide partial pressures. Lot 2691 is a catalyst supplied by Harshaw Chemical Company. It contains 68 percent nickel on a proprietary support.

In Test 38, 1.0 gram of Lot 2691 catalyst was charged and reduced in the BSM unit. The catalyst was then tested at 760 F and 1,000 psig to study the activity.

Initial activity was high and the catalyst showed some deactivation. Reaction rate data for Test 38 are given in Table 24. Figure 35 shows the rate of water production during the test.

(3) Data and Results for BSM Test 39: The purpose of BSM Test 39 was to screen BCR Lot 2903 catalyst for activity and stability at high carbon monoxide partial pressures. Lot 2903 is a catalyst supplied by Harshaw Chemical Company. It is a fluidized-bed hydroforming and dehydrogenation catalyst containing 11 percent molybdenum trioxide on high-activity alumina. The size distribution for Lot 2903 microspheres, as supplied, is given in Figure 36. Catalyst bulk density is 68 lb per cu ft, and the apparent particle density is 110 lb per cu ft.

Three grams of Lot 2903 were charged to the reactor and pretreated under hydrogen. The temperature was brought to 650 F and synthesis gas was introduced into the system. Reaction was initiated at 700 F. Temperature was raised to 800 F and a reaction rate was measured. The temperature was further increased to 850 F and another measurement was taken. Water production data are given in Figure 37 and reaction rates are given in Table 25.

(4) Data and Results for BSM Test 40: The purpose of BSM Test 40 was to screen BCR Lot 2905 catalyst for activity and stability at high carbon partial pressures. Lot 2905 is a catalyst supplied by Harshaw Chemical Company. It is composed of 6 percent nickel and 19 percent tungsten mounted on silica-alumina. This catalyst is generally used for hydrogenation where a cracking function is desired. Three grams of Lot 2905 extrudites were crushed to minus 50 plus 170 mesh size and pretreated under hydrogen in the BSM unit.

TABLE 23. GAS COMPOSITION DATA FOR BSM TEST 37

Component	Feed	Period 1 (First Hour)	Period 2 (Second Hour)
Hydrogen	62.93	54.29	59.28
Nitrogen	2.21	2.91	2.45
Methane	15.51	26.82	20.19
Ethane	0.02	0.38	0.17
Carbon Monoxide	19.33	15.41	17.78
Carbon Dioxide	--	0.19	0.17
	100.00	100.00	100.00

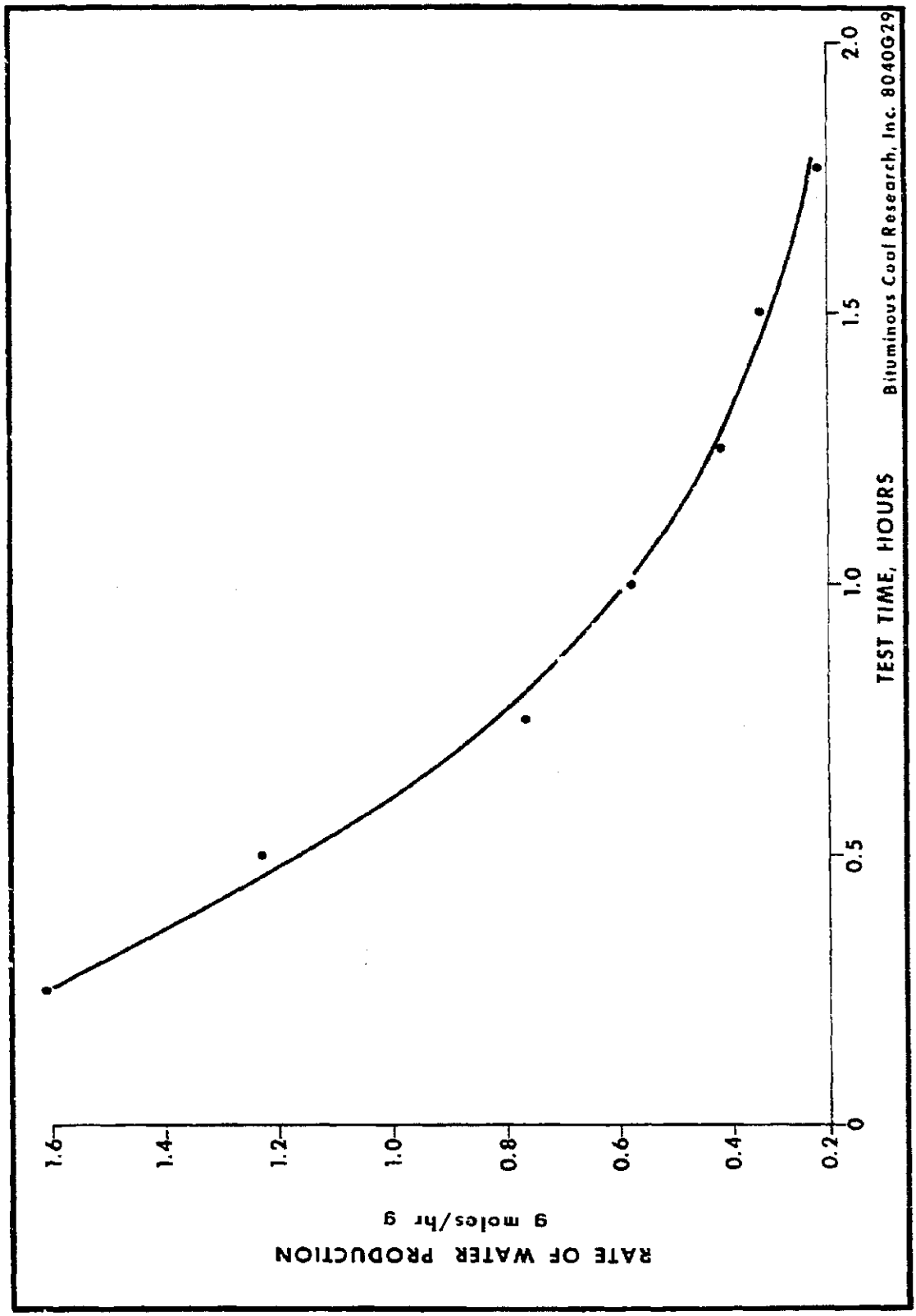

Figure 34. Rate of Water Production for Lot 2731 Catalyst at 650F and 1000 psig (Data from BSM Test 37)

TABLE 24. TEST CONDITIONS AND RESULTS FOR BSM TEST 38

Test Conditions

Catalyst BCR Lot No. 2691	Feed, percent			Period
Mass, g 1.0	Hydrogen	62.9	Flow Rates	1
Size, mesh -50 +170	Nitrogen	2.25	Feed, Orifice Meter, scfh	21.02
System Temperature, F	Carbon Monoxide	19.32	Product	
Period 1 758 F	Carbon Dioxide	0.00	a. Dry meter, scfh	16.07
	Methane	15.51	b. Water, g/hr	31.35
System Pressure, psia	Ethane	0.02		
Period 1 1015				

Material Balance	Results* Period 1
Total Mass In, g/hr	239.7
Total Mass Out, g/hr	242.1
Difference, percent	1.0
Total Nitrogen In, g moles/hr	0.55
Total Nitrogen Out, g moles/hr	0.55
Difference, percent	0.0
Total Carbon In, g moles/hr	8.55
Total Carbon Out, g moles/hr	8.55
Difference, percent	0.0

Conversions and Rates	Product, Mole Percent Period 1	Conversions, g moles/hr Period 1	Rates, g moles/hr/g Catalyst Period 1
Carbon Monoxide	14.61	1.84	1.84
Hydrogen	54.59	4.60	4.60
Methane	26.97	1.55	1.55
Water	-	1.74	1.74
Nitrogen	2.79	-	-
Carbon Dioxide	0.52	0.10	0.10
Ethane	0.52	0.18	0.18

* Normalized Carbon Balance

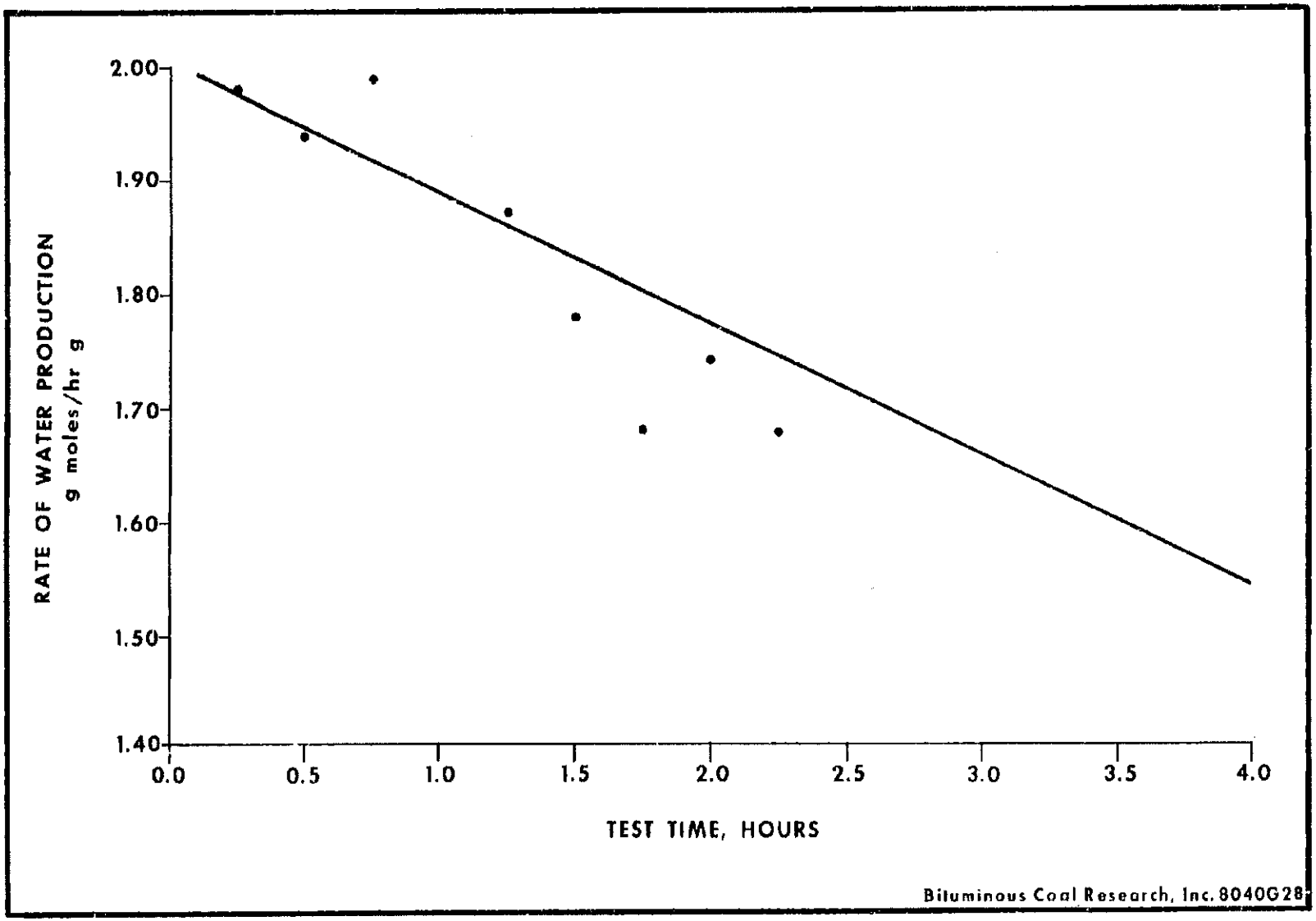

Figure 35. Rate of Water Production for Lot 2691 Catalyst at 760 F and 1000 psig (Data from BSM Test 38)

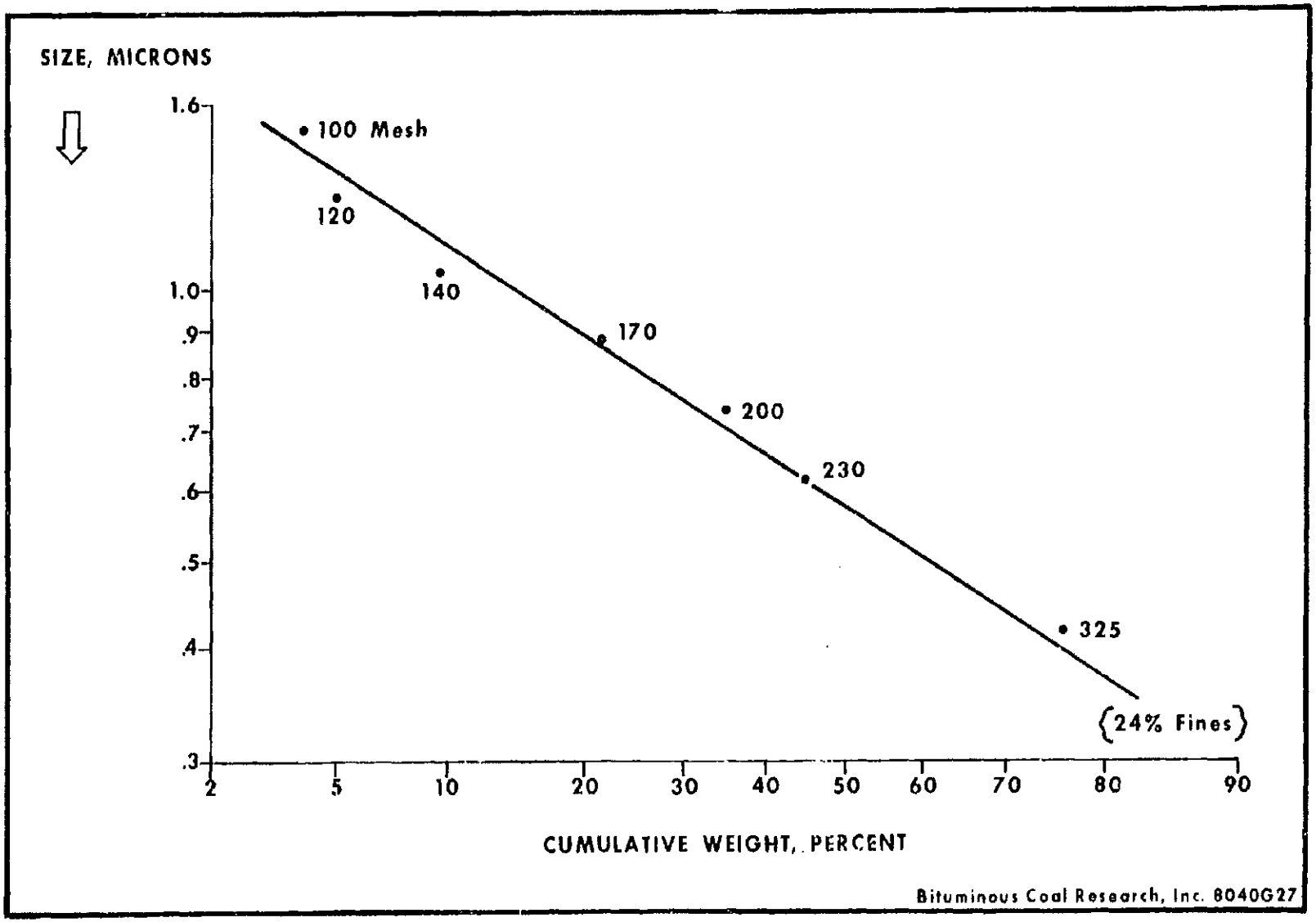

Figure 36. Size Distribution for 2903 Microsphere Catalyst

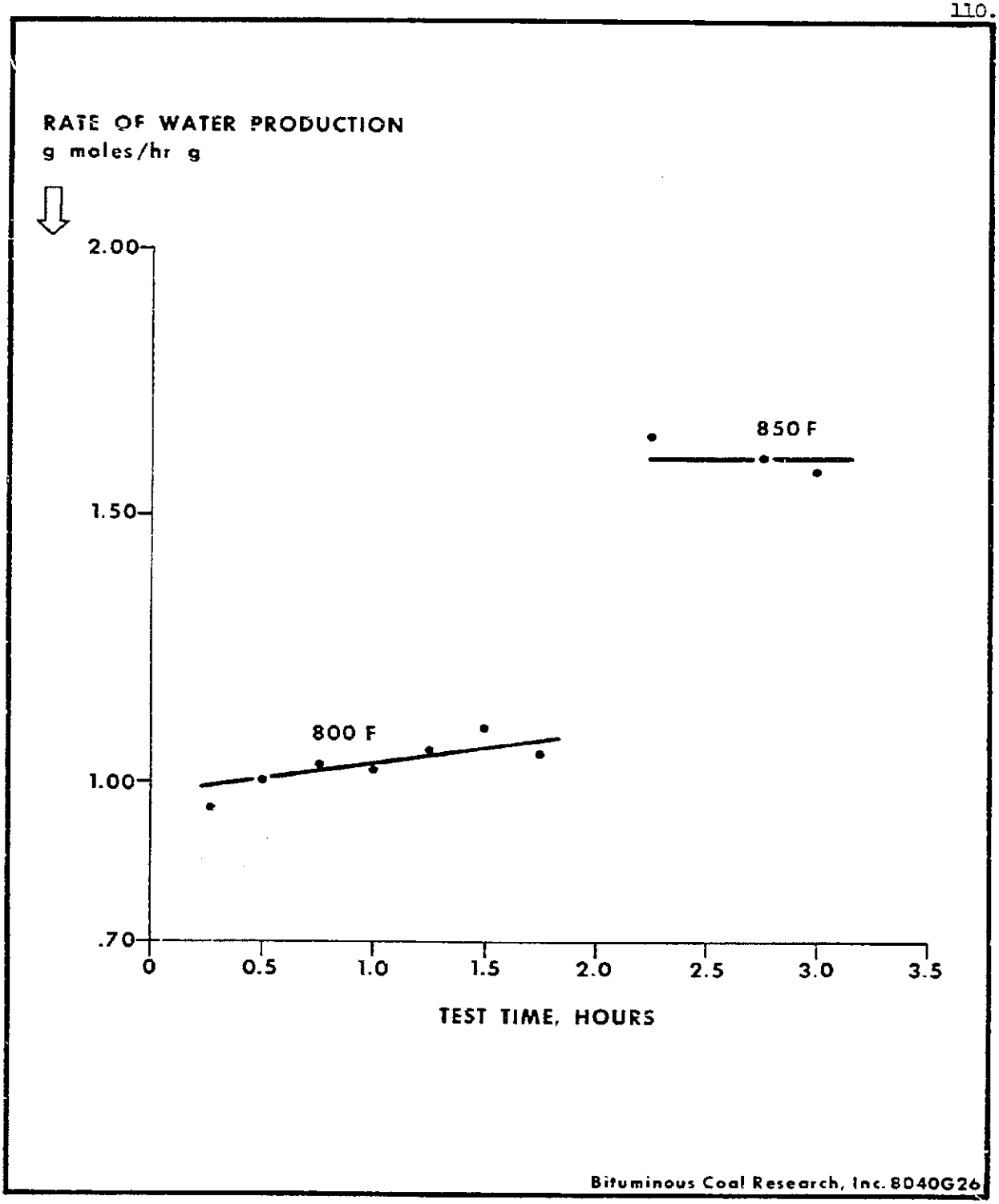

Figure 37. Rate of Water Production for Lot 2903 Catalyst at 800 and 850F and 1000 psig (Data from BSM Test 39)

TABLE 25. TEST CONDITIONS AND RESULTS FOR BSM TEST 39

Catalyst ECR Lot No. 2903
Mass, g 3.0
Size, mesh -50 +170
System Temperature, F
Period 1 805
Period 2 810
Period 3 850
System Pressure, psia
Period 1 1015
Period 2 1015
Period 3 1015

Feed, percent	
Hydrogen	62.94
Nitrogen	2.31
Carbon Monoxide	19.55
Carbon Dioxide	-
Methane	15.20
Ethane	-

Flow Rates	Period 1	Period 2	Period 3
Feed, Orifice Meter, scfh	26.0	26.0	30.1
Product			
a. Dry meter, scfh	16.6	16.6	16.1
b. Water, g/hr	53.5	57.1	86.7

Material Balance	Results* Period 1	Period 2	Period 3
Total Mass In, g/hr	288.5	279.8	334.3
Total Mass Out, g/hr	290.5	289.8	340.5
Difference, percent	0.7	3.6	1.8
Total Nitrogen In, g moles/hr	0.66	0.69	0.78
Total Nitrogen Out, g moles/hr	0.68	0.61	0.82
Difference, percent	3.0	12.3	5.0
Total Carbon In, g moles/hr	10.22	10.31	11.98
Total Carbon Out, g moles/hr	10.22	10.31	11.98
Difference, percent	0.0	0.0	0.0

Conversions and Rates	Product, Mole Percent Period 1	2	3	Conversions, g moles/hr Period 1	2	3	Rates, g moles/hr/g Catalyst Period 1	2	3
Carbon Monoxide	12.15	11.92	8.51	3.19	3.39	4.79	1.06	1.13	1.60
Hydrogen	49.31	47.27	39.56	8.14	9.12	13.08	2.71	3.04	4.36
Methane	33.70	36.02	45.78	2.65	2.78	4.05	0.88	0.93	1.35
Water	-	-	-	2.97	3.33	4.82	0.99	1.11	1.60
Nitrogen	3.11	3.02	3.99	-	-	-	-	-	-
Carbon Dioxide	0.74	0.73	0.76	0.16	0.15	0.16	0.05	0.05	0.05
Ethane	0.90	1.04	1.40	0.38	0.42	0.58	0.13	0.14	0.19

* Normalized Carbon Balance

Reaction began at about 635 F and rates were measured at 700 F and 800 F at 1,000 psig. Measured rates are given in Table 26 and water production data are shown in Figure 38.

(5) Discussion of BSM Tests: During the month, two nickel catalysts, one nickel alloy catalyst, and a molybdenum catalyst were tested in the BSM unit. In Tests 37 and 38, the nickel catalysts were studied. Lot 2731, in Test 37, deactivated as shown in Figure 34. In Test 38, Lot 2691 did not show such extreme deactivation, but loss of activity was apparent, as shown in Figure 35.

Data for the molybdenum catalyst, studied in Test 39, are presented in Figure 37 and Table 25. Reaction rates appear constant over the short intervals shown. For the two temperatures studied, an activation energy of about 35 kcal is apparent.

Rate data for the nickel-tungsten catalyst, studied in Test 40, are presented in Figure 38 and Table 26. This catalyst also shows about a 35 kcal energy of activation.

To obtain some idea of kinetic rates over these latter two catalysts, Figure 39 was developed. Data from Tests 39 and 40 are compared with the results for nickel catalyst and for cobalt-molybdenum catalyst, respectively. Lines are sketched in parallel since all the activation energies are presumed to be the same. Both molybdenum and nickel-tungsten catalysts exhibit rates intermediate between those for nickel and cobalt-molybdenum.

Product distributions for these catalysts are given in Table 27. For the molybdenum catalyst, increasing temperature increases the hydrocarbon yield and reduces carbon dioxide formation slightly. This occurs since equilibrium favors carbon dioxide formations at low temperatures. The same is true for the nickel-tungsten catalyst. Both accelerate the shift to a large extent; and, in a wet environment, each would form appreciable carbon dioxide.

b. Catalyst Life Tests: The purpose of the catalyst life test program is to evaluate methanation catalysts based on their ability to maintain activity under BI-GAS processing conditions.

(1) Catalyst Life Test 2684: In Progress Report No. 1, September, 1971, a test sequence was outlined for catalyst 2684. This material was seemingly the best nickel catalyst screened in the BSM unit in short duration tests. The purpose of the sequence was to systematically reduce the carbon monoxide partial pressure until an acceptable level was found; pressures below 50 psi carbon monoxide were ruled out. The results for the test series are given in Table 28.

Results for all tests were of the same character. The catalyst charge and space velocity were varied, but the reaction rate was so rapid that at no time could a partial conversion be obtained. At the point where

TABLE 26. TEST CONDITIONS AND RESULTS FOR BSM TEST 40

Test Conditions

Catalyst BCR Lot No. 2905
Mass, g 3.0
Size, mesh -50 +170
System Temperature, F
Period 1 702
Period 2 800
System Pressure, psia
Period 1 1025
Period 2 1025

Feed, percent	
Hydrogen	59.67
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	20.38	25.84
Product		
a. Dry meter, scfh	17.30	16.72
b. Water, g/hr	12.7	60.3

Results*

Material Balance	Period 1	Period 2
Total Mass In, g/hr	249.1	315.6
Total Mass Out, g/hr	245.3	315.3
Difference, percent	1.6	0.1
Total Nitrogen In, g moles/hr	0.52	0.66
Total Nitrogen Out, g moles/hr	0.54	0.68
Difference, percent	3.8	3.0
Total Carbon In, g moles/hr	9.11	11.46
Total Carbon Out, g moles/hr	9.11	11.46
Difference, percent	0.0	0.0

Conversions and Rates	Product, Mole Percent		Conversions, g moles/hr		Rates, g moles/hr/g Catalyst	
	Period		Period		Period	
	1	2	1	2	1	2
Carbon Monoxide	18.37	12.58	1.13	3.71	0.38	1.24
Hydrogen	54.78	42.39	2.66	9.16	0.89	3.05
Methane	23.57	39.75	0.90	3.06	0.30	1.02
Water	-	-	0.71	3.35	0.24	1.12
Nitrogen	2.55	3.27	-	-	-	-
Carbon Dioxide	0.39	0.85	0.08	0.18	0.03	0.06
Ethane	0.34	1.16	0.14	0.48	0.05	0.16

* Normalized Carbon Balance

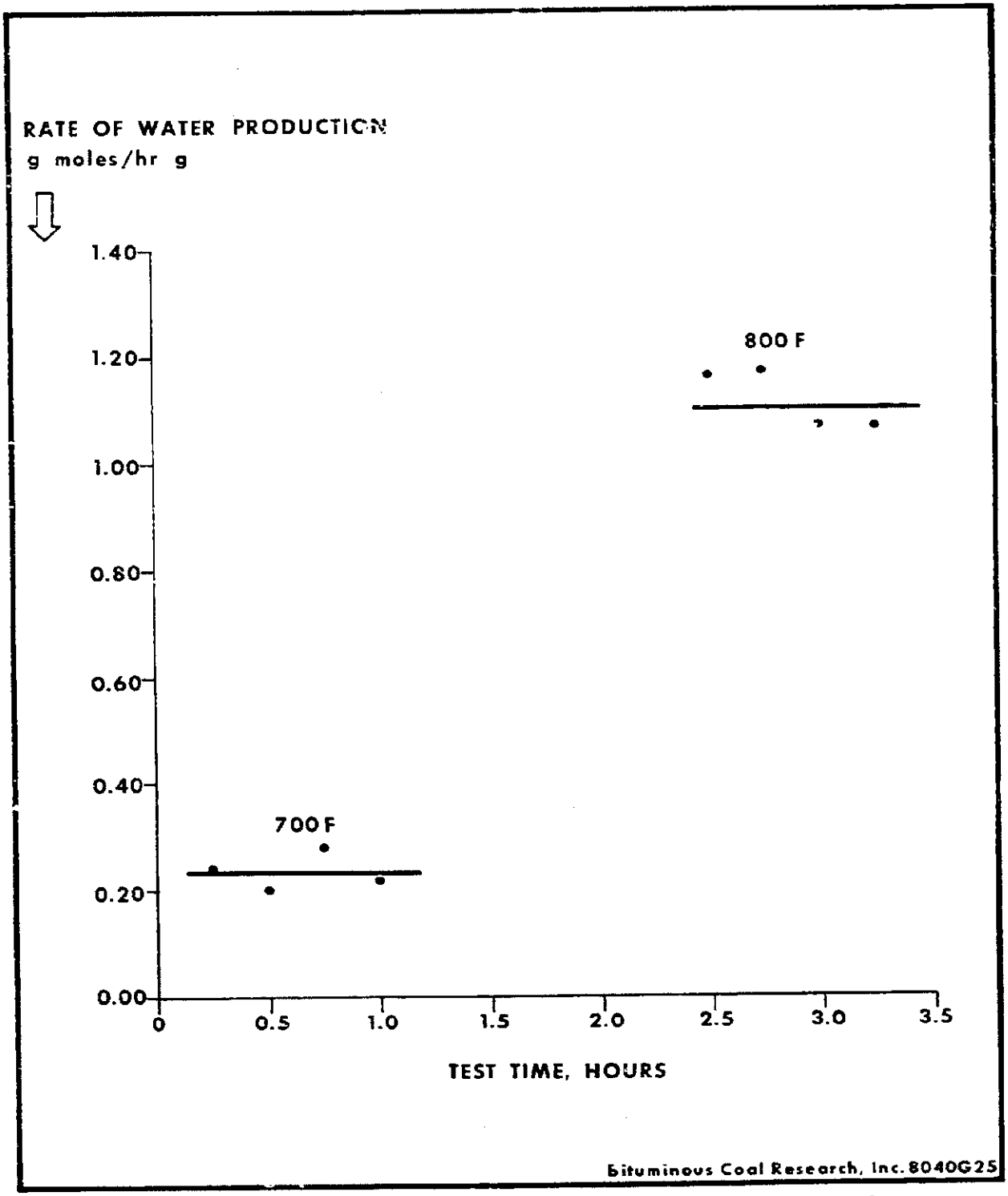

Figure 38. Rate of Water Production for Lot 2905 Catalyst at 700 and 800F and 1000 psig (Data from BSM Test 40)

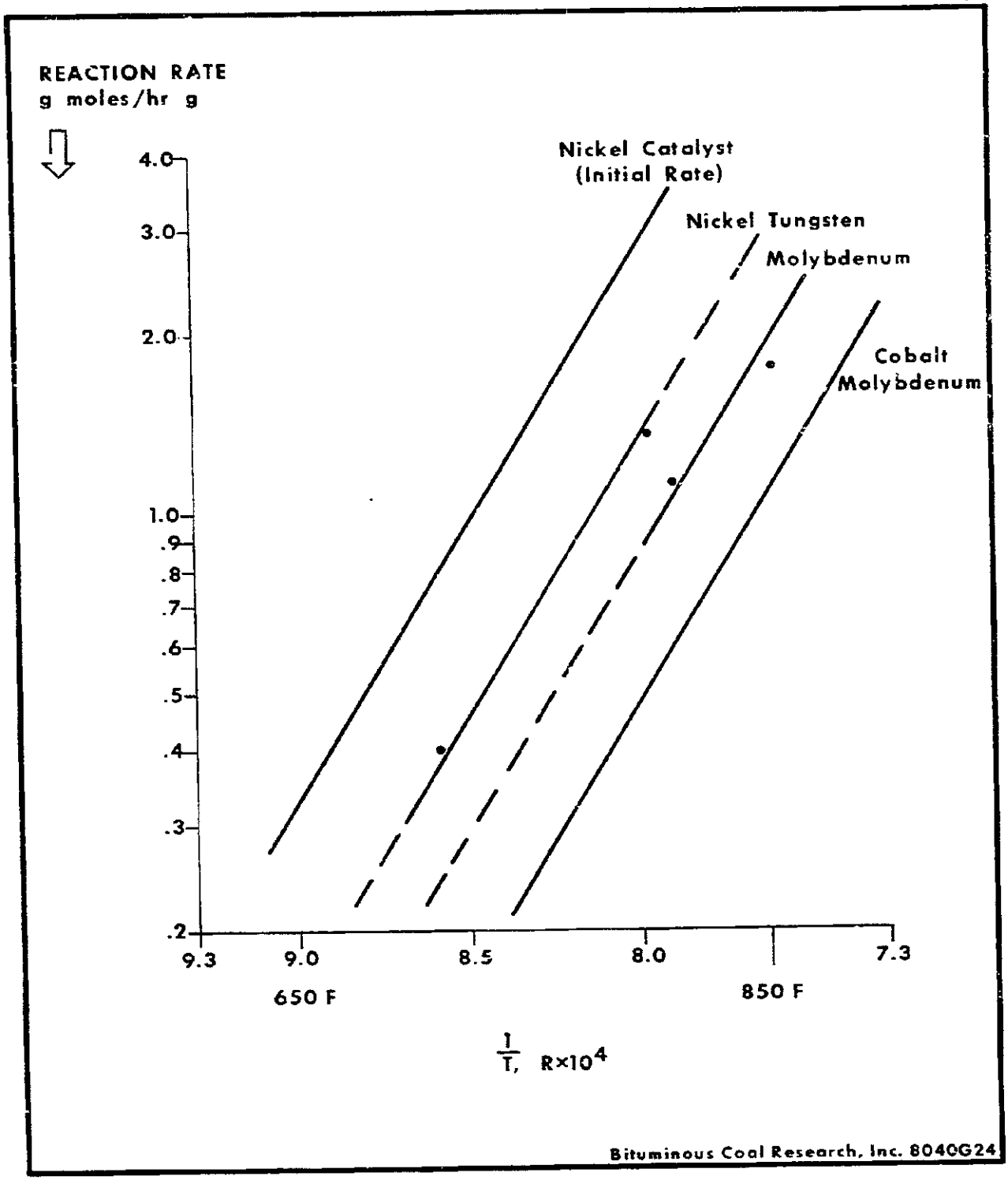

Figure 39. Relative Reaction Rates of Several Methanation Catalysts

TABLE 27. PRODUCT DISTRIBUTION DATA
FOR BSM TESTS 39 AND 40

Test 39	Period 1	Period 2	Period 3
Temperature, F	805	810	850
Pressure, psia	1015	1015	1015
Percent CO → Products	55.5	58.5	73.5
Percent CO → Methane	83.1	82.2	84.5
Percent CO → Ethane	11.9	12.4	12.1
Percent CO → Carbon Dioxide	5.0	4.4	3.4

Test 40	Period 1	Period 2
Temperature, F	702	800
Pressure, psia	1025	1025
Percent CO → Products	22.5	58.7
Percent CO → Methane	79.5	82.3
Percent CO → Ethane	12.4	12.9
Percent CO → Carbon Dioxide	7.1	4.8

TABLE 28. RESULTS FOR LIFE TEST SEQUENCE ON BCR LOT NO. 2684 NICKEL CATALYST AT 700 F

Test No.	CO in Gas, Percent	Partial Pressure CO, psi	Result
2684-1,2	20.0	200	Deactivated Rapidly
2684-3	10.0	100	Deactivated Rapidly
2684-4	10.0	75	Deactivated Rapidly
2685-4	10.0	50	Not Run

the conversion declined below 100 percent, it took only a day for complete catalyst failure. This indicates that the deactivation front moves rapidly down the bed in a piston-like manner, eventually destroying the entire catalyst mass.

(2) Catalyst Life Test 2903: Catalyst 2903 showed good activity in BSM Test 39. An important factor was the fluidizable form of the catalyst. Life Test 2903 was started at 800 F and 1,000 psig to determine the long-term activity of the catalyst.

Three grams of catalyst were charged to the reactor and pre-conditioned. The test schedule selected was as follows:

Part 1: The first portion of Test 2903 was to determine the stable activity of the catalyst. No attempt was made to obtain either complete conversion or to optimize selectivity.

Part 2: Once stable activity was obtained, the gas feed rate was to be reduced to raise the conversion. The purpose was to determine what type of overall product distribution could be obtained.

Part 3: At the conclusion of Part 2, a new synthesis blend containing 15 percent carbon dioxide was to be passed over the catalyst. The purpose was to suppress the shift reaction, should this occur to an appreciable extent.

To date, Part 1 is still being conducted. The catalyst has been in the test unit for almost 430 hours. The results for the test are shown in Figures 40 and 41, which depict overall conversion and product selectivity, respectively. During the test, all conditions have been kept constant. Conversion has, however, continued to increase. It is hypothesized that the increase is due to reduction of the catalyst to metal molybdenum by the following reactions:

$$MoO_3 \xrightarrow{H_2} MoO_2 + H_2O\uparrow \xrightarrow{H_2} Mo + H_2O\uparrow \qquad (1)$$

$$MoO_3 \xrightarrow{CO} MoO_2 + CO_2\uparrow \xrightarrow{CO} Mo + CO_2\uparrow \qquad (2)$$

Data in the literature on the commercial reduction process indicate that the trioxide is reduced to the dioxide at 600 to 700 C. The reduction to the metal occurs at 950 to 1100 C. This is generally carried out at atmospheric pressure under diffusion-controlled conditions. A sample of catalyst was analyzed using BCR's TGA unit under pure hydrogen at atmospheric pressure. No reaction occurred at 800 F. The unit was programmed to increase in temperature. At 1300 F (700 C), noticeable weight loss began.

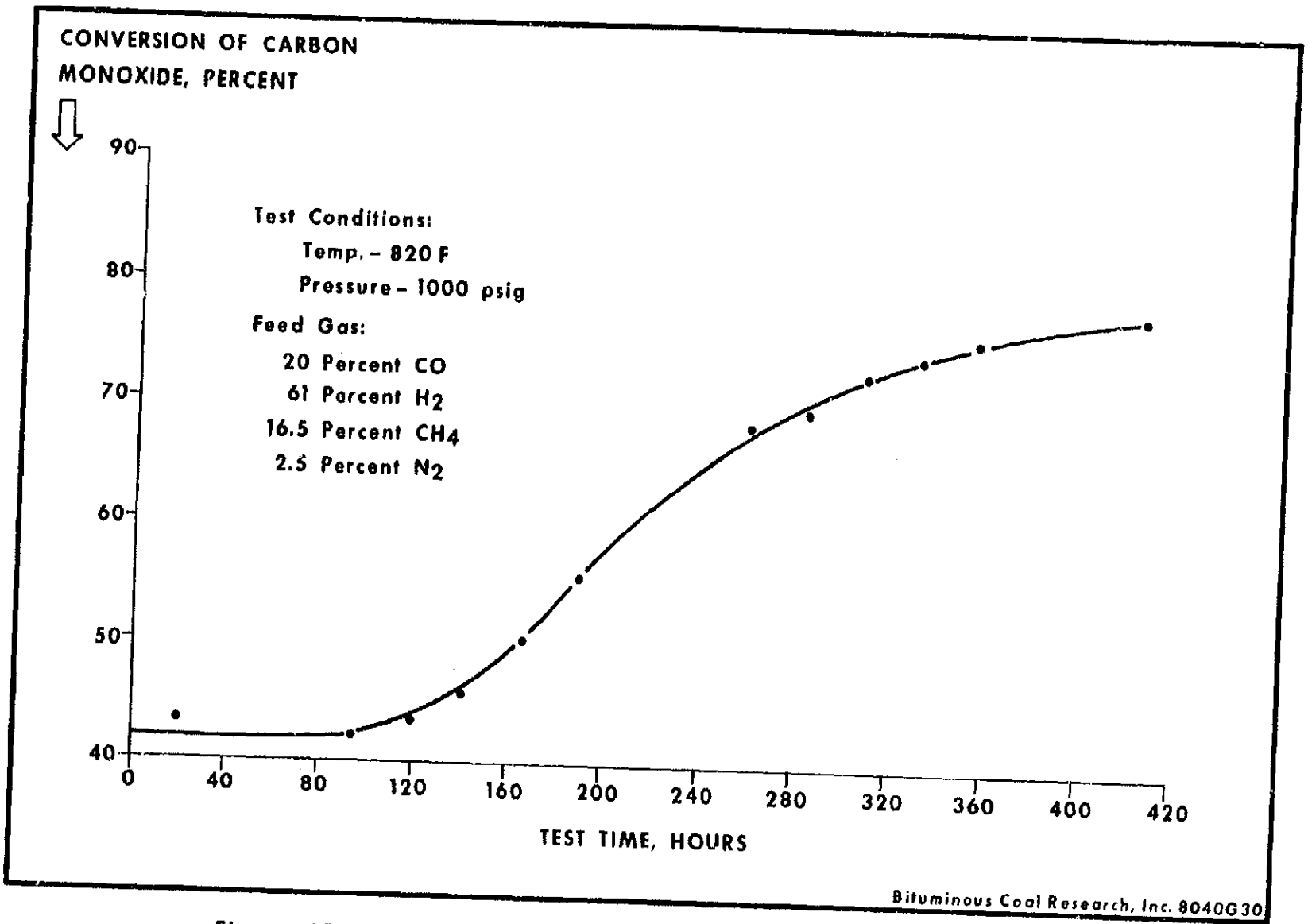

Figure 40. Carbon Monoxide Conversion Data for Life Test 2903

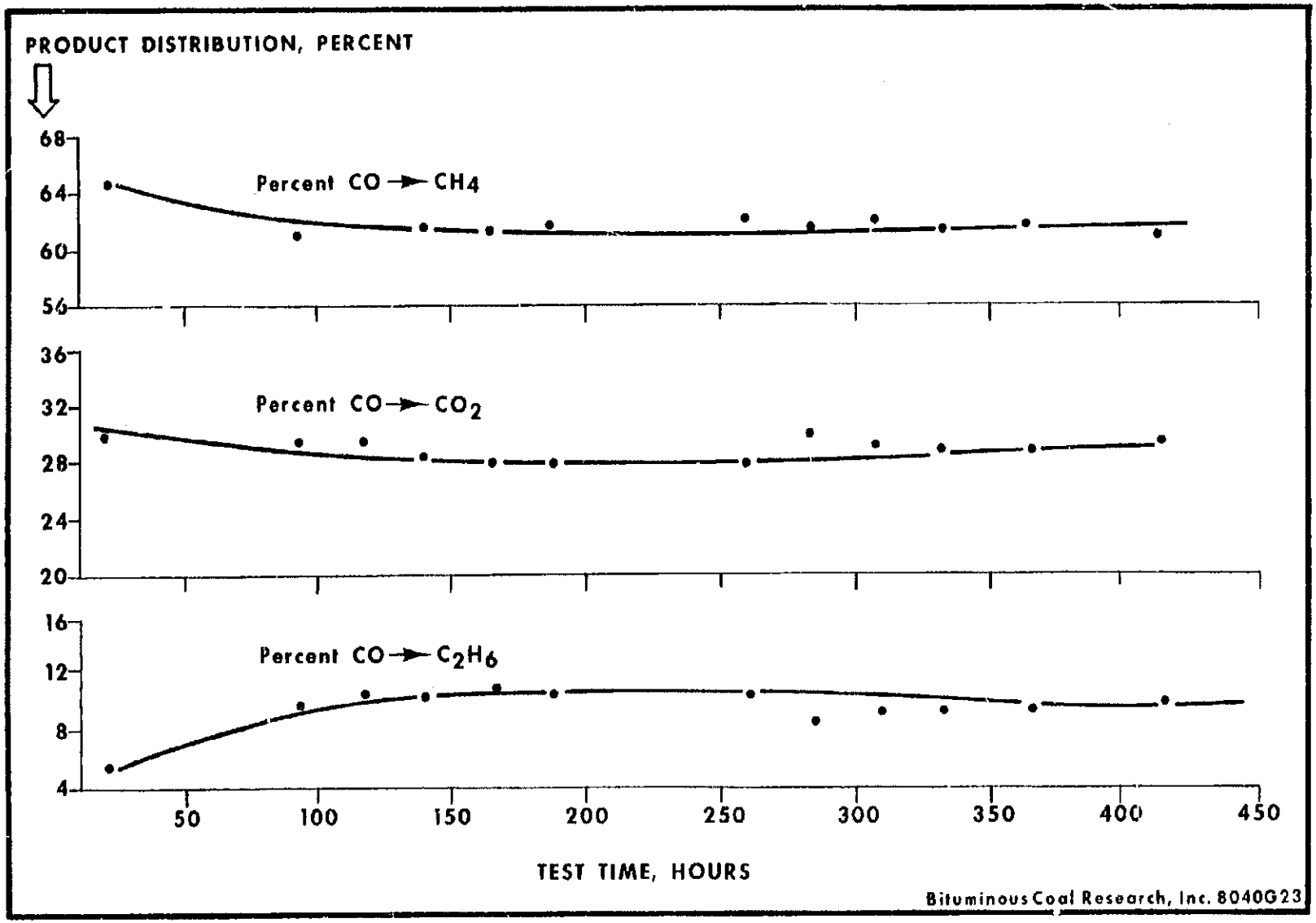

Figure 41. Selectivity Data for Life Test 2903

Since the reduction potential in the life tester is so high, it is fairly evident that slow chemical reduction is taking place. The literature indicates that metallic molybdenum is more catalytic than the oxide. The increased conversion under seemingly constant conditions is the result of an increasing catalyst mass.

While conversion has been increasing, catalyst selectivity has been constant. The degree of shifting by the reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (3)$$

is significant. Tests conducted later will attempt to suppress this function.

The major hydrocarbon products are methane and ethane. No traces of higher hydrocarbons have been found in any samples to date. Product water has almost no organic odor.

c. PEDU Studies. Effort continued during the month in the area of the fluidized-bed PEDU methanator. Work reported here centers about submittal of the "bid package."

The bid package document was submitted to BCR on September 30, 1971. It was reviewed and comments pertaining to the design were returned to Koppers. As a part of the review, a consultant, Dr. Fredrick Zenz, was asked to evaluate the reactor design. His comments are currently being evaluated and changes will be made in the reactor configuration.

Indications from Dr. Zenz are that the cold model program should be expanded. His calculations indicate that slugging should occur in the PEDU. A plastic model is being constructed along with the high pressure steel model to study this phenomena along with other necessary data which need to be gathered. The plastic unit will be studied using sand and freon to get some gross estimates of the slugging regime. More refined studies will be carried out with actual catalyst and argon in the steel unit. In the plastic system, the ratio of particle to gas density will be made the same as in the PEDU, while in the steel unit identical particle Reynolds numbers will be maintained.

d. Conclusions, Recommendations, and Future Work: The results of life tests on nickel catalyst 2648 indicate that a nickel catalyst is not suitable for BI-GAS processing conditions. Work will thus be directed to studying the non-nickel catalysts described in Progress Report No. 1.

During the coming month, BSM tests will screen several new catalysts. The life test on 2903 catalyst will be continued. Work on the PEDU program and model program will be continued.

5. Analytical Services (J. E. Noll): During the past month, 69 samples were analyzed. The number and type of analyses requested were as follows:

Type of Analysis Requested	No. of Samples Analyzed
Gas Chromatography	
100 lb/hr PEDU	15
Methanation Unit	33
Carbon-14	
Gas	18
Liquid	3
Total	69

6. Carbon-14 Procedures (J. E. Noll): The liquid scintillation counter was dismantled and removed from the laboratory. There are no plans for its use in the future.

7. Gas Chromatographic Procedures (J. E. Noll): An on-line gas chromatographic analytical system was set up for cold flow model experiments. The system is described under Section II-C, Cold Flow Model Experiments, of this report.

Future Work: Modification of the above equipment, as necessary, and performing routine sample analyses are the only work planned.