COMBINED SHIFT AND METHANATION IN A
FLUIDIZED-BED REACTOR

QUARTERLY PROGRESS REPORT
FOR THE PERIOD
1 OCTOBER 1979 - 31 DECEMBER 1979
(BCR Report L-1061)

MASTER

by

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350 HOCHBERG ROAD
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JANUARY 1980

WORK PERFORMED UNDER CONTRACT
DE-AC01-79ET14815

for

U.S. DEPARTMENT OF ENERGY
DIVISION OF ENERGY TECHNOLOGY

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Printed in the United States of America

Available from

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy ^{5.40} ~~\$4.00~~
Microfiche \$ 3.00 ⁵⁰

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4. Title Combined Shift and Methanation in a Fluidized-bed Reactor		
5. Type of Document ("x" one) ☒ a. Scientific and technical report ☐ b. Conference paper: Title of conference _____ _____ Date of conference _____ Exact location of conference _____ Sponsoring organization _____ ☐ c. Other (Specify Thesis, Translations, etc.) _____		
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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/14815-4
(BCR Report L-1061)

ABSTRACT

Construction of a new bench-scale methanation reactor is in progress. This system will provide the capability of adding steam to the feed gas.

A bench-scale activity test, employing four samples of a Ni/Mo catalyst, was conducted using the existing life test system. Results showed that a spent catalyst sample containing 18 percent carbon was still as active as the fresh, as-received catalyst, thus confirming an earlier observation based on the results of PEDU Test No. 37.* The activity of one sample that was previously heated at 450 C to remove the carbon seemed abnormally low. However, the results were inconclusive, and this sample will be tested further.

No PEDU tests were scheduled during this report period. Some planned modifications to the PEDU reactor system are being delayed due to late delivery of a water injection pump and malfunctioning of new ball valves intended for installation on the catalyst sampling system.

Arrangements have been made with Dr. Calvin Bartholomew of Brigham Young University to undertake continued studies on carbon deposition and catalyst regeneration. A research proposal submitted by Dr. Bartholomew has been reviewed and approved, and the BYU work is expected to commence early in January 1980.

I. INTRODUCTION AND PROJECT OBJECTIVE

This report presents progress achieved during the period October through December 1979 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-AC01-79ET14815 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.

* Conducted in June 1979 under an earlier contract, and discussed in Report No. FE-1207-66, July 1979

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 catalysts 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: Under an earlier contract,* the activity and thermal stability of methanation catalysts were screened in a bench-scale life test reactor system. The life test system consists of four small parallel fixed-bed reactors, fabricated from 1/8-inch I.D. copper-clad stainless steel tubes, encased in a heated aluminum block.

It was originally planned to modify this system to permit the blending of steam into the feed gas. However, it was subsequently determined that such modifications would require substantial revisions in design of the system, so it was decided to leave the original system intact and build a new reactor system.

The new bench-scale system is shown schematically in Figure 1. The system incorporates a feedwater reservoir and steam boiler, and water flow rate will be measured by means of a level indicator. The synthesis gas mixture is introduced to the reactor tubes through a preheated manifold. Since the program schedule specifies testing of three catalysts at a time, the new reactor system incorporates only three catalyst tubes. The new system also contains larger water traps to compensate for the presence of steam in the feed gas.

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

3.

Figure 1. New Bench-Scale Methanation System

Gas flow will be regulated using three "Norriseal" miniature flow control valves (Dover Corp.).

The entire reactor system is being mounted on a specially constructed metal frame to facilitate portability. Figures 2 and 3 are photographs of the reactor system and sample furnace, respectively, in their present state of development. Construction of the system is expected to be completed by the end of January, 1980.

Also during this report period, the older apparatus was employed in a life test of several samples of the Ni/Mo catalyst, BCR Lot No. 4265, which was evaluated under the earlier contract during PEDU Tests No. 36 and 37. The four samples included in this test were 1) the fresh catalyst (which had been prepared by grinding and sieving the as-received catalyst to minus 100 mesh); 2) the spent catalyst from PEDU Test No. 36, containing 1.7 percent carbon; 3) the spent catalyst from PEDU Test No. 37, containing nearly 18 percent carbon; and 4) a sample of the spent catalyst from PEDU Test No. 37 that had been heated in air at 450 C (842 F) for 2 hours to reduce the carbon content to 1.5 percent.

The objectives of this test were twofold. First, it was desired to confirm the observation, from PEDU Test No. 37, that the presence of the unusually large amount of carbon in the catalyst had no apparent adverse effect on its activity. Secondly, it was necessary to determine whether the heat treatment to remove carbon might have also caused the catalyst to suffer some loss of activity. The test was conducted using a stoichiometric feed gas (20 percent CO, 60 percent H₂, 20 percent CH₄). Catalyst samples were reduced in pure H₂ overnight at 1000 F before the synthesis gas was admitted. As is the usual procedure, the temperature was initially increased through the range of 800 to 1100 F by daily increments of 50 F. This was followed by two cycles where the temperature was raised within a few hours from 800 to 1000 F. The samples were then maintained at 800 F for 4 days, and finally at 900 F for 11 days at the end of the test.

The results of this test are shown in Figure 4 in terms of useful conversion versus reactor temperature. BCR employs the concept "useful conversion" (α) with the belief that this is a more meaningful measure of the efficiency of the methanation process, since both CO and H₂ are included in the expression. Useful conversion is defined as

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

where $K = C_{\text{in}}/C_{\text{out}}$, the gram-atomic ratio of carbon in the feed to carbon in the product. The "in" and "out" terms are moles/hr in the feed and product, respectively. The carbon ratio is used to compensate for small errors in the mass balance by putting all conversion calculations on a common basis so that data from different tests can be compared more consistently. The inclusion of H₂ in the conversion calculation tends to "normalize" for the effect of the shift reaction, since decreases in the CO_{out} term due to water-gas shift

8070P1

Figure 2. New Bench-Scale Methanation Reactor System Under Construction (December 1979)

8070P2

Figure 3. Sample Furnace for New Bench-Scale Methanation Reactor

Figure 4. Life Test Results With Four Samples of Methanation Catalyst
 BCR Lot No. 4265 (H_2/CO Ratio = 3/1)

are offset by equivalent increases in the H_{2out} term. Some other workers base conversion only on the amount of CO reacted, regardless of whether via shift or methanation; we feel this approach can result in misleadingly high conversion numbers.

Figure 4 shows that the sample containing 18 percent carbon performed as well as the fresh catalyst throughout the test, thus confirming the conclusion based on the results of PEDU Test No. 37. On the other hand, the activities of the spent catalyst from PEDU Test No. 36 and the regenerated catalyst, although acceptable initially, tended to decrease after the first 800 to 1100 F heating cycle.

When the reactor tubes were emptied at the conclusion of this test, it was discovered that the regenerated catalyst was mixed with the alundum used as a bed support material. Thus, there was evidently a pressure surge through this reactor tube at some time during the test which resulted in a disturbance of the catalyst bed. Concerning the spent catalyst from PEDU Test No. 36, there was no indication of any disturbance of the catalyst. Since this sample did not show any loss of activity during the PEDU test (and, in fact, it was used again in PEDU Test No. 37, during which gross carbon deposition occurred), its performance in this latest bench-scale activity test appears to be anomalous. It is possible that the catalyst suffered some kind of thermal degradation (e.g., sintering) above 1000 F, since the data show that its activity was the highest of the four samples during the initial 800 to 1000 F phase of the testing. (Catalysts are not normally exposed to temperatures above 1000 F during a PEDU test.) However, this explanation is tenuous since two other samples of the same catalyst survived exposure to the higher temperatures with no apparent adverse effects.

Because of the inconclusive results for the regenerated catalyst, discussed above, it was decided to repeat the test. A new test is currently in progress, and after 4 weeks during which the temperature has ranged from 800 to 950 F, the regenerated catalyst has shown essentially the same level of activity as the fresh catalyst. The results of this test will be presented in the next quarterly report.

B. PEDU Studies: No PEDU tests were conducted during this report period. Work is underway to modify the PEDU system by 1) increasing the capacity of the water injection pump for steam addition, and 2) increasing the reliability of the catalyst sampling system by adding two new ball valves.

A second pump body, which will double the capacity of the existing water injection system, was ordered early in October, 1979. Delivery was originally quoted as 3 weeks. However, the pump supplier later advised that this item was not in stock, and that delivery would be delayed until mid-February, 1980.

The ball valves were originally ordered under the previous contract, and were received early in this report period. After the valves were installed on the catalyst sampling system, however, it was found that one of the valves was leaking badly. The valve was returned to the manufacturer, who reported that further testing failed to reveal any malfunction. The valve was then

reinstalled on the PEDU reactor, but subsequent pressure tests revealed that it was still leaking, regardless of which side of the valve was pressurized. In addition, the second ball valve in the system also began to leak during this testing. At the suggestion of the supplier, both ball valves, as well as the pneumatic actuators, have been returned to the manufacturer for further examination.

C. BYU Studies: A research proposal was received from Dr. Calvin Bartholomew of Brigham Young University (BYU). The proposed program involves work in the following four areas:

1. Kinetic studies of carbon formation using thermogravimetric analysis (TGA) techniques. Studies would be carried out at H_2/CO ratios of 2/1 or lower, over the temperature range of 350 to 500 C (662 to 932 F).

2. Kinetic studies of carbon removal by dilute oxygen mixtures using TGA techniques, over the temperature range of 250 to 350 C (482 to 662 F).

3. Catalyst coking rates at high pressure (1000 psig) using a Bertly CSTR reactor, at temperatures of 400 and 450 C (752 and 842 F).

4. Measurement of catalyst metal surface areas by H_2 chemisorption. This work would be done in conjunction with future BCR studies on possible catalyst degradation in the presence of steam.

The BYU studies are scheduled to commence during the early part of January, pending notification of appropriate DOE personnel.

D. Visitors During October, November, and December 1979

November 2, 1979

Dr. Claus Flockenhaus
Didier Engineering GmbH
43 Essen
Alfredstrasse 28, W. Germany

Dr. Werner Lommerzheim
Thyssengas GmbH
41 Duisburg-Hamborn
Duisburgerstrasse 161, W. Germany

E. Trips and Meetings During October, November, and December 1979

November 13, 1979 (Dr. Clarence Karr) E. K. Diehl
Morgantown Energy Technology
Center, P. O. Box 880
Morgantown, WV 26505

IV. WORK PLAN AND SCHEDULE

Construction of the new bench-scale methanation reactor will continue. The system is expected to be ready for checkout tests early in February.

Efforts are continuing to resolve the problems related to the water injection pump and ball valves for the PEDU reactor. A PEDU test is tentatively scheduled for the latter part of February.

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