

GAS GENERATOR RESEARCH AND DEVELOPMENT

Progress Report No. 1
September 1971
(BCR Report L-432)

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Submitted to the

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

October 25, 1971

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October 1, 1971

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SUBJECT: Monthly Progress Report No. 1
OCR Contract No. 14-32-0001-1207

Dear Mr. Towson,

The final two tests of the 100 lb/hr Stage 2 PEDU were completed in September using Pittsburgh seam coal. One test was made to further determine the effect of changing the position of the coal feed nozzle; the second test was made to determine the effect of a shorter residence time produced by a reduction in the normal volume of the reactor. Preparation of a final summary report on these studies will begin this month.

The summary report on the coal composition and beneficiation studies has been drafted and is being edited.

Evaluation of the bid packages received from Koppers on the fluidized-bed methanation and gasification PEDUs is progressing. Plans are being developed to dismantle the 100 lb/hr Stage 2 PEDU to clear the area for the new PEDUs. Equipment and instrumentation lists are being prepared to determine what can be salvaged for continued use.

Work continues on other phases of the experimental program:

The methanation catalyst evaluation continues; new catalysts are being screened to determine their potential use in the bench-scale methanator.

A new char has been received from Consolidation Coal Company and is being used in the reactivity studies.

Procurement and erection of equipment for the cold flow model studies have been proceeding according to schedule.

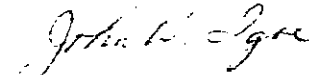
Mr. Paul Towson

- 2 -

October 1, 1971

All possible assistance is being given Koppers in order that they may complete the engineering bid package on schedule.

Yours very truly,


John W. Igoe

JWI:pjc
8006

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BITUMINOUS COAL RESEARCH, INC.
SPONSORED RESEARCH PROGRAM

GAS GENERATOR RESEARCH AND DEVELOPMENT

Progress Report No. 1

(BCR Report L-432)

I. INTRODUCTION

This report summarizes progress achieved during the ninety-third 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 first 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 is shown in Figure 1.

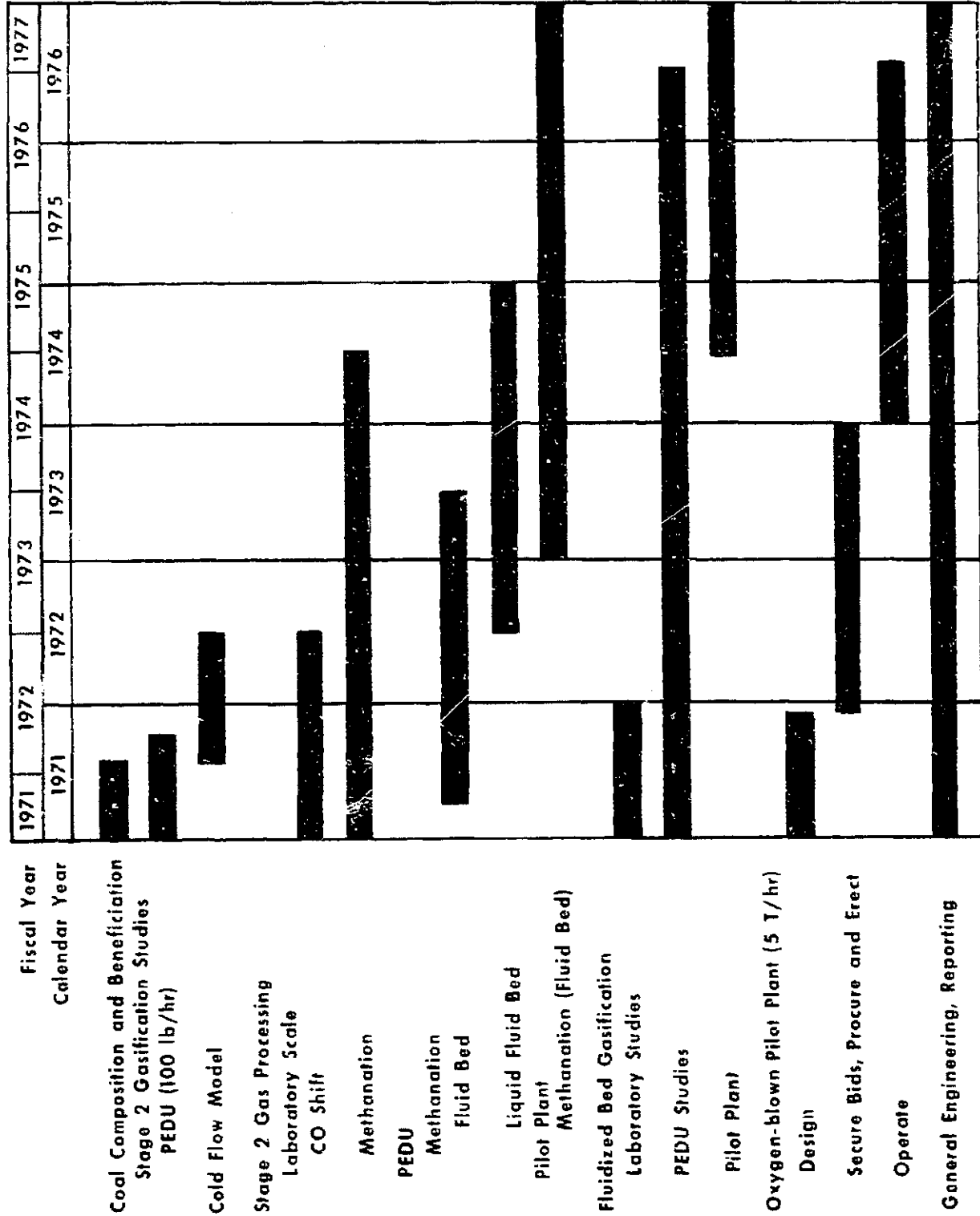
B. Monthly Progress Charts

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 SEPTEMBER 25, 1971

A. Laboratory-scale Process Studies

1. Coal Composition and Beneficiation Studies (R. G. Moses and R. D. Saltsman): Experimental work on this project was discontinued. A summary report on this phase of the work is now being written. It will summarize work performed since September 20, 1970.



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Figure 1. Proposed Work Schedule: Gas General Research and Development Program

2. Laboratory Pyrolysis of Coal (J. E. Noll): A report summarizing work performed on this phase of the project since September, 1970, is in the course of preparation.

3. Fluidized-bed Gasification (E. K. Diehl and J. T. Stewart): Work on the design of the 100 lb/hr char gasification PEDU is nearing completion, and a specification manual prepared by Koppers is expected October 1, 1971.

Laboratory studies on the reactivity of FMC char with both steam and carbon dioxide have been completed and rate equations have been developed. Similar studies on char which is a product of Consolidation Coal's Cresap pilot plant have been initiated.

a. Fluidized-bed PEDU: Koppers has essentially completed the specification manual for the unit, and will submit it to BCR for review and approval.

Utility, equipment, and space requirements have been developed, and Building 3 facilities are being reviewed in light of those requirements.

Plans are being made for disassembling the Stage 2 PEDU to make room for the fluidized-bed and methanation PEDU's. Reusable equipment, controls, and instrumentation will be listed and held for incorporation into the new PEDU systems.

P & I drawings for the fluidized-bed PEDU have been received and are being reviewed. As indicated in last month's report, design for the initial unit covers operation on oxygen/steam and air/steam only. Operation on carbon dioxide will not be conducted until later; only preliminary design of the carbon dioxide system is being considered now.

Koppers has supplied a revised cost estimate for the detail design and for the purchase and erection of the PEDU. Pending OCR approval to continue the PEDU program, the revised estimate has been incorporated in the budget projections for calendar 1972.

b. Laboratory Investigations: Complete rate equations have been given for the reaction of FMC char with both steam and carbon dioxide. Figures 2 and 3 are plots of typical experimental and calculated data and show the significance of the correlation over a wide range of steam concentrations. Similar plots were given in Progress Report No. 92 for a wide range of carbon dioxide concentrations.

Studies were conducted during the month of particle size distribution of FMC char as a function of carbon burn-off and as a function of attrition while in a fluidized condition. It had been previously shown (Progress Report No. 85, pages 3345-3347) that the char particles do not shrink in size as the reaction proceeds to 80 percent carbon burn-off. For the present study, an as-received sample of FMC char was used with an average particle diameter of 0.0087 inches, determined by screen analysis.

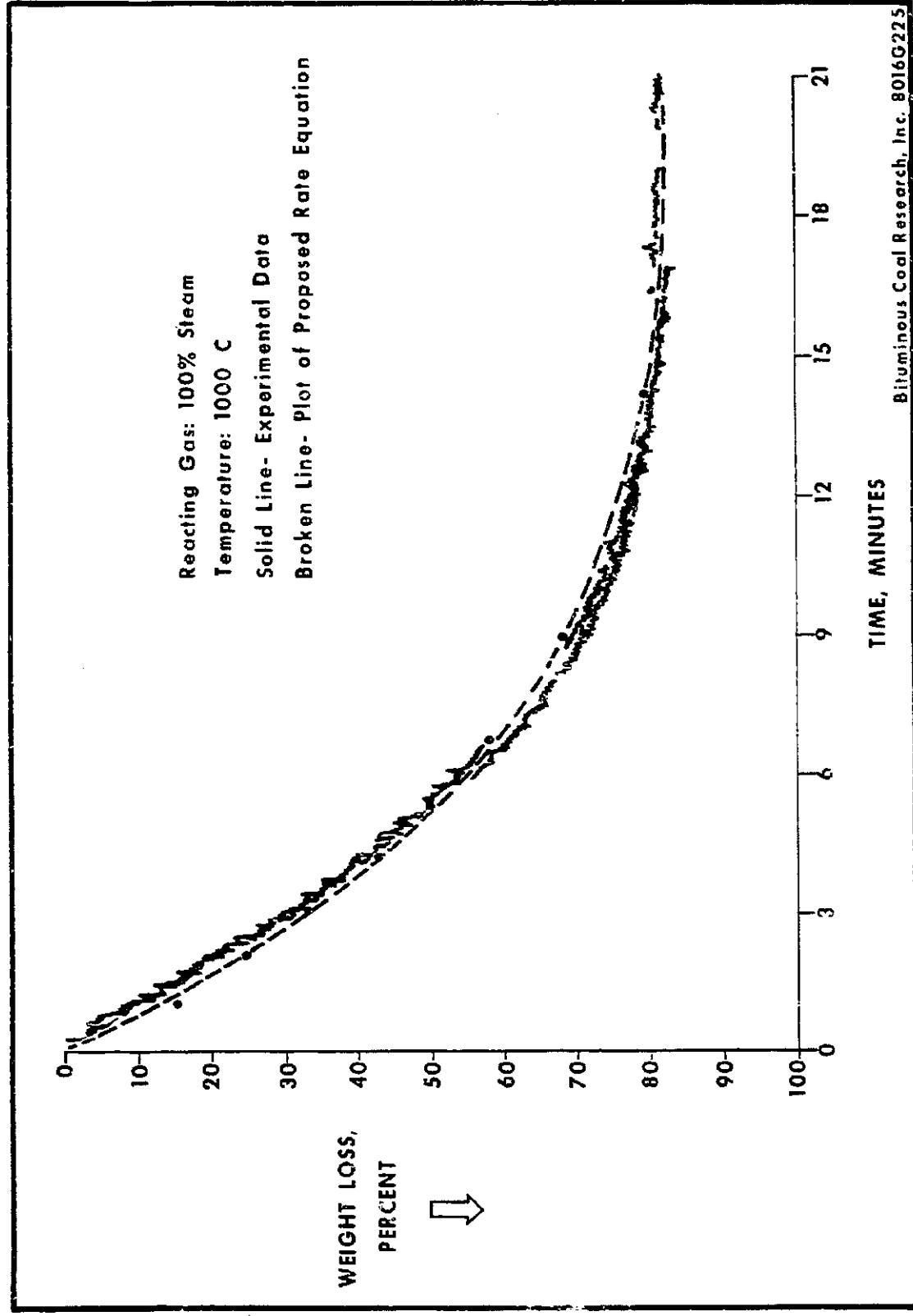


Figure 2. Correlation of FMC Char Reactivity Data

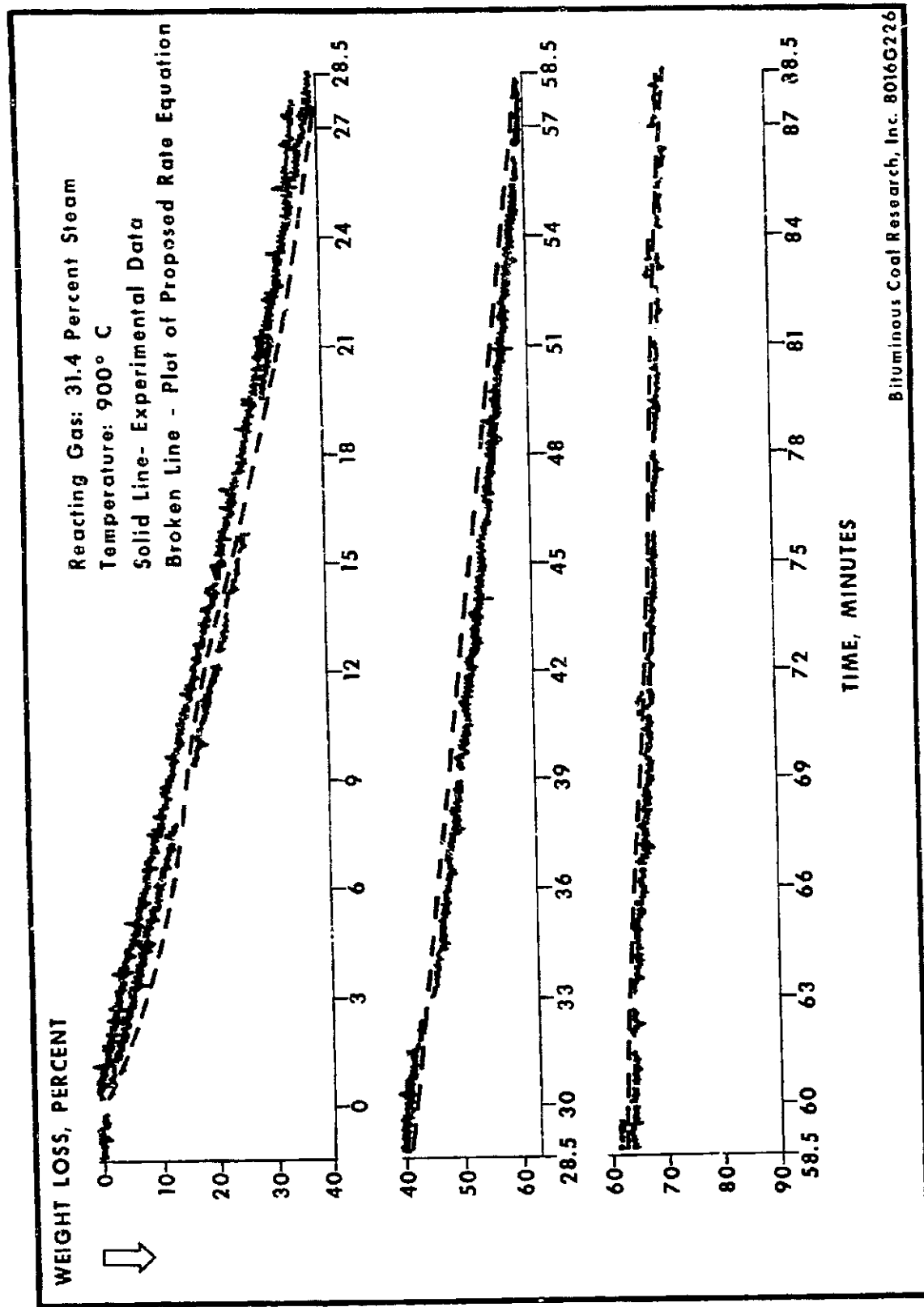


Figure 3. Correlation of FMC Char Reactivity Data at Low Concentrations

This sample was then reacted to 16 percent carbon burn-off and 40 percent carbon burn-off. Screen analysis after each reaction gave an average particle diameter of 0.0087 in.

The 40 percent reacted char particles were fluidized with air in a 1-inch I.D. glass tube at a superficial velocity of approximately 0.2 feet per sec. Screen analysis after 4 hours of fluidization showed that the average particle diameter was still 0.0087 in. This is further evidence that the continuous reaction kinetic model is consistent with experimental observations.

The reaction-rate order of the char/ CO_2 reaction has been given as 0.52 with respect to carbon dioxide. (See Progress Report No. 91, p. 3805.) This fractional order was obtained with carbon dioxide diluted to different concentrations with nitrogen. There was some doubt as to whether or not this same fractional order would apply in the reducing atmosphere that will exist in the gasifier. To answer this question, the series of 48 char/ CO_2 runs was duplicated using carbon monoxide instead of nitrogen as the diluent. Initial results show a fractional order of 0.78 with respect to carbon dioxide. The data are still being interpreted and further discussion will appear in next month's report.

Reactivity studies have begun on a new char, from Consolidation Coal's Cressap pilot plant. This char is much higher in ash content (50 percent) and volatile matter (12 percent) than the FMC char previously investigated. The experimental procedure will be the same as that for the FMC char studies.

c. Future Work: Immediate future work will concentrate on detailed review of the PEDU specification manual and design drawings submitted by Koppers. It is also planned to have the design examined by a fluidization consultant. Reactivity studies of the Consol char will continue.

4. Gas Processing (M. S. Graboski): Work continued in the area of gas processing during the month of September in accordance with the revised time schedule given as Figure 4. 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 various conditions of pressure, temperature, and carbon monoxide contents. During the month, four nickel catalysts were screened and further work was carried out on a cobalt molybdenum catalyst.

The purpose of the screening operation is to determine whether any nickel catalysts available are acceptable for use under BI-GAS methanation conditions. Since the fluidized bed type of unit has been selected, the average carbon monoxide in the reactor might be expected to be low. However, at the distributor plate, a high carbon monoxide content will exist. Since the catalyst may be harmed by such carbon monoxide concentrations, the bench-scale tests have been geared towards conversion at carbon monoxide partial pressure in excess of about 150 psi.

A. Methanation Catalysts

1. Kinetic Rate Studies

2. Attrition Studies

3. Catalyst Life Studies

B. Shift Catalysts

1. Kinetic Rate Studies

2. Catalyst Life Studies

2. PEDU Studies

1. Cold Model Studies

2. Fluidized Bed Reactor System

3. Mathematical Model Development

[illegible]

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Figure 4. Gas Processing Working Schedule for Fiscal 1972

(1) Data and Results for BSM Test 33: The purpose of BSM Test 33 was to investigate BCR Lot 2684 methanation catalyst at 700 F and 1,000 psig under a high carbon monoxide partial pressure to determine whether the catalyst would show rapid reactivation. Lot 2684 is a nickel-alumina formulation supplied by Catalysts and Chemicals Inc., under the trade name of C-13.

In Test 33, 2.5 grams of Lot 2684 were charged to the reactor. The catalyst was reduced with hydrogen in situ and, under operating conditions, carbon monoxide was blended into the reactor feed. Gas samples were taken after several hours of operation. The results of Test 33 are shown in Figure 5.

(2) Data and Results for BSM Test 34: The purpose of BSM Test 34 was to investigate BCR Lot 2688 catalyst at 700 F and 1,000 psig under a high carbon monoxide partial pressure to determine whether the catalyst would show rapid deactivation. Lot 2688 is a selective hydrogenation catalyst supplied by Harshaw Chemical Company under the trade name of Ni-O304T. It contains 32 percent nickel oxide on active alumina.

In Test 34, 2.5 grams of Lot 2688 were charged to the reactor and reduced in situ. Carbon monoxide was fed over the catalyst and batch samples were taken to determine whether the catalyst would show rapid deactivation. The results of Test 34 are shown in Figure 6.

(3) Data and Results for BSM Test 35: The purpose of BSM Test 35 was to investigate BCR Lot 2692 methanation catalyst at 700 F and 1,000 psig under a high carbon monoxide partial pressure to determine whether the catalyst would show rapid deactivation. Lot 2692 is a nickel catalyst supplied by Harshaw Chemical Company under the trade name Ni-3210T. It is composed of 35 percent nickel on a proprietary support.

In Test 35, 2.5 grams of Lot 2692 were charged to the reactor. The catalyst was reduced with hydrogen in situ and carbon monoxide was passed over the catalyst. Data from batch sample analysis are shown in Figure 7.

(4) Data and Results from BSM Test 36: The purpose of BSM Test 36 was to investigate BCR Lot 2693 catalyst at 700 F and 1,000 psig under a high carbon monoxide partial pressure to determine whether the catalyst would show rapid deactivation.

Lot 2693 is a nickel catalyst supplied by Harshaw Chemical Company under the trade name Ni-3250T. No composition analysis is available for this catalyst.

In Test 36, 2.5 grams of 2694 were charged, reduced in situ, and tested. Initial rate was extremely high but the catalyst "burned" itself up within about two hours. No data are tabulated for Lot 2693 catalyst.

(5) Life Test 2687-2: Catalyst 2687 (Harshaw CoMo) had been shown to methanate well in past BSM tests and in Life Test 2687-1 (Progress

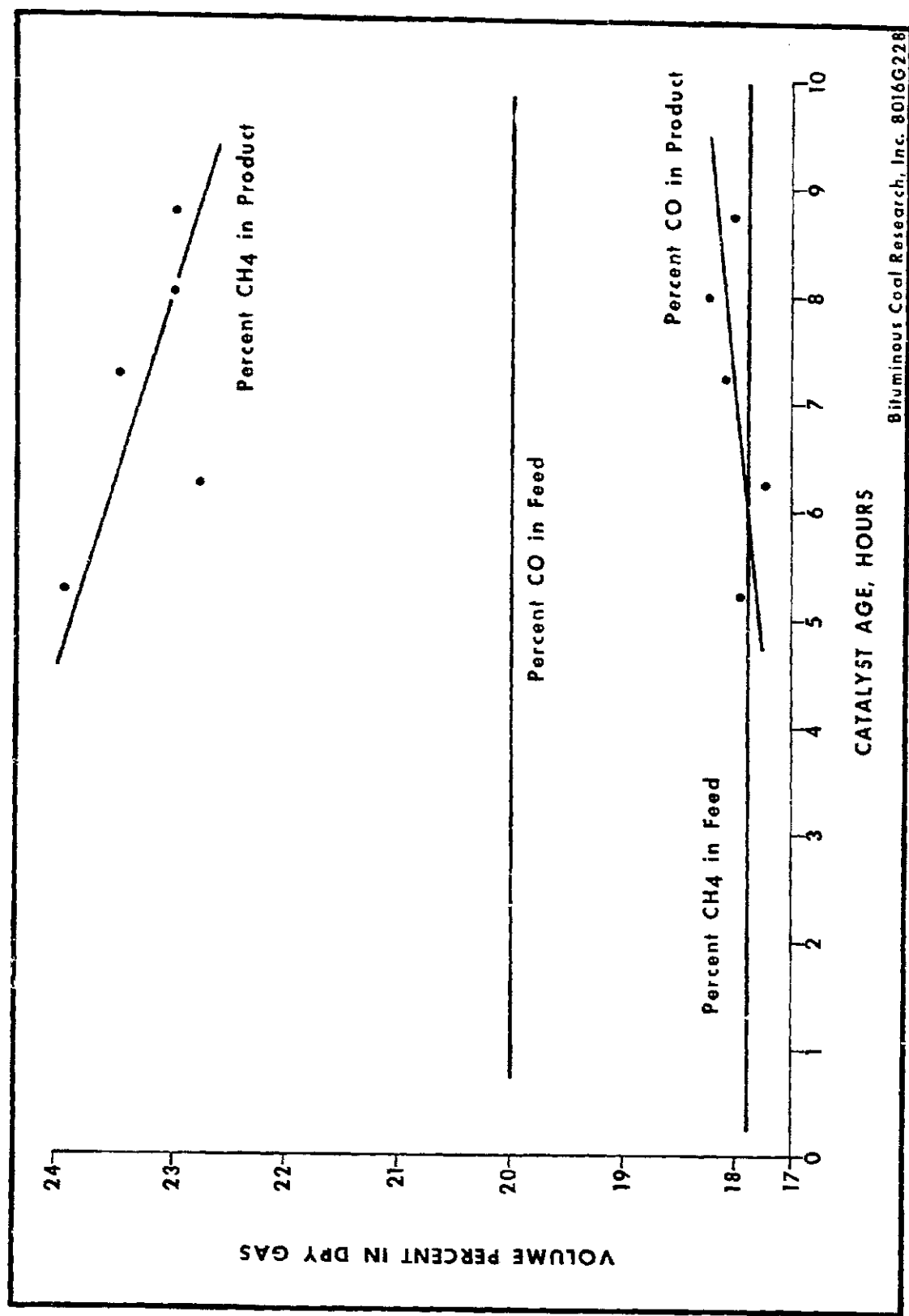
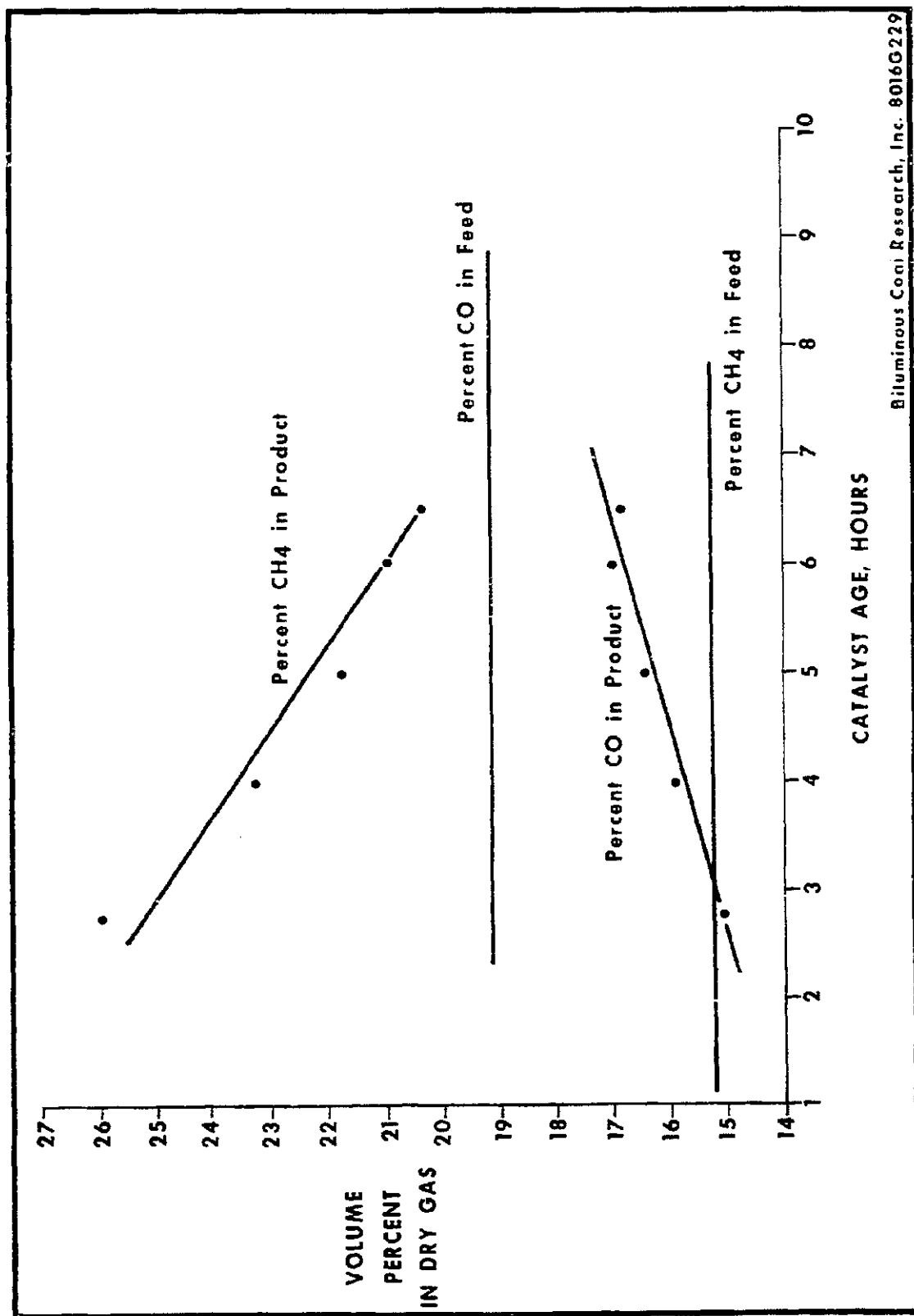
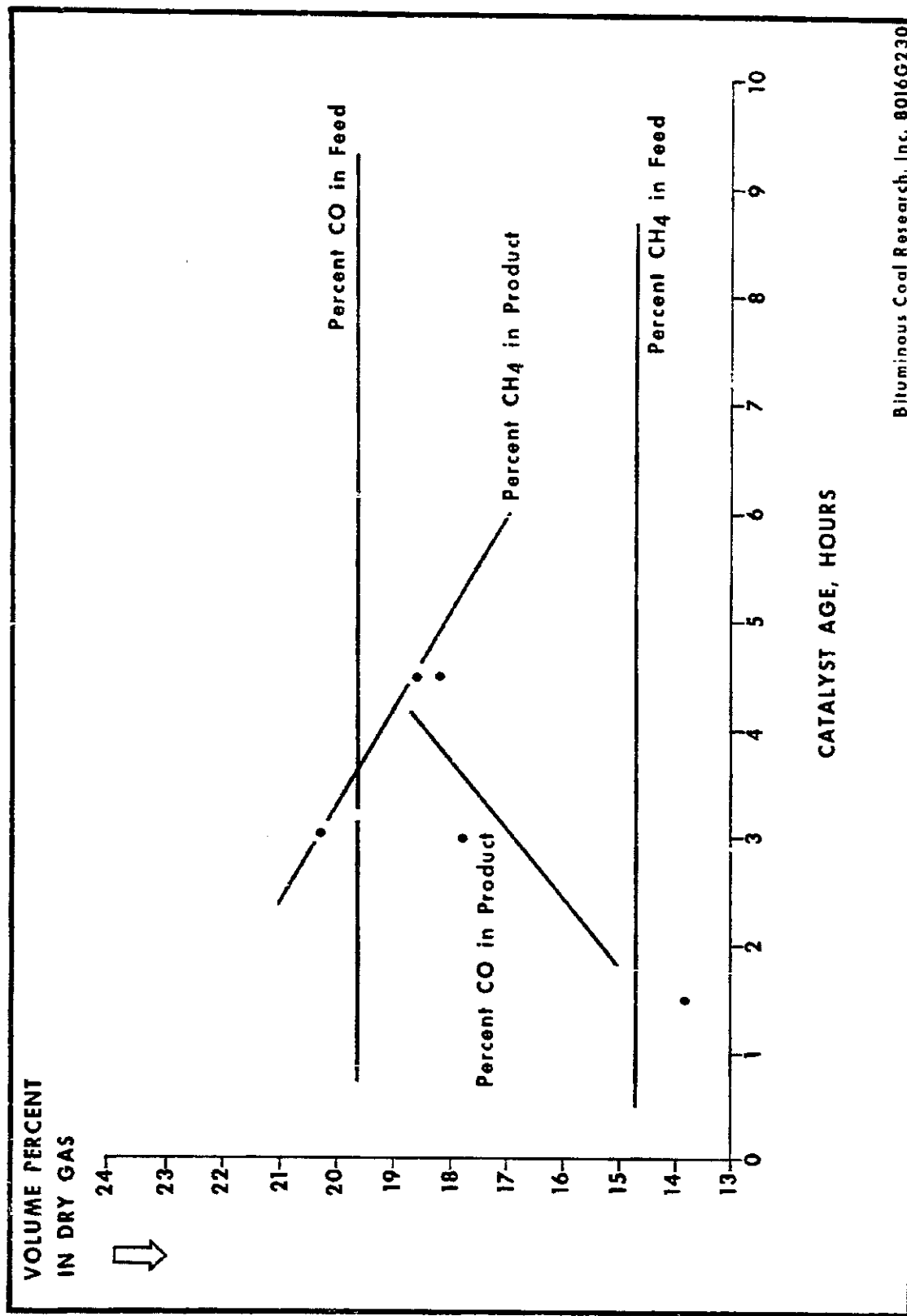


Figure 5. Gas Composition Data from BSM Test 33
(Lot 2684 Catalyst at 700 F and 1000 psi)



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Figure 6. Gas Composition Data from BSM Test 34
(Lot 2688 Catalyst at 700 F and 1000 psi)



Bituminous Coal Research, Inc. 8016G230

Figure 7. Gas Composition Data from BSM Test 35
(Lot 2692 Catalyst at 700 F and 1000 psi)

Report 92, p. 3879). In Life Test 2687-1, however, a fair amount of the carbon monoxide was shifted to carbon dioxide, reducing the useful conversion of carbon to combustible gas.

Life Test 2687-2 was designed to reduce this unwanted conversion by adding carbon dioxide to the feed gas. The desired effect of the carbon dioxide was to start the methanation reaction under conditions approaching shift equilibrium and thus suppress the reaction. The feed gas prepared was the following:

<u>Component</u>	<u>Volume, Percent</u>
Carbon Dioxide	12.31
Carbon Monoxide	17.30
Hydrogen	53.04
Nitrogen	1.79
Methane	15.54
Ethane	0.02

Reaction temperature was 830-870 F and the system pressure was at 1,050 psig.

Since it was determined in Life Test 2687-1 that the activity of Catalyst 2687 stabilized after 200 hours, it was felt that no more information would be gained by a long-term run. Thus, the catalyst was operated for only 42 hours, which was long enough to get two samples taken a day apart. Ten grams of catalyst were used in the test.

Data for Life Test 2687-2 are given in Table 1. In this test, useful conversion of carbon monoxide was about 90 percent while in Life Test 2687-1 it was about 70 percent; this resulted from a threefold reduction in carbon dioxide production. The calculated shift constant was still approximately the same as the thermodynamic constant in the 800 F to 900 F range.

TABLE 1. RESULTS FOR LIFE TEST 2687-2

<u>Product Gas</u>	<u>Volume, Percent</u>	
	<u>24 Hours</u>	<u>42 Hours</u>
Carbon Dioxide	18.59	18.74
Carbon Monoxide	8.11	8.31
Hydrogen	36.58	36.93
Nitrogen	2.36	2.41
Methane	32.68	31.85
Ethane	1.68	1.76
Conversion to CO, percent	66.4	65.2
CO \rightarrow CH ₄ , percent	70.2	66.6
CO \rightarrow C ₂ H ₆ , percent	20.5	22.2
CO \rightarrow CO ₂ , percent	9.3	11.2
Shift Constant K	6.42	6.85

(6) Life Tests 2684-1 and 2684-2: Of the nickel catalysts investigated to date, Catalyst 2684 appeared to deactivate the slowest in BSM tests. It was felt that Catalyst 2684 should be tested to determine whether or not it would show a reasonable lifetime at 700 F and 1,000 psig. Three grams of catalyst were reduced in the life tester and the catalyst was operated under 200 psi carbon monoxide partial pressure. For the first five days of testing, Catalyst 2684 showed complete conversion. Over a weekend, gas sampling did not take place. The Monday sample, after 143 hours, showed the catalyst to be dead. The test was rerun with 1 gram of catalyst. After 66 hours the batch of catalyst died.

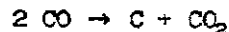
b. Discussion of BSM and Life Tests: During the month, four nickel catalysts were screened in the BSM unit. These ranged in nickel content and support type. This work brings to a total of eight the number of nickel catalysts studied. A summary of tests conducted prior to this month was given in Progress Report No. 92.

Figures 5, 6, and 7 indicate the effect of a short-time test on the catalyst activity. Rapid deactivation is apparent. In BSM Test 36, the catalyst died within several hours of operation. The catalysts from Tests 34 and 35 were analyzed for carbon. The results are given in Table 2.

TABLE 2. RESULTS OF CARBON ANALYSIS OF CATALYSTS
FROM BSM TESTS 34 AND 35

<u>Test No.</u>	<u>Catalyst Lot</u>	<u>Moisture, percent</u>		<u>Carbon, percent</u>	
		<u>Before</u>	<u>After</u>	<u>Before</u>	<u>After</u>
34	2688	0.69	0.64	2.6	4.0
35	2692	0.80	0.91	0.25	0.60

The pickup of carbon is apparently the cause of catalyst deactivation. This carbon formation is due to the reaction:



High partial pressures of carbon monoxide make this reaction kinetically favored. The equilibrium plot, Figure 831, Progress Report No. 92, indicates that a H_2/CO ratio of 3 is just about at the carbon deposition boundary at 80 atmospheres. Non-ideal effects in the gas mixture make the exact location

of the carbon boundary impossible to locate. However, since the mixture being fed to the reactor is so close to the critical ratio, it may be assumed that some carbon formation is favorable thermodynamically. A second, and probably compounding, mechanism for the deactivation is local overheating of the catalyst surface. Although the gas velocity used in the BSM is high, and hence the heat transfer from the solids to the gas is good, one can picture a reaction rate at the surface and in the catalyst pores being so high that the rapid release of energy in the catalyst particle cannot be dissipated. The temperature rise might cause sintering of the catalyst surface, closing off pores and reducing the activity. The effect of rapid thermal deactivation on a Harshaw catalyst similar to BCR Lot 2683 has been documented by Pursley, White, and Sliepcevich¹. Their tests showed a fivefold loss in activity over 100 hours of testing.

The only nickel catalyst tested for extended activity was Catalyst 2684 since it appeared most favorable from the BSM screening. A three-gram batch, initially chosen, proved to be too large a charge for the life tester and complete conversion occurred. The charge was reduced to one gram and the test was repeated in hopes that the conversion would be somewhat less than complete. This was not the case, however. The three-gram batch of catalyst lasted longer than the one-gram batch due to the excess nickel mass percent. Neither batch lasted a significant time under a carbon monoxide pressure of 200 psi.

Several tests with Catalyst 2684 are planned in the life test unit to define more closely what carbon monoxide partial pressure causes deposition.

The partial pressure of carbon monoxide will be reduced systematically until an acceptable level is found. The test sequence is designed as follows:

<u>Test No.</u>	<u>CO in Gas, Percent</u>	<u>Total Pressure, psi</u>	<u>Partial Pressure CO, psi</u>
2684-1,2	20.0	1,000	200
2684-3	10.0	1,000	100
2684-4	10.0	750	75
2684-5	10.0	500	50

It is felt that a carbon monoxide partial pressure below 50 psi would yield a process with a high recycle rate offering no advantages over other processes.

Further testing of Lot 2687 cobalt-moly catalyst continued this month in the life test unit. The purpose of Life Test 2687-2 was to investigate the catalyst's activity under conditions where the shift reaction was not promoted.

¹Pursley, J., White, R., and Sliepcevich, C., "The Rate of Formation of Methane from Carbon Monoxide and Hydrogen with a Nickel Catalyst at Elevated Pressures," CEP Sym. Ser. 4 (48), p. 51-58, 1951.

The data for Life Test 2687-2 are outlined in Table 1. Carbon dioxide-free selectivities for both Life Test 2687-1 and Life Test 2687-2 have been calculated. Test 2687-1 results were reported last month. In that test, no effort was made to control the shift reaction. The methane to ethane ratio for both tests is identical, being 7.2/1 or on a carbon monoxide conversion basis, 3.6/1. The amount of carbon dioxide formed in Test 2687-2 was reduced substantially. Test 2687-1 showed a $\text{CO} \rightarrow \text{CO}_2$ conversion three times greater than Test 2687-2. This indicates that the carbon monoxide conversion by the two reactions can be optimized over the cobalt-moly catalyst by controlling the amount of carbon dioxide in the feed gas.

Tests 2687-1 and 2687-2 were conducted in a sulfur-free environment. Recent talks with a Texaco staff member who has had experience with the BASF cobalt-molybdenum shift catalyst indicate that methanation can also occur on the sulfided catalyst at steam-to-dry gas ratios less than about 0.8/1. While we are not in a position to evaluate sulfided catalysts at present, this is an important factor to study in future tests. Since most methanation catalysts are extremely sulfur-sensitive, it is necessary to reduce sulfur content to the levels required for long catalyst life.

c. Program Planning: It is evident from BSM studies that conventional nickel "methanation" catalysts do not perform well under the conditions of the BCR/OCK BI-GAS process. It is further evident that other potential catalysts could do the job (for example, cobalt-molybdenum). Therefore, a new series of catalysts has been selected for study, primarily for two reasons. The first is based on Sebastian's criteria² and the second is based on commercial availability. In Sebastian's opinion, the "presence of two catalyst types is necessary for the reduction of oxygen compounds, e.g., the conversion of carbon monoxide to methane: (a) hydrogenation catalysts, (b) dehydrating catalysts." Hydrogenation materials include nickel oxide, cobalt oxide, iron oxide, molybdate, molybdenum sulfide, tungsten sulfide, copper chromite, chromic oxide, copper, platinum, and palladium. Dehydrators include tungsten oxide, alumina, chromic oxide, silica, molybdate, and nickel oxide.

The first class of catalysts selected was nickel catalysts not normally used for methanation. The two deactivation mechanisms posed for nickel methanation catalysts are carbonization and thermal deactivation. Both of these could be minimized by the selection of a very low activity catalyst. This could be accomplished effectively by using a low nickel content on a low-surface refractory-type support. The result would be a spreading out of the "active sites" which, in turn, would lower the probability of reaction between chemisorbed carbon monoxide molecules on adjacent sites on the catalyst surface. The low nickel content would also tend to reduce the reaction rate allowing the support to more easily dissipate the heat of reaction. Catalysts in this class are:

(1) C-11-9-02: This is a Catalysts and Chemicals steam forming catalyst. It contains 12 percent nickel on a refractory support. Surface area and pore volumes are low, being 5 to 15 sqm/g and 0.2 to 0.3 cc/g, respectively.

²Sebastian, J., "Catalytic Reduction of Carbon Monoxide to Methane at Atmospheric Pressure," PhD Thesis, Carnegie Tech, May 10, 1935. p. 4.

(2) C-36-1-01: This is a Catalysts and Chemicals selective hydrogenation catalyst. It contains 2 percent nickel on a low surface area alumina support.

The second class of catalysts are hydrogenation catalysts composed of various metals. These are described as follows:

(3) Cu-0202P: This is a Harshaw copper-chromite catalyst containing 82 percent copper oxide and 17 percent chromic oxide. It has a low surface area and pore volume (10-13 sqm/g and 0.5 cc/g, respectively).

(4) Fe-0303P: This is a fluidized-bed microspheroidal catalyst supplied by Harshaw Chemical Co. It contains 20 percent ferric oxide on high activity alumina.

(5) M-1101P: This is a fluidized-bed catalyst supplied by Harshaw Chemical Co. It contains 11 percent molybdenite on high activity alumina.

(6) C-31-1-01: This is a selective hydrogenation catalyst supplied by Catalysts and Chemicals, Inc. It contains a small amount of palladium on a high surface alumina carrier.

The third class selected is dual metal catalysts. The reason for choosing these is based on the success with the cobalt-molybdenum catalyst. In both of these selections, nickel was chosen over cobalt since it is a better methanator.

(7) C-20-7-01: This is a nickel-molybdenum catalyst supplied by Catalyst and Chemicals, Inc. It contains 3 to 4 percent nickel and 13 to 15 percent molybdenum on a high surface alumina support.

(8) Ni-4301-E: This is a nickel-tungsten catalyst supplied by Harshaw Chemical Company. It contains 6 percent nickel and 19 percent tungsten on a silica-alumina support.

A final selection did not quite meet the criteria outlined by Sebastian. However, it was included because of its ability to dehydrogenate.

(9) Cr-1401-P: This is a fluidized-bed catalyst supplied by Harshaw Chemical Company. It contains 19 percent chromic oxide on high activity alumina.

In addition to these, Harshaw has informed BCR that it has available for use, seven nickel fluidized-bed catalysts. Purchase of several of these is being held up until some proof is obtained that a nickel catalyst can perform the job. Two candidates which are similar to the nickels described above, (1) and (2), are 9.6 and 8.7 percent nickel on alundum and sintered alumina, respectively. These meet the low-nickel, low-surface requirements hypothesized above.

Each catalyst will be tested in the BSM for its ability to methanate. Successful candidates will be put into the life test unit for further screening. The choice of catalysts listed, while perhaps not yielding the optimum catalyst, should indicate which metals or combination of metals can supply the methanation needs of the BI-GAS process.

d. Cold Model Unit: Construction of the cold model unit proceeded during the month. Work in this area has been slow due to the lack of success in catalyst studies. The unit is shown in Figure 8. It will be available for studies as catalysts become available. The unit is currently being tested with silica.

e. PEDU Planning: Effort continued during the month in the area of the fluidized-bed methanation PEDU design. The latest detailed time schedule for the unit is shown in Figure 9.

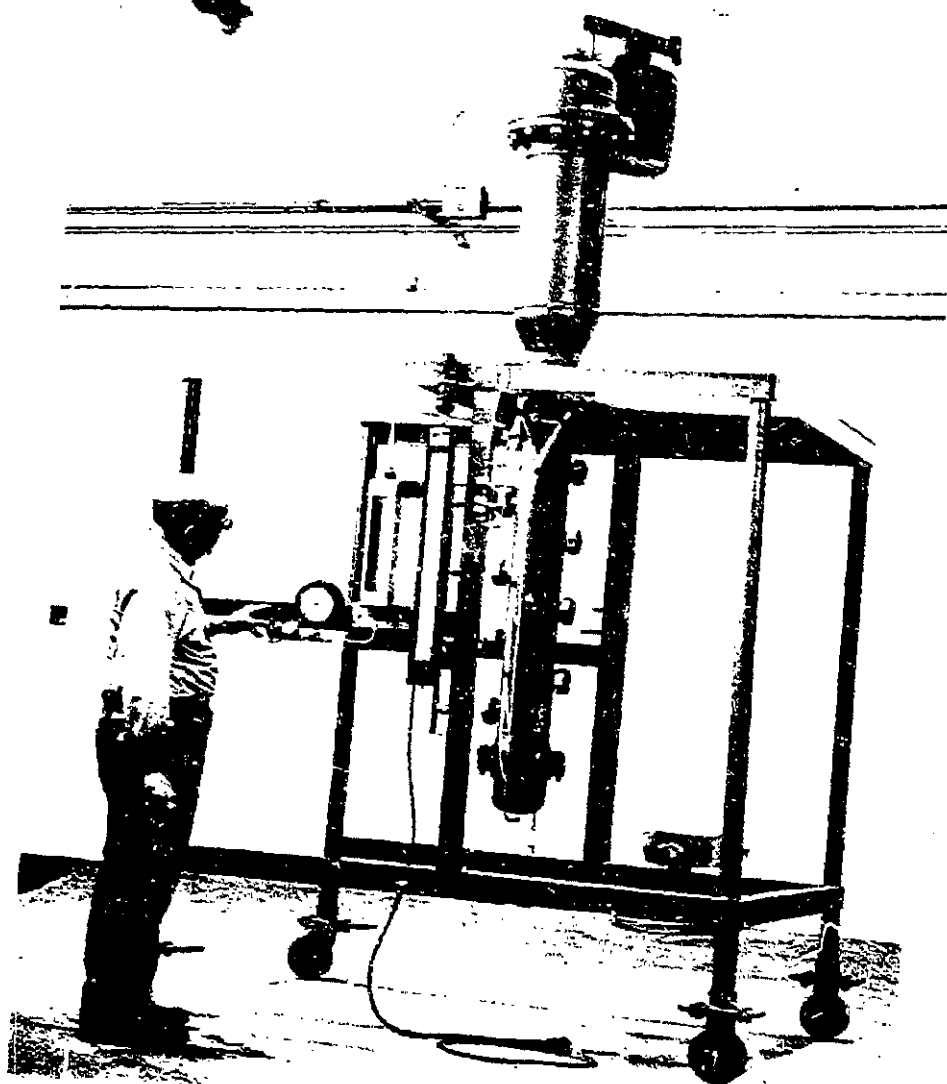
At present, Koppers is channeling all PEDU efforts into the preparation of a "bid package." Some major items included in the package have been reviewed and were discussed in Progress Report No. 92, pages 3888 and 3891. The main technical discussions held this month concerned the design of the gas distributor area. The design agreed upon is shown in Figure 10. The distributor is conical in shape with a drilled sieve plate at the bottom (narrow end) of the cone to obtain:

- (1) a spouting effect which would cause poor solids and gas contact at the distributor; this in turn would reduce reaction and heat release in the area of the bed not filled with cooling coils.
- (2) cooling of the entire distributor area by the therminol oil.

Submission of the complete bid package for review is scheduled for September 30, 1971.

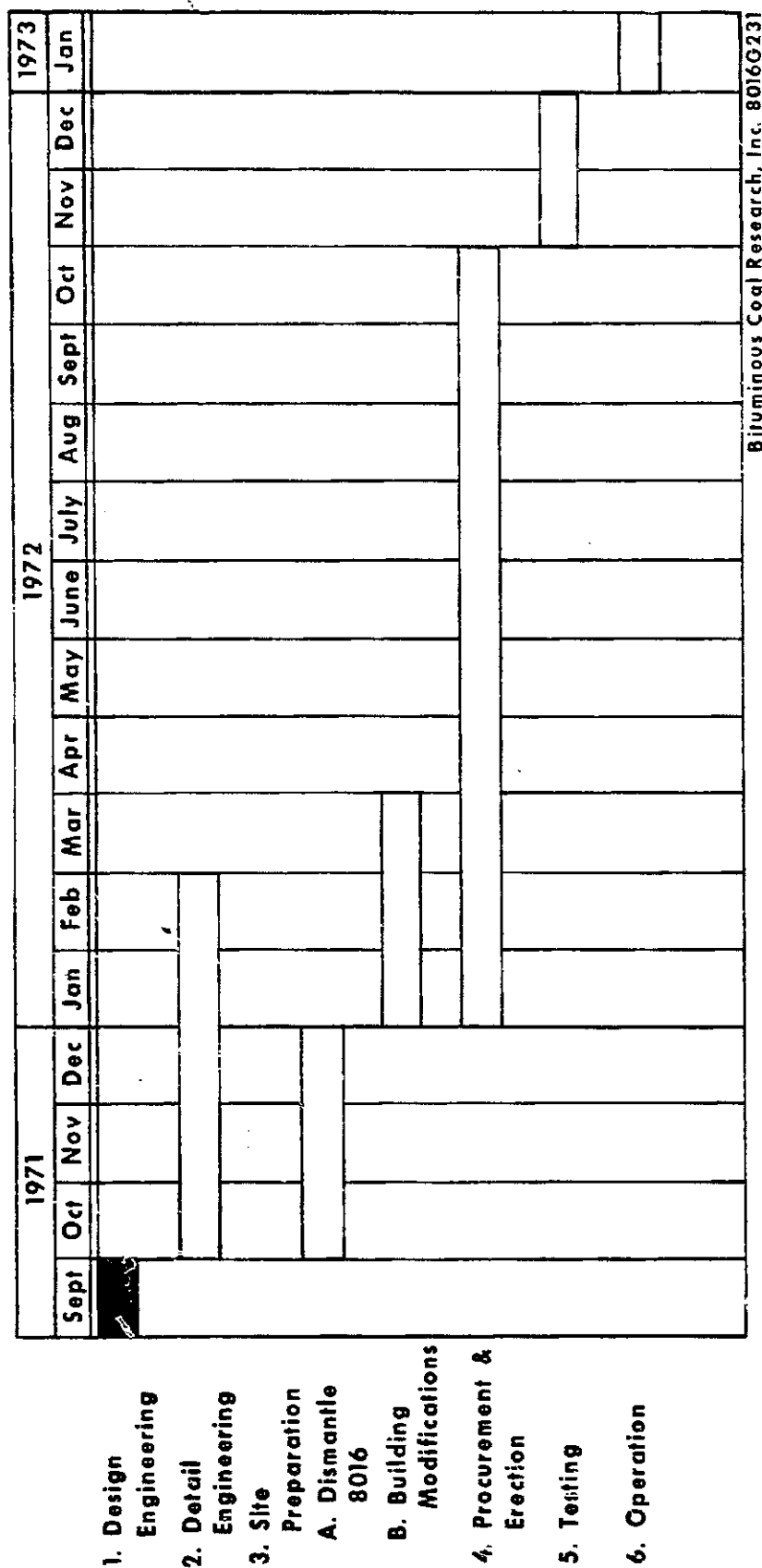
As of September 21, 1971, verbal approval to dismantle the 100 lb/hr Stage 2 PEDU has been received from OCR. Planning is taking place to get the dismantling underway quickly. The major problem areas include the destination of heavy surplus equipment and the storage of reusable materials for both the methanation and fluidized-bed gasification PEDUs. Presently, bids are to be solicited from three contractors for removal of the coal feed tank, gasifier, scrubber unit, structural steel, and the Petrocarb feeder.

Before final technical approval can be given to the PEDU plans by BCR personnel, the methanation reactor design and the fluidized-bed gasifier design must be reviewed by a consulting expert. It is possible that such a review could prevent many problems in the future. Dr. F. Zenz has been contacted and will be available in October to visit BCR for several days.



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Figure 8. Fluidized Bed Methanation Cold Model Unit



Completed Work
 Proposed Schedule

Figure 9. Fluidized Methanator PEDU Time Schedule

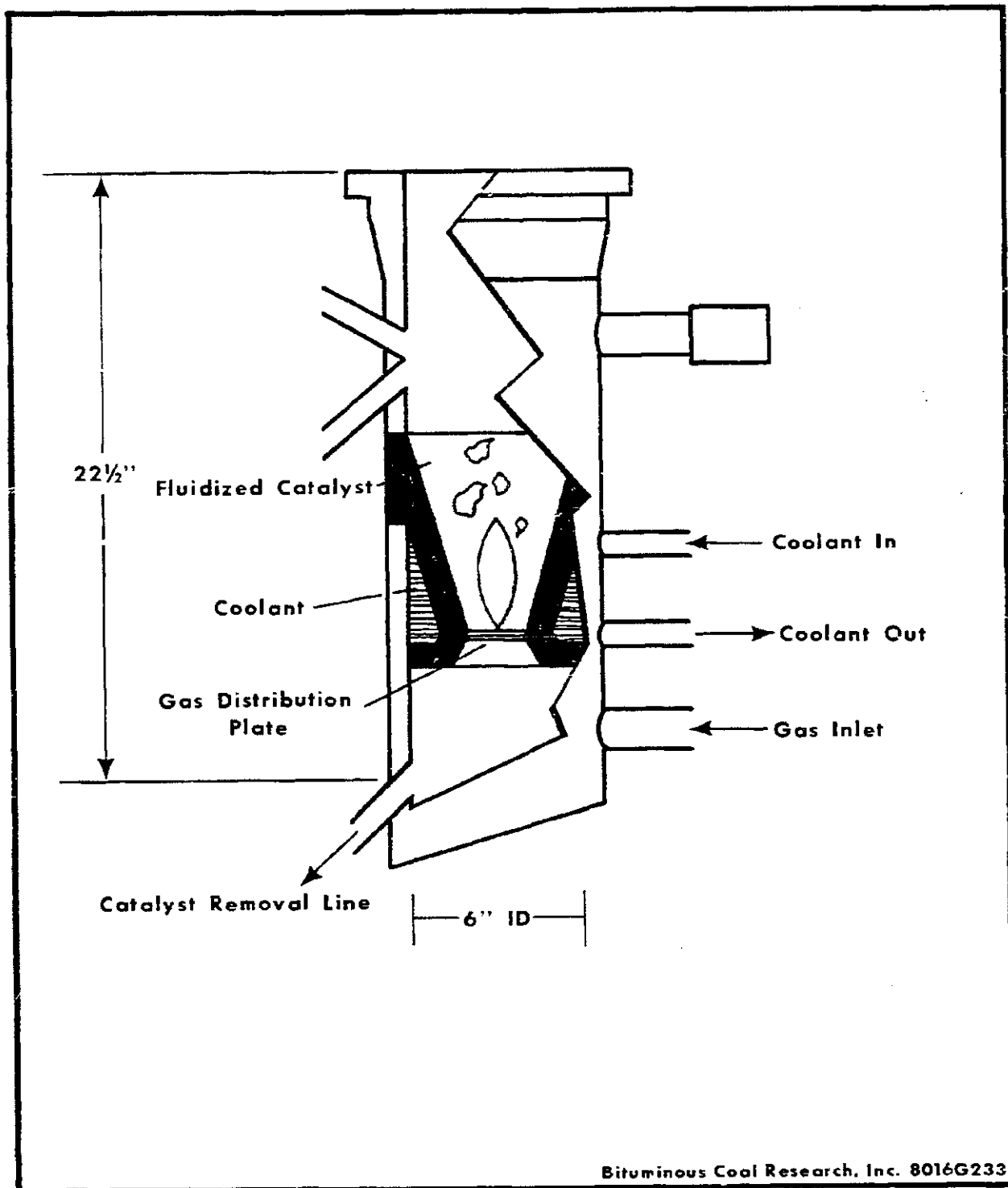


Figure 10. Fluidized Bed Methanation Gas Distributor Design

During the month, Koppers was requested to break down labor hours required for PEDU construction into outside contractor time and BCR labor time. This information has been received. At the time the bid package is submitted, a more detailed breakdown of labor hours will be supplied.

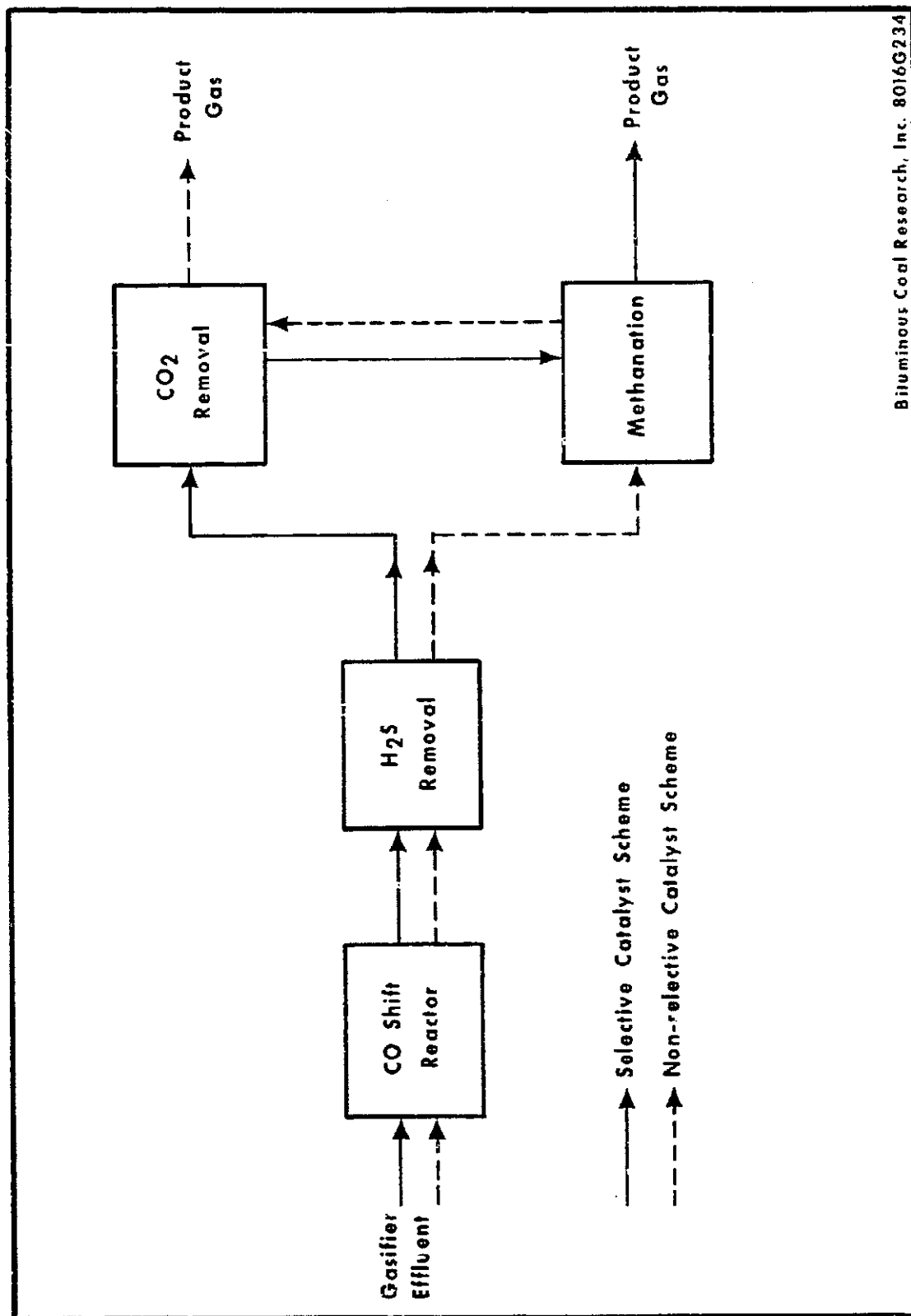
f. Pilot Plant: To date, there has been little attempt to provide a high degree of flexibility in the gasification pilot plant in the area of gas processing. The main reason for this was the lack of data on methanation catalysts. In the last report (Progress Report No. 92, page 3891), an alternate gas processing system for a commercial BI-GAS plant involving a simultaneous shift and methanation synthesis was discussed. While research has not been undertaken to prove the feasibility of such an approach, the discovery of a cobalt-molybdenum catalyst which accelerated both the shift and methanation reactions with a gas which has been preshifted to a hydrogen/carbon monoxide ratio of 3.1/1 has been shown.

In the pilot plant under present design, it has been assumed that a nickel methanation catalyst can be used which will convert carbon monoxide exclusively to methane. To date, no such material has been found; however, this lack of success to date does not admit failure. A reasonable methanation catalyst, cobalt-molybdenum, has been examined in some detail. The use of such a material would not yield acceptable methane contents in the product gas for pipeline quality. The major problem stems from the production of carbon dioxide by the catalyst. To be able to handle such a catalyst in the MPRF, the gas processing train should be slightly modified. Such a revised system, shown in Figure 11, would permit the removal of carbon dioxide either before or after methanation. Scrubbing afterwards would tend to suppress the shift reaction and improve the product gas quality. Selective catalysts could be used in the normal processing train.

g. Conclusions, Recommendations, and Future Work: During the month, progress was made in all areas of methanation studies. Good progress was made on the PEDU design and development. During the month, significant planning in the area of catalyst investigation took place, which should lead to more useful results in the synthesis area.

Work outlined for October includes the following:

- (1) Completion of studies on Catalyst 2684 to determine the critical partial pressure for carbonization.
- (2) Beginning of screening of the new batch of methanation catalysts.
- (3) Increased work in the PEDU area including dismantling of the 100 lb/hr Stage 2 PEDU.
- (4) Further consideration of the pilot plant design based on results from catalyst studies.



5. Analytical Services (J. E. Noll): During the month 68 samples were analyzed. The number of samples and types of analyses requested were as follows:

<u>Type of Analysis Requested</u>	<u>No. of Samples Analyzed</u>
<u>Gas Chromatography</u>	
100 lb/hr PEDU	14
Methanation Unit	34
 <u>Carbon-14</u>	
Gas	17
Liquid	3
Total	68

6. Carbon-14 Procedures (J. E. Noll): No development work was necessary in this area during the month.

7. Gas Chromatographic Procedures (J. E. Noll): No development was necessary in this area during the month.

Future Work: No further work other than routine sample analysis is planned.