GAS GENERATOR RESEARCH AND DEVELOPMENT

Progress Report No. 4
December 1971
(BCR Report L-447)

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Submitted to the

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

January 18, 1972

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January 1, 1972

Mr. Paul Towson, Engineer
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SUBJECT: Monthly Progress Report No. 4
OCR Contract No. 14-32-0001-1207

Dear Mr. Towson,

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

Equipment for the first phase of the cold flow model studies of Stages 1 and 2 of the two-stage gasifier has been installed and some data have been obtained for feed nozzle orientation in an integrated gasifier. Characteristics of chars to be fed are now being studied.

In the bench-scale work on methanation catalysts for use in the BI-GAS process, evaluation studies have shown that further work is justified on non-nickel catalysts. In bench-scale work on char gasification, char obtained from the Stage 2 PEDU is being studied.

While authorization to commit funds for PEDU erection has not yet been received from OCR, further engineering and planning for procurement of equipment for the two PEDUs continues. Estimates regarding design and equipment changes required to modify the fluidized-bed gasifier to (a) process coal, and (b) operate with a second bed in series are being developed with assistance from Koppers.

The draft of the bid package for the Homer City pilot plant as submitted by Koppers on December 3, 1971, was revised under date of December 17, 1971. As approved by OCR, the first mailing was made December 30, 1971.

Yours very truly,

John W. Igoe

John W. Igoe

JWI:mmw
8006

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BITUMINOUS COAL RESEARCH, INC.
SPONSORED RESEARCH PROGRAM

GAS GENERATOR RESEARCH AND DEVELOPMENT

Progress Report No. 4

(BCR Report L-447)

I. INTRODUCTION

This report summarizes progress achieved during the ninety-sixth 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 fourth 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 DECEMBER 25, 1971

A. Laboratory-scale Process Studies

1. Coal Composition and Beneficiation Studies, and Laboratory Pyrolysis of Coal (R. G. Moses, R. D. Saltsman, and J. E. Noll): The summary report covering the work performed since September, 1970, is in the final editing process. The report should be issued in January, 1972.

2. Fluidized-bed Gasification (E. K. Diehl and J. T. Stewart): Work on the project continued during December. Reactivity study on the Consol char was completed.

Detail engineering on the PEDU has been postponed pending Koppers' preparation of several design changes for further consideration.

a. Fluidized-bed PEDU: BCR was given permission to proceed with obtaining bids on the major pieces of equipment for the PEDU without committing the government, and also to have Koppers do the essential drafting and detail engineering needed for construction. A meeting was held with Koppers on December 22, 1971, for the purpose of establishing a priority list for essential PEDU detail engineering. It was reemphasized at the meeting that the present PEDU design provided for both the oxygen-steam and air-steam gasification of various process chars.

As a result of the December 22 meeting, the PEDU detail engineering was postponed to give Koppers time to consider the following:

(1) What additional equipment and changes to the present design are necessary so that the PEDU will be able to process coal as well as char.

(2) What additional equipment and changes to the present design are required to add a second gasifier stage in series.

It should be noted that the above two concepts could add substantially to the PEDU cost. In addition, as discussed previously, no additional design data could be gathered from a second gasifier that would justify the added investment. As currently designed, the PEDU can be used to study second-stage operation if required. The fluidized bed studies for producing industrial gases are important in anticipation of the need for a method of utilizing char that will be available as a by-product from the many coal conversion processes under development. It is doubtful that a medium pressure fluidized-bed gasifier would be competitive with other processes for gasifying coal.

b. Laboratory Investigation: Reactivity studies were concluded for the reaction of steam with a char from Consolidation Coal's Cresap plant (BCR Lot No. 2469). Sixty-eight experimental runs were made at temperatures of 900, 1000, and 1100 C, and at reacting gas concentrations of 32.7, 70, and 100 percent steam in nitrogen. The complete rate equation for the reaction of this char sample with carbon dioxide may be expressed as:

$$(1-x) = \text{Ash} + (1-\text{Ash})\ e^{-k(C_{H_2O})^{.58}t} \qquad (1)$$

$$\text{and } k = 8.64 \times 10^{5}\ e^{-1.93 \times 10^{4}/T} \qquad (2)$$

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, an activation energy of 38 kcal/mole and a pre-exponential factor (Arrhenius constant) of 8.64×10^5 min^{-1} can be found for this reaction. These values correspond to 34 kcal/mole and 9.5×10^6 min^{-1} previously reported for the FMC char-steam reaction. In both cases, the rate was found to be proportional to the steam concentration to the 0.58 power. Figure 66 shows a typical plot of Equations 1 and 2 with the corresponding experimental data.

Table 63 is a comparison of the apparent reactivity, k value from Equation 2, for the two chars. The Consol char is more reactive than the FMC char in the temperature range of interest. This is also shown in the Arrhenius plot in Figure 67.

This study to date has resulted in a procedure to evaluate the relative reactivity of various chars. Chars from both the BI-GAS and the HY-GAS process will be investigated next. The qualitative value of the reactivity test has been demonstrated, but only actual PEDU operation will determine the quantitative value of the complete rate equation in fluidized-bed reactor design.

c. Future Work: Design changes for the PEDU will be evaluated to determine whether their inclusion will add substantially to the research program. Revised cost estimates will be made.

Char reactivity studies will continue. Immediate work will involve the evaluation of several chars produced in the BI-GAS PEDU.

3. Gas Processing (M. S. Graboski): Work continued in the area of gas processing during the month of December 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, two catalysts were tested for activity in the BSM unit. Life testing continued on Lot 2903 molybdenum catalyst.

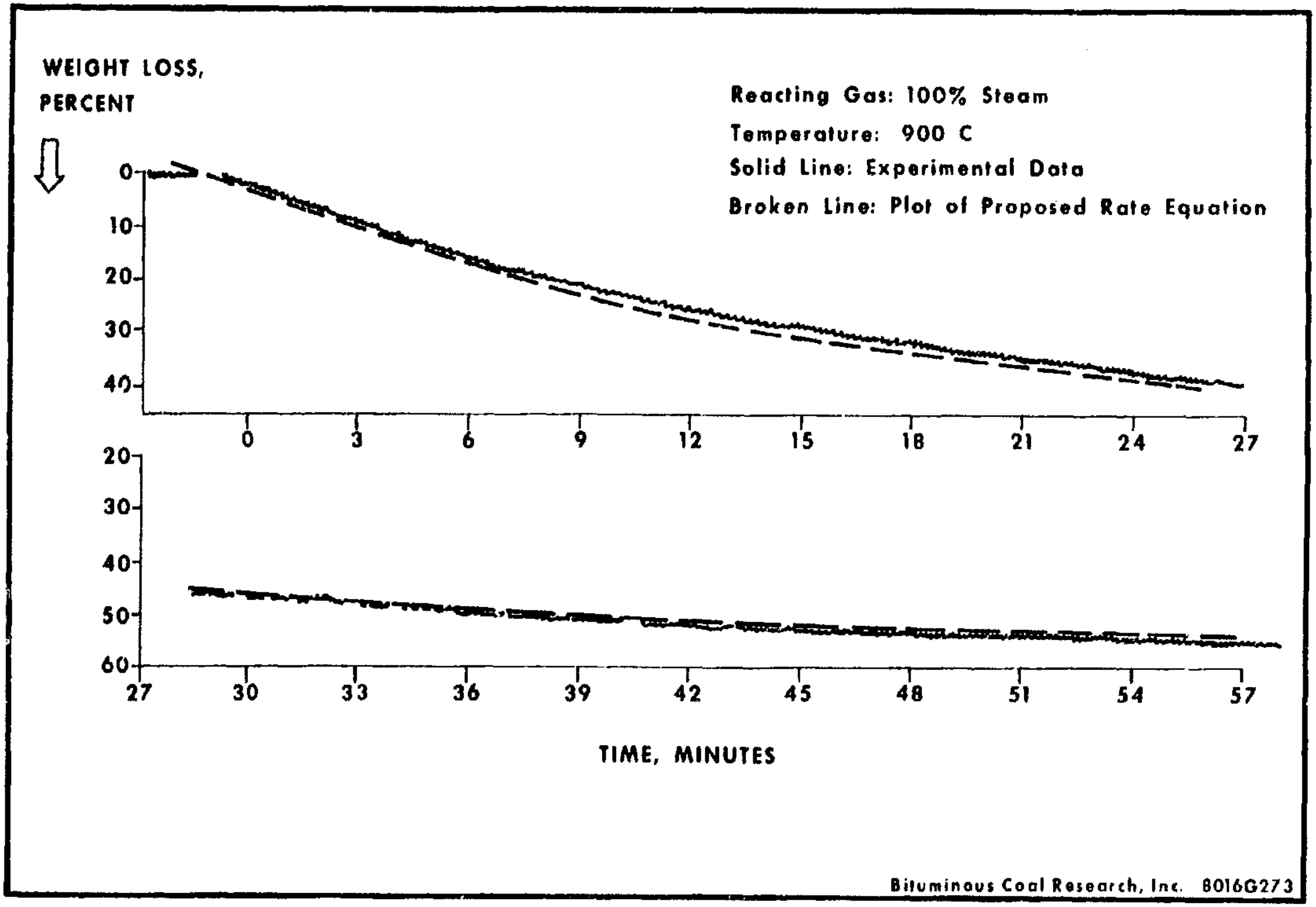

Figure 66. Correlation of Consol Char Reactivity Data

TABLE 63. APPARENT REACTIVITY VALUES FOR FMC AND CONSOL CHAR SAMPLES CHAR + STEAM REACTION

		Temperature, C			
		900	1000	1100	1200
FMC Char (BCR Lot No. 2455)	$k = \frac{\text{lb C reacted}}{\text{lb C inventory - min}}$	.0483	.1507	.3985	.9236
Consol Char (BCR Lot No. 2469)	$k = \frac{\text{lb C reacted}}{\text{lb C inventory - min}}$	.0618	.2250	.6788	1.7626

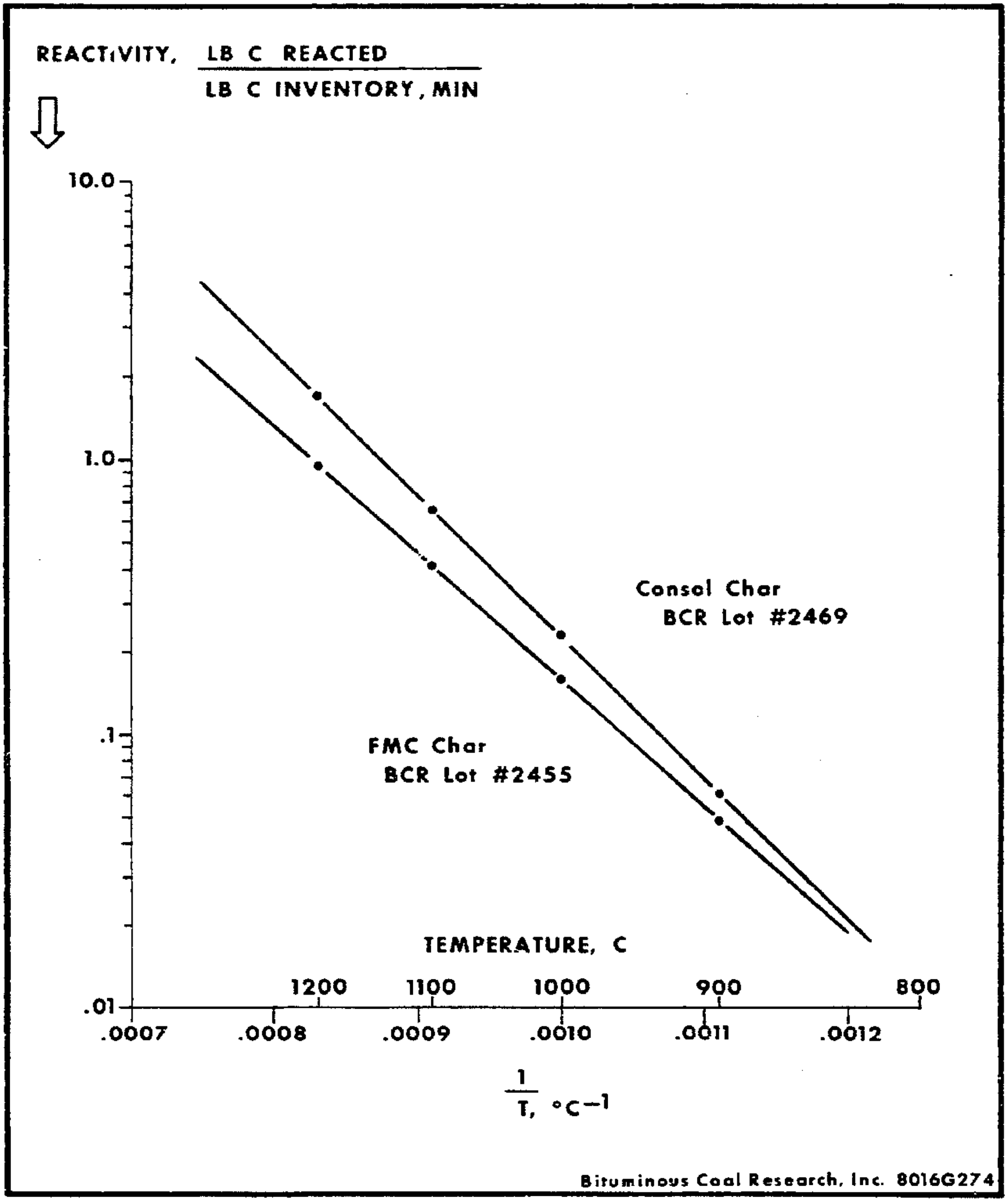

Figure 67. Char Reactivity as a Function of Temperature for the Char Plus Steam Reaction

(1) Data and Results for BSM Test 46: BSM Test 46 was conducted on BCR Lot 2912 catalyst. This material is commercially sold by Catalysts and Chemicals, Inc., as C-36-1-01. It is composed of 2 percent nickel on a very low activity alumina.

Three grams of catalyst 2912 were charged and pretreated. The system temperature was raised to 485 F and synthesis gas was introduced over the catalyst mass. At 550 F, reaction was initiated as evidenced by water in the catchpot. However, within a short period of time, the reaction ceased. The temperature was then slowly increased to 700 F with no signs of reaction reappearing.

(2) Data and Results for BSM Tests 47 and 48: BSM Tests 47 and 48 were carried out on BCR Lot 2913 catalyst. This material is marketed by Catalysts and Chemicals, Inc., as C-31-1-01. It is composed of 0.3 weight percent palladium on an alumina support.

In Test 47, five grams were charged and pretreated. Synthesis gas was introduced at 465 F. The temperature was slowly raised to 750 F without any signs of reaction.

Since palladium is known to be a highly active hydrogenation catalyst, Test 48 was carried out as a repeat of Test 47 except that 15 grams of 2913 were charged. At 400 F, some activity appeared momentarily. The temperature was increased to 650 F with no further signs of reaction.

(3) Discussion of BSM Tests 46 to 48: In the BCR methanation catalyst screening program, two more potential catalysts were tested this month.

Test 46 involved Lot 2912 nickel methanation catalyst. While standard nickel catalysts have been ruled out for BI-GAS use, it was felt worthwhile to investigate 2912 on the basis of the postulate presented in Progress Report No. 1, page 14. This dealt with catalyst deactivation by local overheating. Since 2912 is a very low activity nickel catalyst, it was felt that the support might dissipate the heat sufficiently to prevent deactivation. Test 46 indicates, however, that just diluting the catalyst mass will not enhance the stability of the nickel catalyst.

Tests 47 and 48 were conducted on a palladium-based catalyst (Lot 2913). The noble metals are normally more active catalysts for hydrogenation than nickel. This is also true for methanation as witnessed by the low initiation temperature of reaction. However, deactivation was even more rapid for palladium than for nickel catalysts. Apparently, noble metal catalysts will not suffice for the highly exothermic and rapid methanation synthesis.

(4) Life Test of Catalyst 2903: Data were reported last month for life testing of molybdenum oxide catalyst 2903 till 1100 hours of operation. During the past month, data were collected beyond 1600 hours as shown in Figure 68. At 1440 hours, the space velocity was decreased for Phase 2 of the test as described in Progress Report No. 2, page 118. Throughout Phase 1 and Phase 2 periods, the activity has remained stable.

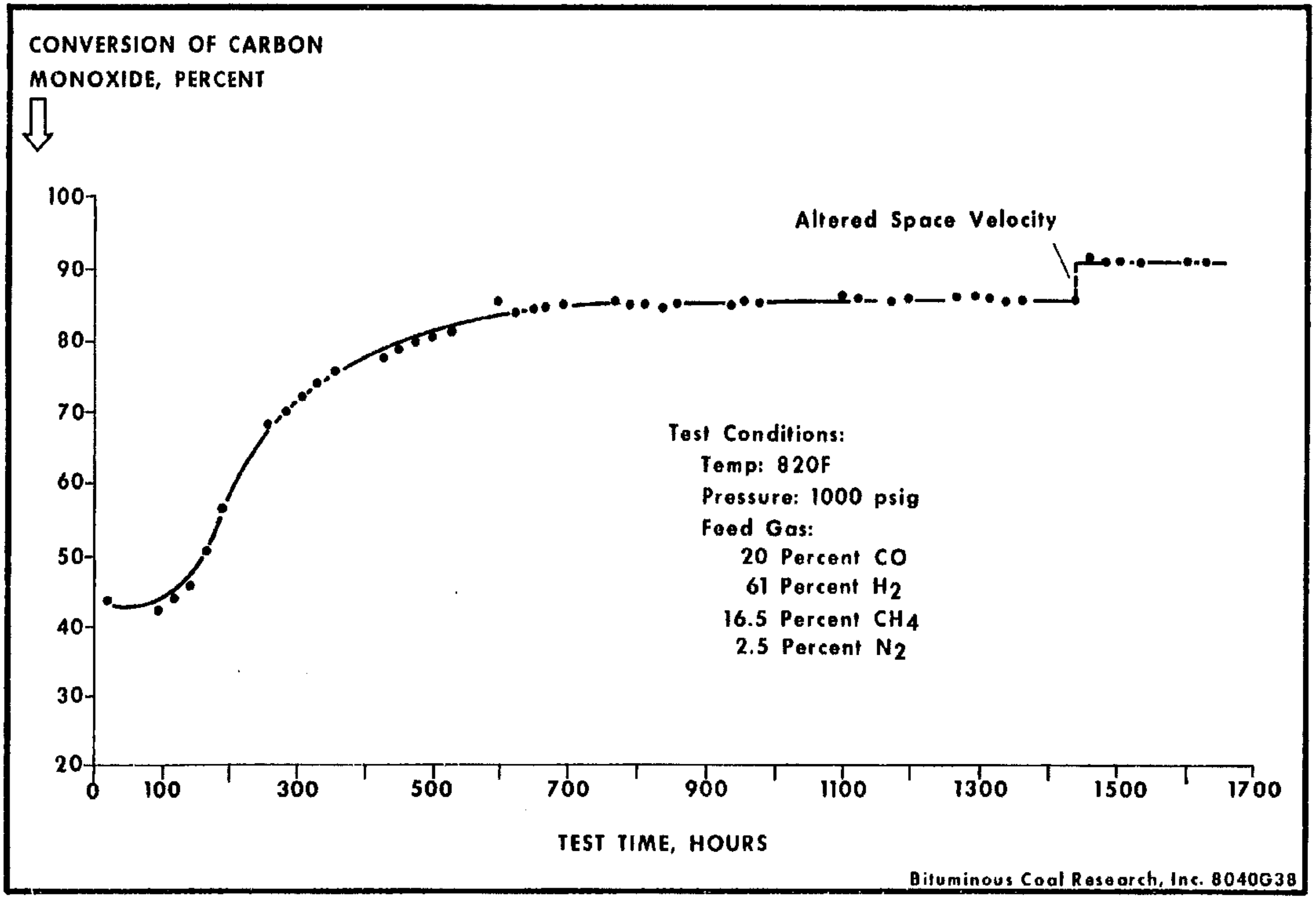

Figure 68. Carbon Monoxide Conversion Data for Life Test 2903

Product selectivity data are shown in Figure 69. Increasing the conversion has increased the useful amount of products slightly at the expense of carbon dioxide. It is very possible that the carbon dioxide could be shifted back and methanated with a sufficiently large charge of catalyst. This will be studied at a later date.

Gas for Phase 3 of the life test has been mixed. It contains roughly 30 percent carbon dioxide with proportionally reduced amounts of carbon monoxide, methane, and hydrogen. This will simulate the methanation of the shifted and desulfurized gas from the gasifier. Phase 3 will begin early in January.

Phase 4 has been added to the life test program. This involves sulfiding of the molybdenum catalyst under the Phase 3 gas composition with one percent hydrogen sulfide added. Sulfided operation is important from several aspects, but the area of greatest importance is whether sulfur poisoning will occur or whether the catalyst will be enhanced in activity.

b. PEDU Program: Work continued in the area of PEDU planning, and preliminary tests were started on the cold model program.

(1) PEDU Status: During the month, there were several major developments in the area of the methanation PEDU program.

(a) On Tuesday, December 14, a work crew began dismantling the Stage 2 PEDU in preparation for the methanation and char gasification PEDUs.

(b) By phone on December 14, BCR obtained approval to solicit bids on PEDU equipment.

(c) By phone on December 14, BCR obtained clearance to permit Koppers to do detail engineering on the methanator.

As a direct result of the latter two clearances, BCR and Koppers met on December 22 to outline the detail engineering and to determine which vessels and major equipment items are already sufficiently detailed for bidding purposes. Presently, Koppers is supplying BCR with specification sheets, and a list of recommended suppliers of equipment for the PEDU.

(2) Cold Model Program: During the month, the cold model unit was extended to 10 feet in height. Pressure tests were conducted on the unit and some preliminary studies were carried out with air. Work was limited due to a shift of manpower to the dismantling operation.

The unit was routinely operated at 45 psig and pressure-tested to 75 psig.

The tests carried out suggested several modifications of the unit. The pressure tap above the distributor has been eliminated and grid pressure drop will be determined in the empty bed as a function of flow rate. The pressure tap in the bed above the distributor constantly plugged and was therefore useless.

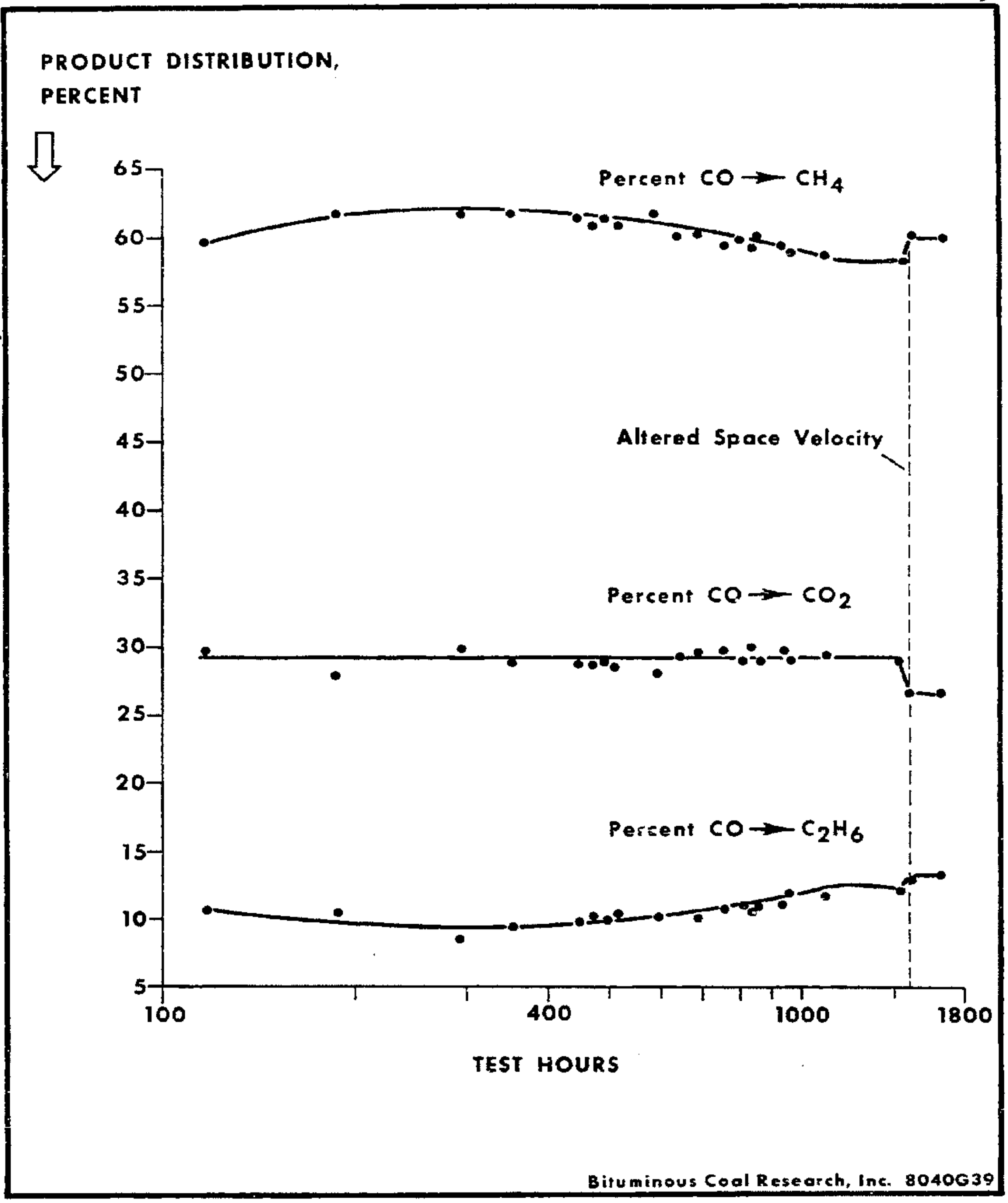

Figure 69. Selectivity Data for Life Test 2903 Catalyst

The actual bed drop will be calculated by subtracting the grid pressure drop from the total system pressure drop. Also, the distributor cone has been modified to permit one to watch the grid plate. This has been accomplished by lining the cone with Plexiglas and cutting a portion of the cone away. A new three-hole distributor plate is being constructed to model the grid selected for the pilot plant methanator.

c. Other Work

(1) Status of BCR Suggestion 193: BCR Suggestion 193 dealt with operation of a combined shift converter and methanator. A report is being prepared on this suggestion. In addition, material balance data have been developed and a complete literature search is underway pertaining to the subject matter of this suggestion.

(2) Status of BCR Suggestion 194: BCR Suggestion 194 dealt with modifications to the pilot plant gas processing scheme to handle different types of methanation catalysts. A report is in preparation and will soon be submitted.

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

At the bench-scale level, kinetic measurements will be made in the BSM unit on a copper chromite catalyst. Further rate data will be gathered on the molybdenum (Lot 2903) catalyst and on the chrome (Lot 2904) catalyst. In the Life Test Program, Phases 3 and 4 will be carried out on Catalyst 2903. These involve operation under conditions designed to suppress the shift reaction under both unsulfided and sulfided conditions.

Work on the PEDU will continue. Bids on equipment will be solicited and Koppers will conduct detail engineering. If approval for construction is received early in January, the time schedule as outlined for the PEDU can still probably be met (operation by Jan. 1, 1973). Further delay will cause setbacks in the program.

PEDU model studies will continue.

Work on followup reports on BCR Suggestions 193 and 194 will be conducted.

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

5. Analytical Services (J. E. Noll): During the past month, 19 samples were analyzed by gas chromatography and 4 samples by special procedures. The manner and type of analyses requested were as follows:

Type of Analysis Requested	No. of Samples Analyzed
Gas Chromatography	
Methanation Unit	19
Special Procedures	
Apparent particle density for fluidization	4
Total	23

6. Gas Chromatographic Procedures (J. E. Noll): No work was required in this area during the past month.

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

B. Stage 2 Process and Equipment Development Unit--100 lb/hr (R. J. Grace, E. E. Donath, and R. L. Zahradnik)

During the month, time was distributed between: checking process descriptions and piping and instrumentation drawings from the Koppers Company for the bid package for the multipurpose research pilot plant facility (MPRF); preparation of a report for the Subcommittee Work Group for the AGA Materials Evaluation program; supervision of dismantling operations of the Stage 2 100 lb/hr PEDU; and preparation of the final summary report. Also, checking special "equipment" design by Foster Wheeler Corporation as requested by OCR.

1. Inspection of Reactor Refractories and Internal Metal Surfaces in PEDU: During dismantling operations of the PEDU, the flange covering the Stage 1 section was removed for inspection of the internals of Stage 1. Slag in the base of the 6-inch diameter, 18-inch length of the cylindrical Stage 1 section had accumulated to a depth of about two inches. Figure 70 is a view through the front of Stage 1 showing the slag accumulation. Above the base area, the slag covering averaged about 1/2 inch in thickness over the entire surface.

The bends in the cooling water tubes in Stage 1, shown in Figure 71, were corroded most extensively in the upper section just adjacent to the covering flange. Apparently the seal in this area was not tight and moisture penetrated the area which, along with other gaseous components (air and combustion products), promoted a highly corrosive condition.

Figure 72 is a close-up view of one of the two tube bends shown in Figure 71 and indicates the extent of the surface corrosion. Figure 73 shows the average condition of most of the other tube bends, which Figure 74 is a close-up view of one of these three tube bends and indicates relatively little surface deterioration.

Specifications for the cooling coils were given on Blaw-Knox Reactor Dwg. 2239-35001-1, Rev.-5 as: coils are to be 1 inch O.D. with minimum wall thickness of 0.16 inch.

Inspection of the refractory brick inner lining, Harbison and Walker Co., Korundal XD, aside from the slag covering over all areas, showed very little deterioration, and slag penetration into the brick was slight. Figure 75 pictures the refractory lining after removal of a portion of the brick from Stage 1 and shows the slight penetration of the slag below the surface of the brick.

Arrangements have been made for Mr. J. Bialosky, Metallurgy Section, Koppers Co., to inspect the Stage 1 components at a later date, when a complete section of the Stage 1 water cooling coils has been exposed. It may be that a complete section of the cooling tubes will be cut from Stage 1 to provide for a more complete metallurgical inspection by Koppers.

2. Future Work: Future work will include:

a. Further inspection of the internals - cooling coils and refractories - of Stage 1 of the PEDU by Koppers Co. personnel,

b. Necessary work to expedite final dismantling of the 100 lb/hr PEDU,

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Figure 70. Slag Accumulation in Stage 1 after Test 58

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Figure 71. Corroded Cooling Water Tube Bends, Stage 1

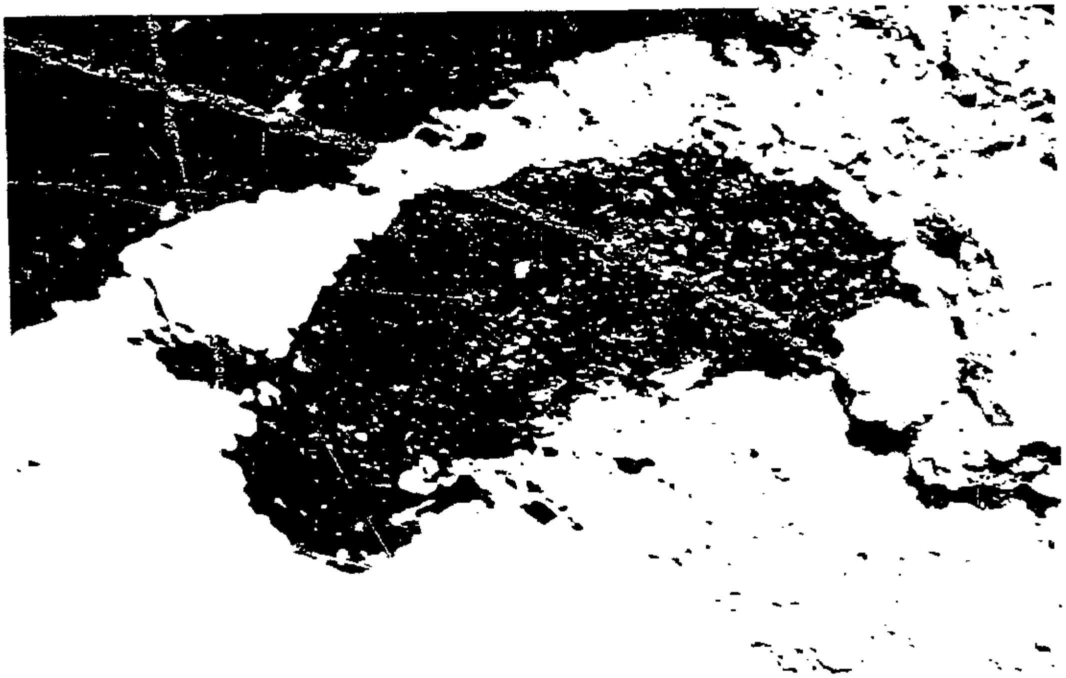

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Figure 72. Close-up of Cooling Water Tube Bends, Stage 1

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Figure 73. Average Condition of Cooling Water Tube Bends, Stage 1

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Figure 74. Close-up of Average Condition Tube Bends, Stage 1

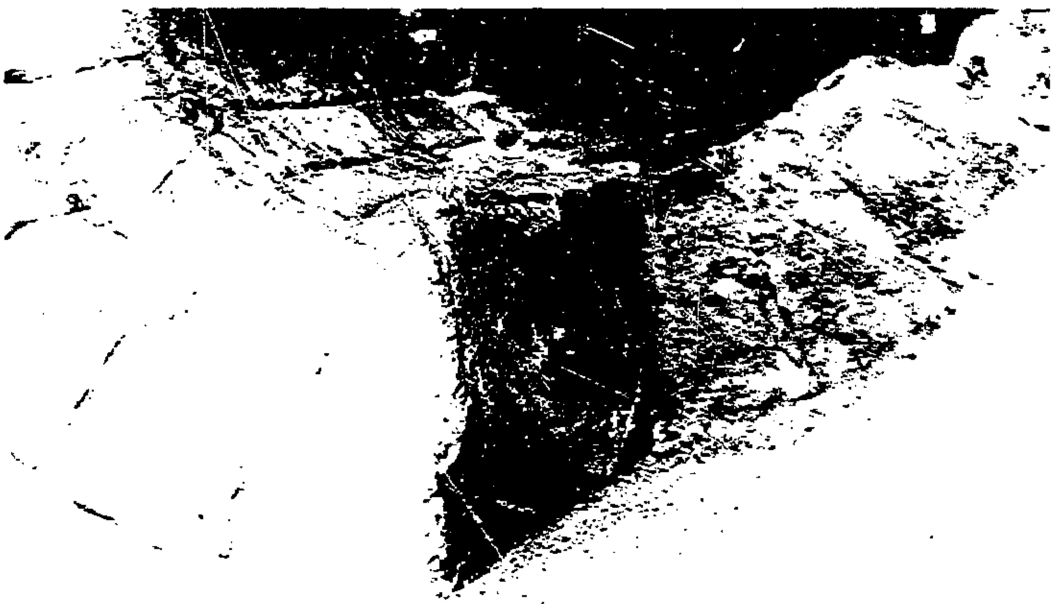

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Figure 75. Refractory Lining Condition, Stage 1