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COMBINED SHIFT AND METHANATION IN A FLUIDIZED-BED REACTOR

Quarterly Progress Report for April 1-June 30, 1980

By
Robert C. Streeter

July 1980

Work Performed Under Contract No. AC01-79ET14815

Bituminous Coal Research, Inc.
Monroeville, Pennsylvania

U. S. DEPARTMENT OF ENERGY

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**COMBINED SHIFT AND METHANATION IN A
FLUIDIZED-BED REACTOR**

**QUARTERLY PROGRESS REPORT
FOR THE PERIOD
1 APRIL 1980 - 30 JUNE 1980
(BCR Report L-1122)**

by

Robert C. Streeter

**BITUMINOUS COAL RESEARCH, INC.
350 HOCHBERG ROAD
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JULY 1980

**WORK PERFORMED UNDER CONTRACT
DE-AC21-79ET14815**

for

**U.S. DEPARTMENT OF ENERGY
DIVISION OF ENERGY TECHNOLOGY**

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BITUMINOUS COAL RESEARCH, INC.
DOE-SPONSORED RESEARCH PROGRAM

COMBINED SHIFT AND METHANATION IN A FLUIDIZED-BED REACTOR

Report No. DOE/ET/14815-12
(BCR Report L-1122)

ABSTRACT

Only one bench-scale reactor test was completed during this report period. The Harshaw Ni/Cu/Mo and UCI (composition undisclosed) catalysts were evaluated over a 12-day period at 800 F and a feed gas H_2/CO ratio of 2/1. Initial conversions with both catalysts were about 33 percent; and the activities of both samples declined steadily during the test, with final conversion values in the 15 to 20 percent range.

During this test, problems were experienced with water carryover into the Drierite traps, necessitating some major design changes in the water let-down system.

Two subsequent attempts to initiate a second test at 950 F with these catalysts were unsuccessful when 1) a reactor temperature controller malfunctioned following a weekend power failure, and 2) difficulties in controlling gas flow were traced to contamination of the flow-control valves, which presumably occurred during the earlier problems with water carryover.

A 5-day PEDU test (Test SM-2) was conducted during the week of April 14 to 18, 1980, using the spent Harshaw Ni/Cu/Mo catalyst from Test SM-1 in February. The purpose of Test SM-2 was to continue the data period at $H_2/CO = 1/1$ that was terminated prematurely during the earlier PEDU test. After a brief baseline period ($H_2/CO = 3/1$), during which catalyst activity appeared to be normal, the feed gas was changed to approximately 31 percent H_2 , 31 percent CO , 22 percent CO_2 , and 16 percent CH_4 ; and steam was added to the feed. Some difficulty was experienced in maintaining high bed temperatures, with the result that the steam flow had to be gradually decreased. This may have enhanced catalyst coking, since the catalyst activity generally declined slowly throughout the test, and the final carbon content of the catalyst was 3.6 percent (vs. 2.0 percent at the beginning of the test).

A second 5-day PEDU test (Test SM-3) was conducted during the week of June 23 to 27, 1980, using the Climax Ni/Mo catalyst. Prior to the test, the catalyst was heated for 20 hours in N_2 -diluted air to remove 18 percent carbon that had accumulated during an earlier PEDU test. The rejuvenated catalyst showed very high activity under combined shift and methanation conditions. Once again, however, significant carbon deposition occurred at H_2/CO ratios of 2/1 without steam and 1/1 at a steam/gas ratio of 0.18. On the other hand, this same steam/gas ratio appeared to be effective in inhibiting carbon formation at a H_2/CO ratio of 1.4. The rate of carbon formation under various test conditions was monitored by the periodic removal of catalyst

samples from the reactor. The carbon content of the catalyst increased from 0.4 to 11.3 percent during the test, although, as in the previous PEDU test with this catalyst, this did not impair the catalyst activity. To the contrary, the data indicate that the activity of the catalyst was gradually increasing during the 5-day test.

A brief letter report from Dr. Calvin Bartholomew of Brigham Young University indicates that the BYU support studies on rates of carbon deposition and catalyst regeneration are on schedule.

I. INTRODUCTION AND PROJECT OBJECTIVE

This report presents progress achieved during the period April through June 1980 on the program "Combined Shift and Methanation in a Fluidized-bed Reactor," being conducted by Bituminous Coal Research, Inc., for the U.S. Department of Energy. The program was initiated under Contract No. DE-AC21-79ET14815 on September 25, 1979.

The continuing objective of this program is to demonstrate the feasibility of employing a gas-phase catalytic fluidized-bed reactor to carry out water-gas shift and methanation in a single pass. Successful attainment of the objective will permit methanation of a nonstoichiometric feed gas in an SNG process.

II. SCOPE OF WORK

Tests will be conducted using both bench-scale equipment and a process and equipment development unit (PEDU). The PEDU reactor is a 6-inch I.D., 15-foot long vessel with a reaction zone of approximately 8 feet. The nominal catalyst charge is about one cubic foot.

The combined bench-scale and PEDU studies will be conducted to develop a fluidized-bed process for use in upgrading a coal-derived synthesis gas. Tests will involve the use of synthesis gases with H_2/CO ratios of 2/1 and 1/1, containing CO_2 and CH_4 , to simulate the gasifier products (sulfur-free basis) of several first- and second-generation coal gasification processes. Some tests will involve the addition of steam to the feed gas in an effort to determine its role in inhibiting carbon deposition, as well as its possible adverse effects on the catalyst (e.g., sintering). Nominal test conditions will be 1000 psig pressure and temperatures in the range of 800 to 1100 F.

Additional studies will be undertaken at Brigham Young University on the effects of gas composition, catalyst composition, and support material on the kinetics of carbon formation under representative reaction conditions, and on the kinetics of carbon removal by oxygen. Information from these studies will afford a comparison of the relative sensitivities of the catalyst to carbon fouling, and may provide sufficient basis for an in situ catalyst regeneration process.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Bench-scale Studies: The new bench-scale reactor system, described in the first quarterly report (Report No. DOE/ET/14815-4), was employed during this report period in a test of two catalyst samples. The catalysts evaluated were BCR Lots No. 4533 from Harshaw (Ni/Cu/Mo on alumina) and No. 4438 from United Catalysts, Inc. (undisclosed composition).

After the catalyst samples (2 cc each) were loaded into the fixed-bed reactor tubes, the system was pressurized to 1000 psig and the catalysts were reduced in pure H₂ overnight at 1000 F. The temperature was then decreased to 800 F, and a synthesis gas composed of 40 percent H₂, 20 percent CO, 30 percent CO₂, and 10 percent CH₄ (H₂/CO = 2/1) was admitted to the reactor. The temperature was held constant at 800 F throughout the 12-day test, and no steam was added to the feed gas.

The results of this bench-scale reactor test are shown in Figure 1, in terms of useful conversion* with time. Both catalysts gave essentially the same (although low) initial conversions, and it is evident that conversions decreased steadily throughout the course of the test. The activity of the UCI catalyst was slightly higher than that of the Harshaw catalyst, although the difference is not considered to be significant. The catalyst deactivation was presumably due to coking, since the carbon contents of the spent UCI and Harshaw catalysts were 4.0 and 1.7 percent, respectively.

During this bench-scale test, some problems were experienced with water carryover and condensation in the Drierite traps (the Drierite traps are necessitated by the fact that the flow transducers must operate at a dew-point of at least -60 F). At the conclusion of the test, the traps were found to be plugged. Initially, the product-gas piping was repositioned to allow better gravity flow of water into the water letdown traps.

A second bench-scale test to evaluate the UCI, Harshaw, and Climax (Ni/Mo) catalysts at 950 F (H₂/CO = 2/1) was started on Friday, May 9. During the following weekend, a short power failure occurred while the system was unattended. When power was restored, the reactor temperature controller evidently failed to hold the setpoint and continued to drive the temperature above 950 F. Strip-chart recorder tracings indicated that the reactor temperature exceeded 1200 F during this upset. The catalyst samples were found to be fused inside the tubes and had to be drilled out. There were also further problems with water carryover into the Drierite tubes, even though the

*

$$\text{Useful conversion } (\alpha) = \frac{(\text{CO} + \text{H}_2)_{\text{in}} - K(\text{CO} + \text{H}_2)_{\text{out}}}{(\text{CO} + \text{H}_2)_{\text{in}}} \times 100 \text{ (percent)}$$

where $K = C_{\text{in}}/C_{\text{out}}$. The rationale for this expression was discussed in the quarterly report for October-December 1979 (No. DOE/ET/14815-4).

USEFUL CONVERSION (a), PERCENT

BCR 8070G5

Figure 1. Useful Conversion vs. Time with Catalysts BCR Lots No. 4438 and 4533 at 800F and Feed H_2/CO Ratio 2/1

product-gas piping had been repositioned before the test in an effort to minimize this problem. Consequently, it was decided to redesign the water-trap system. New traps were fabricated from 1-inch Schedule 40 pipe (316 SS) and positioned immediately downstream of the water condensers. The furnace temperature controller was replaced with a less sensitive controller, and the latter was found to function normally following several simulated power interruptions.

The water-trapping system was subsequently tested by operating the steam boiler at pressure with the catalyst sample tubes empty. Although some minor problems were encountered with the level indicators for the steam boiler and water reservoir, the redesigned water traps appeared to be functioning normally. However, considerable difficulties were experienced in adjusting the flow-control valves. The valves were disassembled and found to be contaminated with a pinkish solid, presumably cobalt chloride carried over from the indicating Drierite columns during the previous upsets of the system. The valves were cleaned ultrasonically and reassembled, although one of the valves is still not operating properly. Because of the lengthy delay in putting this system back into operation, it has been decided to proceed with the bench-scale tests using only two of the three catalyst tubes. As in the earlier test at 800 F, the UCI and Harshaw catalyst samples will be employed in the forthcoming test at 950 F.

The indicating Drierite has been replaced with type 4A molecular sieves (4-8 mesh beads), and heat tracing has been added to the desiccant tubes to permit regeneration of the molecular sieves between tests.

B. PEDU Studies

1. PEDU Test No. SM-2: PEDU Test No. SM-2* was conducted over the 5-day period of April 14 to 18, 1980, using the spent Harshaw Ni/Cu/Mo catalyst (BCR Lot No. 4533) recovered following PEDU Test SM-1 in February. The primary objective of Test SM-2 was to continue operation of the system at a feed H_2/CO ratio of 1/1, since operation under these conditions was terminated prematurely during Test SM-1 due to a leak in the main Dowtherm pump.

a. Catalyst Activation: A catalyst charge of 66 pounds (1.16 cu ft at minimum fluidizing velocity) was employed. During startup on April 14, the reactor was purged initially with N_2 , followed by CH_4 ; H_2 and CO from the steam reformer were then gradually blended into the CH_4 until a stoichiometric synthesis gas composition was obtained (60 percent H_2 , 20 percent CO, 20 percent CH_4 ; $H_2/CO = 3/1$). The addition of H_2 and CO to the feed gas was initiated at 3:15 p.m., with bed temperatures at about 480 F. Bed temperatures rose rather slowly over the next two hours to 600 F, then increased more rapidly over the following 3 hours, leveling out at about 950 F. Thus, the catalyst behavior during the activation process was essentially identical to that observed during Test SM-1. The first data period was started at 8:30 p.m.

* SM denotes combined shift/methanation.

b. Summary of PEDU Test No. SM-2 Results: Data on test conditions, feed and product compositions, material balances, and conversions are summarized in Table 1 for the various data periods of PEDU Test No. SM-2. For reasons to be described later, Periods 2 and 3 were divided into shorter data periods. In all of the data periods, the feed gas was introduced entirely through the bottom inlet (distributor zone) of the reactor, with the result that significant bed-temperature differentials (>100 F) were measured in some periods. Consequently, for those particular periods, the average bed temperature has been arbitrarily re-defined as the average of the middle bed and distributor zone temperatures only.

Period 1 was a brief baseline activity check with stoichiometric synthesis gas ($H_2/CO = 3/1$). The results, shown in Table 1, are virtually identical to those obtained in the initial baseline period of Test SM-1 with this catalyst under the same conditions; useful conversion in Period 1 was actually slightly higher (88.6 percent) compared with that from the previous PEDU test (86.0 percent). Thus, the data show that the activity of the catalyst had not declined during previous operation of the catalyst at H_2/CO ratios of 2/1 (36 hours) and 1/1 (14 hours) during Test SM-1.

Period 2, at $H_2/CO = 1/1$, was actually conducted over a time span of 39 hours. The desired feed gas for this period was 31 percent H_2 , 31 percent CO , 22 percent CO_2 , and 16 percent CH_4 on a steam-free basis. However, as the feed-gas composition was being changed in preparation for this period, some difficulty was experienced in attempts to achieve high catalyst-bed temperatures. Under these conditions, bed temperatures are rather sensitive to the amounts of steam and CO_2 in the feed. Consequently, the steam flow was initially decreased to about 7 percent (compared to 11 percent in the $H_2/CO = 1/1$ period of Test SM-1) and the feed-gas temperature was raised to 830 F, 100 degrees higher than in the corresponding data period of Test SM-1.

After Period 2 was initiated, two minor problems were experienced. First, the pressure drop on the catalyst filters began to increase, indicating gradual plugging of the filters. Although several attempts were made to blow back the filters, they were only marginally successful. As the ΔP on the filters increased, flow through the reactor tended to decrease; and efforts were made to compensate for this by incremental increases in the feed-gas pressure. Secondly, a temporary leak developed through the packing of the water-injection pump, resulting in a decrease in the steam flow. Because of these problems, the system was unstable during the early part of the data period. In addition, several changes were made during the course of the period in an effort to optimize catalyst activity. It was decided, therefore, to select for data reduction certain time intervals within the period during which the system was in reasonably steady-state operation.

Period 2A represents an 8-hour data block starting 6.5 hours after the period was formally initiated. As shown in Table 1, bed temperatures were abnormally low, around 820 F. As a consequence, the catalyst activity was also lower than usual, as shown by the decrease in useful conversion and the comparatively large amounts of H_2 and CO in the product gas. Following Period 2A, both the steam and CO_2 in the feed were decreased in an effort to increase bed temperatures.

TABLE 1. PROCESS MATERIAL BALANCE DATA FOR
METHANATION PEDU TEST NO. SM-2

DATA PERIOD	1	2A	2B	2C	3A	3B	4
PERIOD DURATION, hours	3	8	3	2	7	7	3
TEMPERATURES, F							
Feed	764	831	834	832	838	837	843
Distributor	962	815	988	880	948	926	850
Middle Bed	938	826	941	873	928	912	854
Top Bed	864	818	860	841	876	870	835
Bed Average	950*	817	964*	854	938*	888	840
PRESSURE, psia	1017	1031	1017	1014	1016	1016	1011
COMPOSITION DATA, mole percent							
Feed							
Hydrogen	60.8	30.7	34.3	36.1	49.3	49.7	61.3
Carbon Monoxide	21.0	29.1	31.7	29.5	24.0	23.5	20.4
Carbon Dioxide	1.1	19.3	15.0	15.3	15.8	16.2	1.1
Methane	16.9	14.3	15.6	14.9	10.9	10.6	17.2
Ethane	0.2	0.0	0.0	0.0	0.0	0.0	0.0
Steam	--	6.6	3.4	4.2	--	--	--
Product (dry basis)							
Hydrogen	19.3	9.0	2.3	11.3	15.3	16.0	39.8
Carbon Monoxide	0.2	5.1	2.6	5.0	4.2	5.2	2.2
Carbon Dioxide	5.9	48.0	47.0	41.5	37.3	37.6	8.0
Methane	73.2	36.0	46.8	40.5	41.7	39.7	48.7
Ethane	1.4	1.9	1.3	1.7	1.5	1.5	1.3
HYDROGEN/CARBON MONOXIDE RATIO IN FEED	2.90	1.06	1.08	1.22	2.05	2.11	3.01
MASS FLOW RATES, lb/hr							
Gas In	87.7	159.6	163.6	160.2	149.6	150.2	77.6
Steam In	--	9.7	5.3	6.6	--	--	--
Total Out	88.2	169.1	168.6	166.9	150.0	151.1	78.2
Gas Out	61.5	159.6	161.3	156.5	133.8	135.1	62.6
Water Out	26.7	9.5	7.3	10.4	16.2	16.0	15.6
USEFUL CONVERSION (α), percent	88.6	84.2	95.3	83.7	84.3	83.0	67.7
FEED, scfh (dry basis)							
Distributor	3204	2891	3206	3209	3447	3470	2878
Middle Zone	0	0	0	0	0	0	0
Total	3204	2891	3206	3209	3447	3470	2878
SPACE VELOCITY, hr^{-1}	2762	2492	2764	2766	2972	2991	2481
PRODUCT, scfh (dry basis)	1530	2081	2083	2205	2025	2036	1807

* Average bed temperature based on distributor and middle bed temperatures only (see text).

Period 2B represents a 3-hour data block 27 hours into the period. The data in Table 1 show that considerably higher bed temperatures had been achieved (compared with Period 2A), resulting in a significant increase in useful conversion to 95 percent. This conversion level is identical to that achieved during Period 3 ($H_2/CO = 1/1$) of Test SM-1 at an average bed temperature of 912 F and, essentially, the same mass-flow rate (although, as noted earlier, the steam-flow rate was about three times higher during the previous PEDU test). On a CO_2 -free basis, the CH_4 content of the product gas was 88.5 percent in Period 2B, comparable to 89.3 percent in Period 3 of Test SM-1.

During the last 12 hours of Period 2, bed temperatures began dropping, indicating gradual deactivation of the catalyst.

Period 2C includes data from the last two hours of the 39-hour period. At this point in time, pressure in the CO tube trailer had dropped to a level where the flow of supplemental CO was gradually decreasing, resulting in an increase in the feed H_2/CO ratio to 1.2. Even though bed temperatures were slightly higher than at the beginning of the period (e.g., Period 2A), useful conversion had once again dropped to 84 percent, further confirming that the catalyst had suffered some deactivation.

It was then decided to raise the feed H_2/CO ratio to 2/1 in an attempt to duplicate conditions for Period 2 of Test SM-1 (40 percent H_2 , 20 percent CO, 30 percent CO_2 , 10 percent CH_4 , no steam).

Period 3 conditions, like those in Period 2, tended to remain unstable; bed temperatures tended to gradually decrease throughout the period. Thus, although the overall duration of the data period at $H_2/CO = 2/1$ was nearly 17 hours, the period was arbitrarily divided into two segments to show the effect of temperature on conversion.

Period 3A includes data from the first 7 hours of Period 3. It should be noted that the desired level of 30 percent CO_2 in the feed was never achieved. Attempts to increase the feed CO_2 above 16 percent resulted in immediate decreases in the catalyst bed temperature. As shown in Table 1, useful conversion during Period 3A was only 84 percent, with 15 percent H_2 and 4 percent CO in the product, and a product gas CH_4 content of 66 percent on a CO_2 -free basis. By contrast, under comparable conditions during Period 2 of Test SM-1 (e.g., average bed temperature of 940 F, but 30 percent CO_2 in the feed as noted above), useful conversion was 97 percent with 2 percent H_2 and 1 percent CO in the product, and a product gas CH_4 content of 92 percent CH_4 (CO_2 -free basis).

Period 3B includes data from a 7-hour time span near the end of Period 3. The data show that a 50 F drop in the average bed temperature (relative to Period 3A) resulted in a further decrease in useful conversion with corresponding increases in the amounts of H_2 and CO in the product.

Period 4 was a final baseline activity check at a feed H_2/CO ratio of 3/1. Although an effort was made to duplicate the conditions of Period 1, it was not possible to achieve the same high bed temperatures. Consequently, the average bed temperature for the final baseline period was 140 F lower than in the initial period (the feed flow was also lower by about 10 percent). The data in Table 1 clearly show that the catalyst had suffered some deactivation during the test; useful conversion dropped to 68 percent versus 89 percent at the beginning of the test.

c. Changes in Catalyst Properties: It had been planned to withdraw periodic catalyst samples during PEDU Test No. SM-2 to monitor accumulation of carbon with time. However, although the ball valves in the catalyst sampling system were operable, early attempts to collect catalyst samples were unsuccessful; it was confirmed, following shutdown, that the tube leading from the reactor to the catalyst sampling system had become plugged.

The carbon content of the as-charged catalyst (i.e., following the earlier Test SM-1) was 2.0 percent. The carbon content of the bulk spent catalyst from Test SM-2 was 3.6 percent. Earlier experience with this Harshaw catalyst in prior PEDU tests has shown that its activity is adversely affected when the carbon content exceeds about 3 percent. Thus, there is little doubt that the gradual decline in catalyst activity observed throughout Test SM-2 was due to continuing carbon deposition. Furthermore, the results indicate that this occurred fairly early in the test, soon after the H_2/CO ratio was lowered to 1/1.

The particle-size distributions of the as-charged and bulk spent catalyst samples from PEDU Test No. SM-2 are shown in Table 2. These data show that, within the limits of experimental error, there was essentially no change in the size distribution of the catalyst during Test SM-2. The apparent decrease in the amount of fines (<325 mesh) may be due to the fact that a certain amount of this material is entrained and trapped in the inspection ports at the top of the reactor. The results shown in Table 2 are consistent with earlier observations that the Harshaw catalyst tends to approach a limiting size distribution during fluidization, with a fines content in the range of 55 to 60 percent.

d. General Conclusions Concerning PEDU Test No. SM-2: The data from PEDU Test No. SM-2 suggest that a "borderline" situation existed when the catalyst, already containing 2 percent carbon, was exposed to a synthesis gas with a 1/1 H_2/CO ratio. Initial activity data from Period 1 indicate that the catalyst was still highly active after 14 hours of operation at $H_2/CO = 1/1$ during Test SM-1, with 11 percent steam in the feed. However, attempts to return to those conditions during Test SM-2 were unsuccessful, since high bed temperatures could not be maintained at the higher steam inlet flows. It is probable, therefore, that the combination of low bed temperatures and low steam flows accelerated the carbon-deposition process, since the lower activity of the catalyst was immediately apparent after the H_2/CO ratio was increased to 2/1 in preparation for Period 3.

TABLE 2. SIZE DISTRIBUTION OF AS-CHARGED AND BULK SPENT
 SAMPLES OF CATALYST BCR LOT NO. 4533 BEFORE AND AFTER PEDU TEST NO. SM-1

Mesh Size (U.S. Series)	Cumulative Weight, percent*		Mesh Size Fraction	Amount in Designated Mesh Size Fraction, percent	
	No. 4533 As-charged	No. 4533 Bulk Spent		As-charged	Bulk Spent
+ 100	0.3	0.1			
+ 120	0.7	0.8	> 120	0.7	0.8
+ 140	1.3	1.1			
+ 170	3.6	3.4	120 x 170	2.9	2.6
+ 200	6.0	5.7			
+ 230	20.6	20.7	170 x 230	17.0	17.3
+ 270	24.4	23.7			
+ 325	40.3	44.4	230 x 325	19.7	23.7
- 325	100.0	100.0	< 325	59.7	55.6
Mean Particle Diameter, microns	29.5	30.4			

*Determined by dry sieve analysis

From the data obtained in the last two PEDU tests with the Harshaw catalyst, it is concluded that this catalyst can be effectively employed to yield high conversions at a H_2/CO ratio of 2/1 without steam, although a longer period of operation under these conditions would be desirable to confirm this. Operation at $H_2/CO = 1/1$ will apparently lead to fairly rapid deactivation of the catalyst through carbon deposition; such deactivation might be controlled through steam addition, although the data are not sufficiently conclusive to indicate what the optimum steam addition rate should be (e.g., carbon deposition was evidently controlled to some extent during Test SM-1 during 14 hours of operation at a steam/gas ratio of 0.12). In any event, there is no doubt that this catalyst is quite sensitive to deactivation through coking, since it can only tolerate up to about 3 percent carbon by weight. In striking contrast, a different Mo-promoted Ni catalyst was found to tolerate significantly higher carbon levels during PEDU Test No. SM-3, discussed below.

2. PEDU Test No. SM-3: PEDU Test No. SM-3 was conducted over the 5-day period of June 23 to 27, 1980, using the Climax Ni/Mo catalyst (BCR Lot No. 4265). The objective of this test was to evaluate the performance of the catalyst at feed H_2/CO ratios of 2/1 (without steam addition) and 1/1 (with steam addition) over extended time periods.

The catalyst employed in Test SM-3 had been employed in two previous 5-day PEDU tests in April and June, 1979, under an earlier DOE contract.* In the first of these earlier tests (PEDU Test No. 36), all data periods were conducted using a stoichiometric synthesis gas ($H_2/CO = 3/1$), and the carbon content of the spent catalyst was 1.7 percent. The second test (PEDU Test No. 37) included 5-hour and 8-hour data periods at H_2/CO ratios of 2/1 and 1.6/1, respectively, and featured a 43-hour data period with a feed composition simulating the feed to the BI-GAS shift converter on a steam-free basis, based on Stearns-Roger process flow diagrams (H_2/CO ratio = 1.4/1). No steam was added to the feed, and results of a final baseline period ($H_2/CO = 3/1$) at the end of the test indicated that the activity of the catalyst was significantly higher than at the beginning of the test. Surprisingly, the spent catalyst was found to contain nearly 18 percent carbon, although a subsequent bench-scale test confirmed the observation that this unusually high carbon loading had no adverse effect on catalyst activity (e.g., see Quarterly Report No. DOE/ET/14815-4 for October-December 1979, pp. 4-7). Subsequent analytical tests by the catalyst supplier have so far failed to identify the form of carbon present in the catalyst.

Because of the apparent propensity of this Ni/Mo catalyst to promote carbon deposition, one of the particular objectives of Test SM-3 was to monitor this phenomenon by periodic withdrawal of catalyst samples during

* Gas Generator Research and Development - BI-GAS Process: Contract No. EF-77-C-01-1207.

the test. Toward this end, new higher-torque actuators were installed on the ball valves of the catalyst-sampling system prior to the PEDU test to assure that the valves would operate properly.

a. Catalyst Preparation and Activation: Before Test SM-3 was undertaken, the first task was to regenerate the spent catalyst from PEDU Test 37 (i.e., remove the 18 percent carbon). Preliminary bench-scale tests had indicated that this could be accomplished, without adversely affecting catalyst activity, by heating the catalyst in the presence of oxygen (air) at 450 C (842 F). Because of the large amount of material involved (approximately 78 pounds), it was decided to attempt this operation by fluidizing the catalyst in the Stage 1 vessel of the TRI-GAS PEDU system. This approach also permitted monitoring of CO₂ in the product stream to determine when the oxidation was essentially completed.

The carbon burnoff was carried out over a 20-hour period. The oxygen content of the feed was kept below 2 percent initially by blending nitrogen into the feed. During the early part of this process, frequent temperature adjustments were required to maintain a fairly constant reactor temperature of 842 F. The reaction gradually became more sluggish, and the air flow was raised to compensate. Near the end of the burnoff period, the oxygen content of the feed had been raised to about 8 percent, and the catalyst bed temperature was raised to 900 F for about 4 hours.

The bulk of the recovered catalyst had a grayish-green color, indicating that carbon had been effectively removed. A small portion of the catalyst, apparently trapped in dead spots near the grid plate, was still black in color. This material was collected separately and processed further by heating small batches overnight at 842 F in a large muffle furnace.

Although flows were intentionally kept low during the carbon oxidation process, an appreciable amount (approximately 30 percent) of the catalyst was lost during the treatment, presumably as catalyst fines entrained out of Stage 1. Some of this material was recovered from the Stage 1 catchpot, although it was found to be contaminated with coal fines and was discarded. Altogether, about 43 pounds of usable catalyst was recovered from the carbon burnoff operation. The balance of the catalyst charge for Test SM-3 was obtained by crushing and sieving to minus 60 mesh the remaining amount (19 pounds) of the virgin, as-received catalyst which was still on hand. Thus, the total catalyst charge for Test SM-3 was 62 pounds (1.03 cu ft at minimum fluidizing velocity). The carbon content of the mixed, as-charged catalyst was 0.4 percent.

The catalyst activation procedure was basically the same as that described previously for Test SM-2, except that on the advice of the catalyst supplier, the feed H₂/CO ratio was maximized to a value of about 10 during the early part of the process. Once reactor temperatures were above 550 F, the H₂/CO ratio was gradually decreased to 3/1 over a period of about 6 hours, during which time catalyst bed temperatures increased steadily and smoothly to about 875 F. The rate of the methanation reaction did not appear to become significant until bed temperatures were above 800 F.

During this time interval, a catalyst sample was taken, and the new ball valves and actuators were found to be functioning properly.

b. Summary of PEDU Test No. SM-3 Results: Data on test conditions, feed and product compositions, material balances, and conversions are summarized in Table 3 for the various data periods of PEDU Test No. SM-3. As in Test SM-2, all of the feed gas was introduced through the bottom inlet; and, in periods when the temperature differential through the bed was greater than 100 F, the average bed temperature was calculated as the average of the middle-bed and distributor-zone temperatures.

Period 1 was an initial baseline activity check with a stoichiometric synthesis gas ($H_2/CO = 3/1$). The results shown in Table 3 were basically the same as those obtained in earlier PEDU tests under similar conditions. For example, in the first period of PEDU Test No. 36 with the same feed-gas composition, the product-gas composition was 36 percent H_2 , 2 percent CO, 7 percent CO_2 , 54 percent CH_4 , and 1 percent C_2H_6 , with a useful conversion of 71 percent. Thus, the data from Period 1 confirm that the carbon burnoff process prior to Test SM-3 had no adverse effect on catalyst activity.

Period 2 was conducted over a 36-hour period with a feed H_2/CO ratio of 2/1 and no steam addition. As shown in Table 3, a significant reduction in product H_2 occurred, resulting in a useful conversion of 96 percent. On a CO_2 -free basis, the CH_4 content of the product gas was 88 percent. As will be discussed later, the carbon content of the catalyst increased to nearly 8 percent during this data period, without any apparent effect on catalyst activity. In fact, the Dowtherm temperature had to be lowered several times during this period to maintain constant bed temperatures, indicating that the catalyst activity was increasing with time.

Period 3 was conducted at a H_2/CO ratio of 1/1, and steam was added at the maximum achievable rate of 26 pounds/hour, corresponding to a steam/gas ratio of 0.18 in the feed. Once again, a high useful conversion was achieved (95 percent), and the CH_4 content of the product was again 88 percent on a CO_2 -free basis. It had been intended to maintain Period 3 conditions for about 40 hours. However, analysis of catalyst samples taken during this period showed that carbon deposition was continuing at a significant rate. Consequently, it was decided to raise the feed H_2/CO ratio to 1.4. In effect, the objective was to repeat the extended data period of the earlier PEDU Test No. 37 using a feed gas simulating that to the shift converter in the BI-GAS process (41 percent H_2 , 29 percent CO, 22 percent CO_2 , and 9 percent CH_4 on a steam-free basis), and maintaining maximum steam flow in an effort to control carbon deposition.

Period 4, using the BI-GAS shift converter feed with a steam/gas ratio of 0.18, was continued for 19 hours. As shown in Table 3, useful conversion decreased slightly to 92 percent, suggesting that the presence of steam in the feed tended to retard the methanation reaction. In PEDU Test No. 37, under the same conditions, but without steam in the feed, a useful conversion of 98 percent was achieved, with a product gas composition of 1.6

TABLE 3. PROCESS MATERIAL BALANCE DATA FOR
METHANATION PEDU TEST NO. SM-3

DATA PERIOD	1	2	3	4	5
PERIOD DURATION, hours	3	36	22	19	2.5
TEMPERATURES, F					
Feed	762	798	806	784	708
Distributor	907	985	982	982	950
Middle Bed	900	906	927	928	912
Top Bed	858	784	836	840	843
Bed Average	874	946*	954*	955*	931*
PRESSURE, psia	1035	1036	1036	1035	1028
COMPOSITION DATA, mole percent					
Feed					
Hydrogen	62.2	40.1	26.0	33.5	59.0
Carbon Monoxide	20.1	19.9	26.0	24.1	19.4
Carbon Dioxide	0.0	29.2	18.5	18.4	0.0
Methane	17.6	9.8	13.5	7.6	20.7
Ethane	0.1	1.0	0.9	0.8	0.9
Steam	--	--	15.1	15.6	--
Product (dry basis)					
Hydrogen	36.2	2.9	3.2	7.0	18.7
Carbon Monoxide	1.5	0.9	0.9	1.0	0.5
Carbon Dioxide	6.7	55.0	51.5	51.6	4.7
Methane	53.5	39.7	42.7	39.0	74.5
Ethane	2.1	1.5	1.7	1.4	1.6
HYDROGEN/CARBON MONOXIDE RATIO IN FEED	3.09	2.01	1.00	1.39	3.05
MASS FLOW RATES, lb/hr					
Gas In	73.8	171.0	173.0	162.0	74.5
Steam In	--	--	25.6	26.7	--
Total Out	73.1	169.5	197.0	185.8	72.9
Gas Out	57.6	154.7	172.8	155.1	55.1
Water Out	15.5	14.8	24.2	30.7	17.8
USEFUL CONVERSION (α), percent	73.8	96.1	95.3	92.4	87.6
FEED, scfh (dry basis)					
Distributor	2866	3073	3030	3056	2757
Middle Zone	0	0	0	0	0
Total	2866	3073	3030	3056	2757
SPACE VELOCITY, hr^{-1}	2782	2983	2942	2967	2677
PRODUCT, scfh (dry basis)	1640	1872	2157	1971	1391

* Average bed temperature based on distributor and middle bed temperatures only (see text).

percent H_2 , 0.2 percent CO , 55.3 percent CO_2 , 42.8 percent CH_4 , and 0.1 percent C_2H_6 . However, during that earlier test, the carbon content of the catalyst also rose to 18 percent, as noted previously.

Period 5 was the final baseline activity check at a feed H_2/CO ratio of 3/1. By comparison with the results of Period 1, the data show that the catalyst activity had increased significantly during the course of the 5-day test; a useful conversion of nearly 88 percent was obtained in the final baseline period. Once again, these results parallel the performance of the catalyst in PEDU Test No. 37, where useful conversion increased from 80.0 percent in the initial baseline period to 87.5 percent in the final baseline period (despite the presence of 18 percent carbon). This tendency toward increasing activity with time is believed to be due to the slow reduction of molybdenum-containing sites.

c. Carbon Deposition and Changes in Catalyst Properties: The accumulation of carbon on the catalyst with time during Test SM-3 is shown in Figure 2. The shaded areas indicate the relative durations of the five steady-state data periods.

It can be seen that carbon buildup began during Period 2 ($H_2/CO = 2/1$) and that the rate was increasing markedly with time. The addition of steam during Period 3 ($H_2/CO = 1/1$) apparently decreased the rate of carbon deposition, although carbon formation was still occurring at an essentially linear rate with time.

Despite some scatter in the data points, possibly due to nonrepresentative samples, the results for Period 4 indicate that steam addition at a steam/gas ratio of 0.18 was effective in inhibiting any further carbon buildup at a H_2/CO ratio of 1.4. The carbon content of the bulk spent catalyst was 11.3 percent, essentially the same as that of samples taken during Period 4.

The particle size distributions of the as-charged and bulk spent catalyst samples from PEDU Test No. SM-3 are shown in Table 4. Also shown in Table 4 is a normalized particle-size distribution for the spent catalyst, which was calculated by assuming that all of the carbon was in the minus 325-mesh fraction (i.e., the calculated values approximate the size distribution of the spent catalyst on a carbon-free basis).

The data show that the fines content (<325 mesh) increased by 11 percent absolute (4 percent on the carbon-free basis). This compares favorably with results of the two previous 5-day PEDU tests; increases of 5 percent and 14 percent were observed in PEDU Tests 36 and 37, respectively. It may be recalled that about 31 percent of the initial catalyst charge was from previously unused material. Thus, an increase in the fines content of 4 to 5 percent over a 5-day period is considered quite acceptable; even though the fines content of this silica-alumina catalyst approached 40 percent during the test, this is well within operating limits, considering that similar PEDU tests with certain alumina-supported catalysts have resulted in fines contents in the range of 55 to 60 percent (e.g., see Table 2).

Figure 2. Accumulation of Carbon on Catalyst BCR Lot No. 4265
During PEDU Test No. SM-3

TABLE 4. SIZE DISTRIBUTION OF AS-CHARGED AND BULK SPENT
SAMPLES OF CATALYST BCR LOT NO. 4265 BEFORE AND AFTER PEDU TEST NO. SM-3

Mesh Size (U.S. Series)	Cumulative Weight, percent*			Amount in Designated Mesh Size Fraction, percent			
	No. 4265 As-charged	No. 4265 Bulk Spent	Bulk Spent, Normalized†	Mesh Size Fraction	As-charged	Bulk Spent	Bulk Spent, Normalized†
+ 100	2.0	0.2	0.2				
+ 120	3.5	0.7	0.8	> 120	3.5	0.7	0.8
+ 140	4.5	1.3	1.4				
+ 170	10.3	6.3	7.1	120 x 170	6.8	5.6	6.3
+ 200	16.7	11.9	13.4				
+ 230	45.9	36.3	41.0	170 x 230	35.6	30.0	33.9
+ 270	52.1	42.9	48.3				
+ 325	67.3	56.1	63.3	230 x 325	21.4	19.8	22.3
- 325	100.0	100.0	100.0	< 325	32.7	43.9	36.7
Mean Particle Diameter, microns	39.9	34.8	37.6				

* Determined by dry sieve analysis.

† Calculated on a carbon-free basis, assuming all carbon is in the minus 325-mesh fraction.

d. General Conclusions Concerning PEDU Test No. SM-3: During PEDU Test No. SM-3, the Climax Ni/Mo catalyst continued to show its propensity to undergo carbon formation at lower H_2/CO ratios. Just as importantly, however, the presence of carbon (in this case up to 11 percent) had no adverse effect on the catalyst activity. To the contrary, the catalyst activity actually increased gradually throughout the test.

It is known from previous experience with this catalyst (i.e., PEDU Test No. 37) that it can tolerate at least 18 percent carbon. This raises the interesting question as to what the upper limit of tolerance might be; this question also involves ramifications concerning reactor volume, bed pressure drop, and fluidization properties of the catalyst as the carbon content increases.

Although Period 4 was of limited duration, the data therefrom indicate that a steam/gas ratio as low as 0.18 was effective in inhibiting carbon formation at a H_2/CO ratio of 1.4. By implication, carbon formation should be controllable at lower H_2/CO ratios through increased steam flow.

Apart from its tendency to promote carbon formation, the catalyst showed very high activity under combined shift and methanation conditions. Since the possibility of catalyst "regeneration" (i.e., carbon removal) has been demonstrated, perhaps the most suitable application in terms of shift/methanation operation would be a process involving catalyst regeneration and recycle, the feasibility of which has been well established in the technology of fluid-bed reactors.

C. BYU Studies: A brief letter report, dated June 30, 1980, was received from Dr. Bartholomew. Progress on Task 1 (measurement of carbon deposition rates) is on schedule. Preliminary studies are still in progress on Task 2 (measurement of rates of carbon removal with O_2). Tasks 3 and 4 (measurement of deactivation rates and changes in metal surface area) are underway, although catalytic wall effects have been identified in the Berty CSTR reactor at temperatures above 400 C (752 F), and these will have to be quantified to correct existing data.

D. Visitors During April, May, and June 1980

April 15, 1980

Dr. Clarence Karr, Jr.
DOE-METC
Morgantown, WV 26505

April 23, 1980

Dipl.-Ing. Klaus Weinzierl
Dipl.-Ing. Jürgen Poller
VEW Hauptverwaltung
Postfach 941
4600 Dortmund 1, W.Germany

May 16, 1980

Dr. Edmond Tucci
Johnson Matthey, Inc.
4 Malin Road
Malvern, PA 19355

E. Trips and Meetings During April, May, and June 1980

May 28-30, 1980

Pittsburgh Catalysis Society
Annual Spring Symposium
Monroeville, PA 15146

R. C. Streeter

IV. WORK PLAN AND SCHEDULE

Bench-scale reactor tests will be continued as planned.

A PEDU-scale sample of the UCI catalyst, based on BCR Lot No. 4438, is expected to be delivered by the end of July. Accordingly, a PEDU test to evaluate this catalyst is tentatively scheduled for the week of August 11 to 15, 1980.

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