

RECENT DEVELOPMENTS IN
FLUIDIZED-BED METHANATION RESEARCH

By

Robert C. Streeter
Supervising Scientist

Bituminous Coal Research, Inc.
350 Hochberg Road
Monroeville, Pa. 15146

Presented at

NINTH SYNTHETIC PIPELINE GAS SYMPOSIUM
October 31 - November 2, 1977

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represent that its use would not infringe privately owned rights.

SPONSORED BY

AMERICAN GAS ASSOCIATION

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

AND

INTERNATIONAL GAS UNION

RAMADA O'HARE INN
CHICAGO, ILLINOIS

RECENT DEVELOPMENTS IN FLUIDIZED-BED METHANATION RESEARCH

by

Robert C. Streeter*

INTRODUCTION

The evolution of the BCR dry (vapor-phase) fluidized-bed methanation process has been described in three earlier papers presented at these symposiums.^{1,2,3} Development of the fluidized-bed methanation process has been necessarily tailored to meet the requirements of the BI-GAS coal gasification process. Thus, to avoid the cost of final pipeline gas compression, the methanator was designed to operate at a pressure of 1000 psig. In addition, it is desirable to operate the methanator at as high a temperature as practicable to recover the heat of reaction as useful steam for the process. These rather severe operating conditions impose some difficult requirements relative to the temperature stability of the catalyst as well as the heat removal capability in the methanator.

Early in the formulation of the BI-GAS program, BCR elected to proceed with the development of the fluid-bed methanation concept because of the following potential advantages over the existing fixed-bed methanation technology:

1. Temperature gradients are minimized and hot spots are less likely to occur due to the turbulence within the catalyst bed.
2. Higher heat-transfer coefficients are possible because of the motion of catalyst particles past internal heat-transfer surfaces. Thus, control of exothermic reactions is much easier.
3. The superior heat removal capability of the fluid-bed system permits the use of higher partial pressures of reactant gases and eliminates the need for product gas recycle for temperature control.
4. Continuous addition and removal of catalyst is possible, eliminating the need to shut down the methanator to replace the catalyst charge.

Because of the high reactant concentrations (e.g., approximately 20 percent carbon monoxide in the feed) anticipated in the fluid-bed methanator, it was foreseen that conventional fixed-bed methanation catalysts, such as the CRG-types, would not be suitable for fluid-bed operation due to their

*Supervising Scientist, Bituminous Coal Research, Inc.

higher metal loadings; these catalysts, designed for treating synthesis gases with carbon monoxide contents on the order of 5 percent or less, would simply have been too active for our Fluid-bed application. Consequently, a major emphasis in the BCR program has been to evaluate fluid-bed methanation catalysts, developed by commercial catalyst suppliers, specifically designed to provide the desired levels of activity and thermal stability under the process conditions outlined earlier.

Fluid-bed methanation tests are carried out in the Process and Equipment Development Unit (PEDU) at BCR. The PEDU reactor has been described in detail in earlier publications.^{1,3} In our presentation at the Eighth Symposium last year,³ we noted that the dry fluidized-bed methanation process had been proven feasible for methanating, with high conversions, synthesis gases containing up to 25 percent carbon monoxide without recycle, and with very acceptable heat removal capability using internal heat-transfer surface immersed in the catalyst bed.

This paper will discuss the results of several PEDU tests using the BI-GAS pilot-plant methanation catalyst, including recent data on catalyst attrition and reactor heat-transfer characteristics.

PEDU OPERATION

We are still actively evaluating new catalyst samples at the bench-scale level. However, with the advent of BI-GAS pilot plant startup operations at Homer City, Pa., attention in the PEDU test program was logically turned toward a more thorough evaluation of the methanation catalyst originally selected for use at Homer City. This is a Harshaw catalyst, containing nickel, copper, and molybdenum on an alumina support.⁴

During the past year, five PEDU tests have been conducted using four separate splits of the Homer City methanation catalyst. These tests have resulted in a combined 30 days of operating experience with the catalyst under a wide variety of conditions.

The first PEDU test was designed as a factorial experiment to investigate the effects of temperature, pressure, feed-gas flow rate, and carbon dioxide addition to the feed on conversions. The data showed that temperature was the most important variable, with conversions increasing by about 12 percent (absolute) for an increase in bed temperature of 100 F. Succeeding PEDU tests have been designed to more closely duplicate the actual conditions being encountered during startup operations at Homer City, as illustrated by the following examples:

1. Preliminary tests of the gasifier operation are being conducted at a pressure of 750 psig, rather than the normal design pressure of 1000 psig. Accordingly, several data periods in recent methanation PEDU tests have been conducted at this lower pressure to establish whether this would affect the

behavior of the catalyst. Results to date indicate that operation of the methanator at the reduced pressure is feasible, with no substantial decreases in the conversions obtained.

2. In the PEDU reactor system at BGR, catalysts are normally activated (reduced) in a hydrogen-rich synthesis gas (hydrogen/carbon monoxide ~ 9/1). At Homer City, however, there is no provision for generating and blending supplemental hydrogen into the methanator feed-gas stream. Therefore, it became important to determine whether the catalyst could be activated using (1) normal synthesis gas at design operating conditions, and (2) a synthesis gas predicted from actual gasifier operation, under the nonideal conditions obtained in preliminary startup tests.

In the first instance, the catalyst was successfully activated using a feed gas of 60 percent hydrogen, 20 percent carbon monoxide, and 20 percent methane at 1000 psig with a feed-gas temperature of 750 F. In the second instance, catalyst reduction was accomplished using a feed gas of 47 percent hydrogen, 16 percent carbon monoxide, 14 percent carbon dioxide, 8 percent methane, and 15 percent nitrogen (the basis for this feed composition will be discussed below) at 750 psig and a feed-gas temperature of 520 F. In both cases, catalyst bed temperature was found to be a critical variable, and catalyst activity was very low until a "light-off" temperature of about 600 F was exceeded. Thereafter, the catalyst reduction proceeded smoothly without any sudden temperature excursions, and the catalyst appeared to reach its maximum activity within a few hours under both sets of conditions.

3. Gasifier tests were initiated before the Selexol acid gas removal system was completely operational. Consequently, some consideration was given to the possibility of either partially or completely bypassing the Selexol system, on an interim basis, with the result that the methanator feed would have an abnormally high carbon dioxide content. In addition, initial gasifier tests have required the use of nitrogen as purge gas for the coal spray-drying system. Although this is only a temporary situation, it will lead to higher than normal nitrogen concentrations in the methanator until integrated plant operations can be achieved. In view of these considerations, it was decided to attempt operation of the PEDU methanator under somewhat unconventional conditions, using a feed gas based on preliminary BI-GAS plant analyses (47 percent hydrogen, 16 percent carbon monoxide, 14 percent carbon dioxide, 8 percent methane, and 15 percent nitrogen).

During the last two PEDU tests, several data periods have been completed while operating with this unconventional feed gas (as well as some variations of it). Again, reactor temperature was found to be an important variable, and achieving the desired bed temperatures was slightly more difficult because of the abnormally high concentration of inerts (nitrogen, methane,

carbon dioxide) in the feed. Nevertheless, with bed temperatures close to 900 F, useful conversions* on the order of 90 percent were obtained and product carbon monoxide concentrations were about 1.5 percent.

CATALYST ATTRITION

One of the most frequent concerns expressed about the reliability of the fluid-bed methanation process is whether destruction of the catalyst through attrition will be a serious problem. Throughout the BCR catalyst evaluation program, we have tested the attrition resistance of the more promising catalysts in a small laboratory-scale unit. Although these tests are useful for comparing the attrition resistance of different catalyst types, it is difficult to translate the results to actual methanator operation since the lab-scale test is a short-term, accelerated attrition test, conducted with air at ambient pressure and temperature on a sample of the catalyst from which the fines have been removed.

We have also routinely measured the particle size distribution of catalyst samples before and after each PEDU test. Figure 1 shows typical results of these measurements for the Homer City catalyst before and after an 8-day PEDU test, and it is evident that the fines (minus 325 mesh fraction) increased and the relative amounts of all other size fractions decreased during the test. Again, however, this information tells nothing about how the size changes occurred throughout the course of the test.

Near the end of 1976, a catalyst sampling system was added to the PEDU reactor, as shown in Figure 2. It consists of two 1-inch graphite-seated ball valves with pneumatic actuators separated by a heavy-walled pipe nipple approximately 3/4-inch I.D. and 11 inches long. The internal volume of the sample chamber is roughly 4 cu in., permitting the withdrawal of about 100 grams of catalyst at each sampling. The sampling system is located near the mid-point of the catalyst bed.

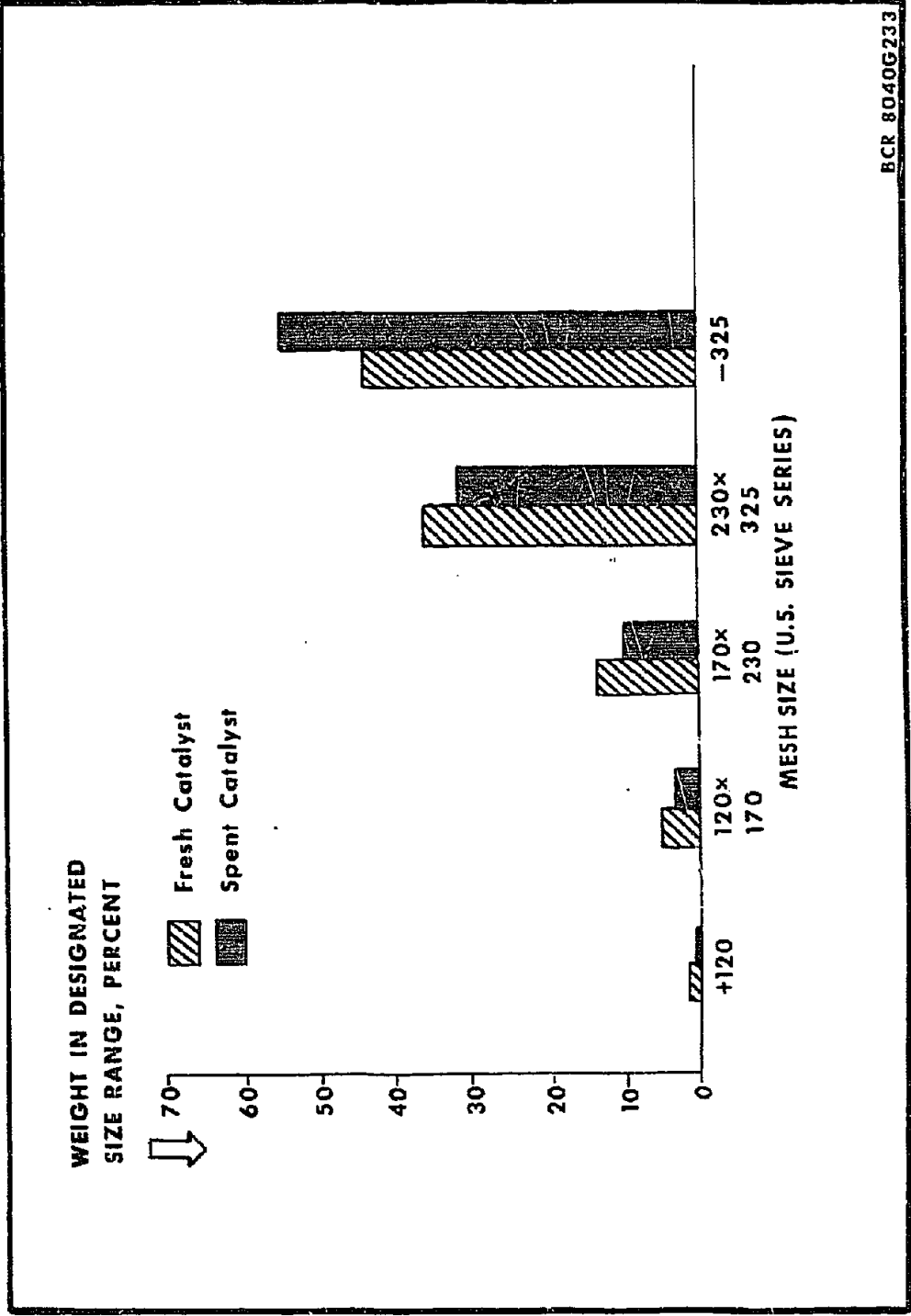
Not surprisingly, after a short period of operation, abrasion of catalyst in the valve seats caused slow leakage through the valves. This was overcome by pressurizing the sampling system with nitrogen to slightly above reactor pressure, so that any leakage would be nitrogen into the reactor.

$$* \text{ Useful Conversion (\%)} = \frac{(\text{CO} + \text{H}_2)_{\text{in}} - K(\text{CO} + \text{H}_2)_{\text{out}}}{(\text{CO} + \text{H}_2)_{\text{in}}} \times 100$$

where $(\text{CO} + \text{H}_2)_{\text{in}}$ = moles/hr of CO and H₂ in the feed

$(\text{CO} + \text{H}_2)_{\text{out}}$ = moles/hr of CO and H₂ in the product

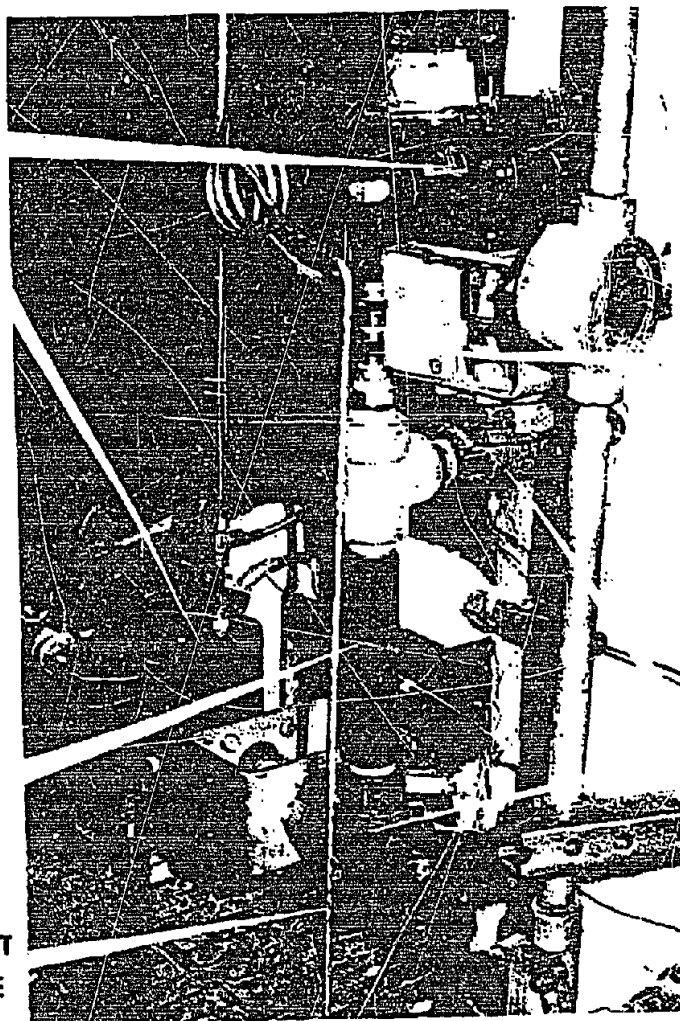
$K = C_{\text{in}}/C_{\text{out}}$, carbon ratio



BCR 8040G233

Figure 1. Particle Size Distribution of Catalyst BCR Lot No. 3631 Before and After PEDU Test No. 22

**PNEUMATIC
ACTUATORS**



**FRITTED
METAL
FILTER TUBE**

**REACTOR
OUTLET**

**BALL
VALVES**

**CATALYST
SAMPLE
CHAMBER**

**VENT
LINE**

8040P168

**Figure 2. Methanation PEDU Catalyst
Sampling System**

After the catalyst sampling system was installed, it was operated at frequent intervals during two succeeding PEDU tests with the Homer City catalyst. The samples were sieved, and the results of the sieve analyses are shown in Figure 3. Once again, it can be seen that the fines content of the catalyst increased with time while the amounts in the coarser size fractions decreased (although in one instance, the amount of the 230 x 325 mesh fraction remained reasonably constant). However, the most notable feature of the data shown by Figure 3 is that the size changes took place within the first few hours of fluidization; the catalyst appeared to reach a limiting size distribution which then remained essentially unchanged throughout the duration of the test. These results are consistent with data reported by Forsythe and Hertwig on attrition characteristics of fluid-bed cracking catalysts.⁵ These earlier investigators observed marked decreases in the attrition rate with time during laboratory accelerated attrition tests. This behavior was attributed to the early buildup of fines in the catalyst bed as the weaker particles broke apart and rough edges were smoothed off the coarser particles. These authors concluded that the fines tend to reduce the severity of attrition in two ways; by a cushioning effect which lessens the force of impact between coarser particles, and by dilution which reduces the number of coarse particles available for attrition.

Initially, there was some question as to the validity of the data shown in Figure 3, since it is possible that there is some stratification of particle sizes in the catalyst bed, raising doubt as to whether samples withdrawn from the center of the bed are representative of the bulk catalyst. This was checked prior to the last PEDU test. The reactor was charged with fresh catalyst and a sample was withdrawn before the bed was fluidized. The bed was then fluidized with nitrogen and additional catalyst samples were withdrawn after 5- and 40-minute intervals. The size distributions of the 5-minute sample and the sample before fluidization were not significantly different from that of the bulk fresh catalyst. On the other hand, the size distribution of the 40-minute sample had definitely changed in the same fashion as shown by Figure 3 (increased fines, generally decreasing amounts of coarser size fractions).

In summary, the evidence available to date for this catalyst indicates that attrition is not a significant problem after the first few hours of methanator operation. However, it should be recalled that the PEDU reactor is not designed for catalyst makeup and recycle; fines are trapped out on sintered metal filters. No attempt has been made yet to estimate the potential losses of fines through the cyclone in the BI-GAS pilot-plant methanator.

REACTION PROFILES

As an added bonus with the catalyst sampling system, described above, we now have the capability to withdraw batch samples of gas from the middle zone of the reactor. Full use has been made of this capability during the three most recent PEDU tests, and analyses of these mid-zone gas samples have led to some interesting conclusions as to what is happening inside the reactor.

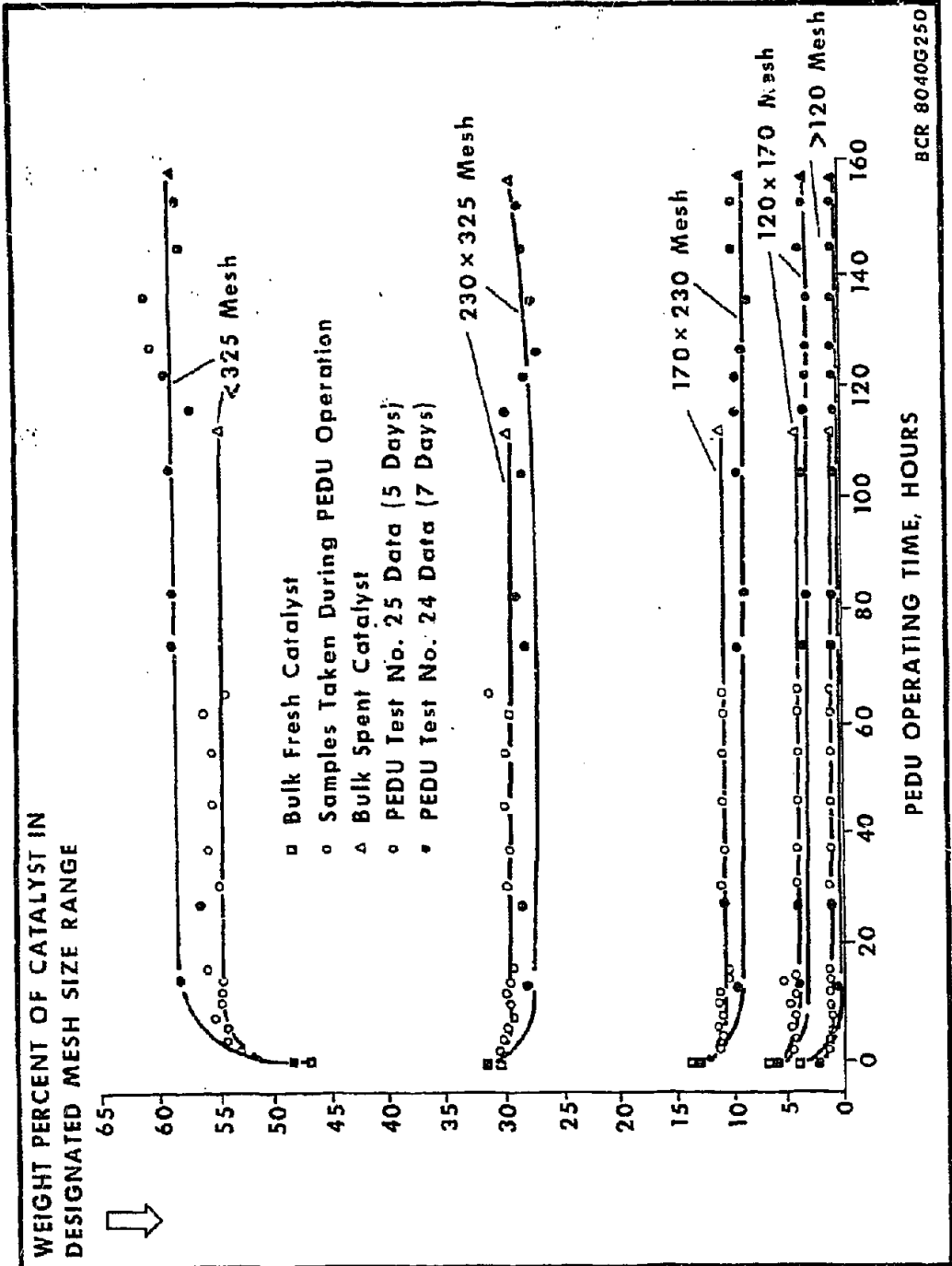


Figure 3. Change in Catalyst Particle Size Distribution with Time During PEDU Operation

To interpret these results, it is useful to consider the reactor as a series of two fluid beds. The intermediate "product" flow from the lower catalyst bed can be estimated from the mid-zone gas composition using a forced carbon balance and the known feed flow and composition at the bottom of the reactor. This intermediate "product" is then also the feed to the upper catalyst bed; or, in cases where the feed is split, it is added to the middle-zone feed (which is measured separately) to obtain a composite upper-zone feed gas. With these data, plus the known flow and composition of the final product gas, it is possible to calculate material balances for both the upper and lower parts of the catalyst bed.

Results of these calculations for four selected data periods are shown in Table 1. The hydrogen/carbon monoxide ratio of the feed was approximately 3/1 in each of these data periods. In the first case, where all of the feed was introduced at the bottom of the reactor, practically all of the reaction was taking place in the lower part of the catalyst bed. Of the amount of carbon monoxide available for reaction at the middle of the bed, nearly 80 percent passed through the upper part of the bed unreacted, with the result that the useful conversion in the upper zone of the reactor was practically nil. In the last three cases, increasing proportions of the feed were introduced at the middle part of the bed. As shown in Table 1, conversions in the upper part of the bed increased progressively with the amount of synthesis gas introduced. In addition, from the relative amounts of carbon dioxide produced in the upper zone, it appears that the shift reaction predominates originally when the proportion of the feed gas introduced to the upper zone of the reactor is small; as the percentage of the feed to the upper zone increases, the methanation reaction becomes more pronounced.

Regardless of the amount of synthesis gas fed to the middle part of the reactor, most of the methanation evidently takes place in the lower (hotter) part of the catalyst bed. This was always suspected, but never confirmed until the collection of middle-zone gas samples became possible. Based on this finding, we reasoned that it should be possible to operate with less than the normal catalyst charge and still obtain acceptable conversions. To verify this, approximately 40 percent of the original catalyst charge was intentionally removed from the reactor near the end of PEDU Test No. 25. As a result, the space velocity in the following data period was higher than that normally achieved by a factor of 1.6. In spite of this, a high useful conversion (81 percent) was still obtained and only 1 percent carbon monoxide remained in the product (i.e., 95 percent of the feed carbon monoxide reacted).

The available PEDU data on reaction profiles suggest that it would be desirable to utilize the intermediate feed spargers on the Homer City methanator. Splitting the feed appears to offer the advantages of more efficient utilization of the catalyst, potentially higher throughputs, and more nearly isothermal temperatures in the catalyst bed.

TABLE 1. CALCULATED LOWER AND UPPER ZONE CONVERSIONS FOR SELECTED DATA PERIODS
FROM FEDU TESTS NO. 24 AND 25

Test No., Zone	Temperature, F	Percentage of Feed Gas Introduced	Feed H ₂ /CO Ratio	CO Fed, scfh	CO Converted, mole percent			CO Unreacted, mole percent	Useful Conversion, percent
					CH ₄	CO ₂	C ₂ H ₆		
Test No. 24, Period 2									
Lower Zone	785	100	3.1	540.2	69.2	22.5	4.3	4.0	70.3
Upper Zone	748	---	29.5	21.4	15.7	5.1	2.2	77.0	4.1
Test No. 25, Period 2									
Lower Zone	861	85	2.9	528.9	88.0	8.4	2.7	0.9	86.5
Upper Zone	839	15	5.6	95.9	5.0	75.5	4.5	15.0	16.4
Test No. 24, Period 7									
Lower Zone	845	81	2.8	389.2	86.6	10.4	2.2	0.8	88.6
Upper Zone	811	19	4.5	93.1	57.7	35.4	3.2	3.7	46.7
Test No. 24, Period 6									
Lower Zone	892	60	2.9	431.4	88.3	10.2	0.7	0.8	89.9
Upper Zone	874	40	3.4	286.8	70.0	24.8	2.2	3.0	62.7

HEAT-TRANSFER DATA

In our status report for 1976,³ we discussed attempts to fit our heat-transfer data to a correlation originally developed by Wender and Cooper⁶ for fluid-bed reactors. At that time, we acknowledged that although a correlation was apparent, it did not fit the one predicted based on the Wender and Cooper approach. In essence, the discrepancy arose from the fact that the predicted bedside heat-transfer coefficients were from 2 to 10 times higher than those actually measured. To explain this discrepancy, we speculated that the cause was due to one (or possibly a combination) of three reasons:

1. The close spacing of the vertical-finned heat exchanger tubes in the PEDU reactor may have been interfering with good solids mixing.
2. The non-axial location of some of the tubes might have reduced the overall efficiency of the heat-transfer system.
3. The fins themselves may have been preventing good catalyst contact at the tube surface.

In an effort to resolve these discrepancies in the heat-transfer data, some of the finned tubes were removed from the reactor prior to PEDU Test No. 23, resulting in more free space between the remaining finned tubes. However, the data from PEDU Test No. 23 showed that there was no significant change in the heat-transfer coefficients due to the wider spacing of the tubes.

The next step was to install a bare (unfinned) heat-transfer tube in the lower zone of the PEDU reactor. This bare tube was fabricated from the same material, and had the same dimensions, as the finned tube remaining in the reactor lower zone. The two tubes were mounted adjacent to each other in the methanator.

Both the bare and finned tube loops were in use during PEDU Tests No. 24 and 25, and a dramatic difference was observed in the heat-transfer characteristics of the system. Overall heat-transfer coefficients for the finned tube remained at about 25 Btu/(hr)(sq ft)(°F) whereas the overall coefficient for the bare tube was higher by a factor of four at about 100 Btu/(hr)(sq ft)(°F). Moreover, as shown in Figure 4, the data for the bare tube show a much better fit to the predictive correlation of Wender and Cooper than do the data for the finned tube.

The large difference in the heat-transfer characteristics of the bare and finned heat exchanger tubes confirms that in the PEDU reactor, the vertical fins are not necessary to achieve adequate heat transfer. To the contrary, the advantage of greater heat-transfer surface from the addition of the fins is offset by the close spacing (approximately 1/8-inch) between the fins, which presumably restricts the rapid exchange of catalyst particles with the tube surface. This finding has significant implications relative to the scale-up design of fluid bed heat-transfer systems.

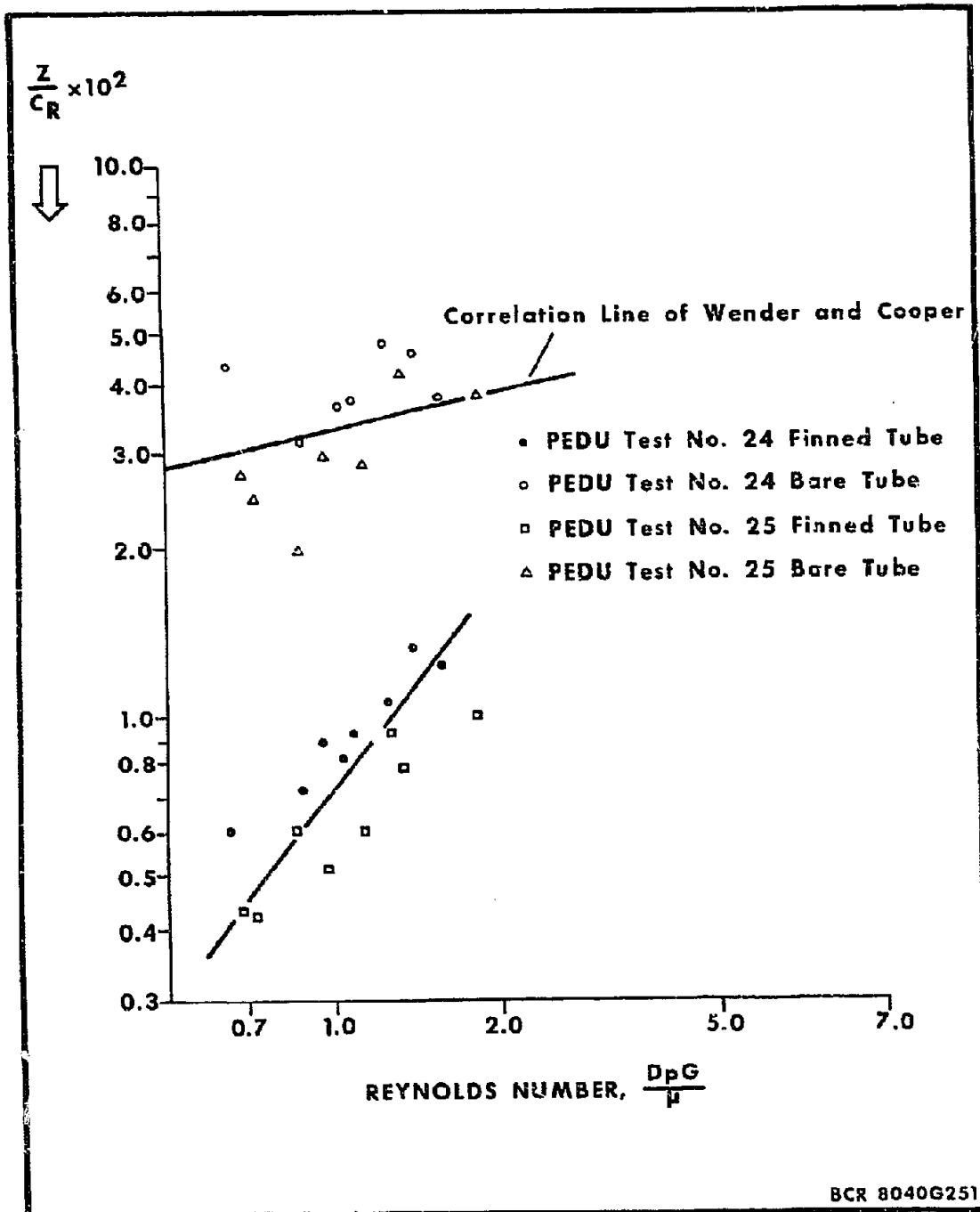


Figure 4. Z Factor Correlation for Data from PEDU Tests No. 24 and 25

CARBON DEPOSITION

As noted earlier, recent PEDU tests have involved operation of the methanator with some unconventional feed gases. These gas compositions can be represented graphically on a triangular diagram in terms of the atom-percentages of carbon, hydrogen, and oxygen present in the mixture,⁷ as shown by Figure 5. The isotherm on the graph is a boundary above which carbon deposition is thermodynamically possible at the designated temperature and pressure.

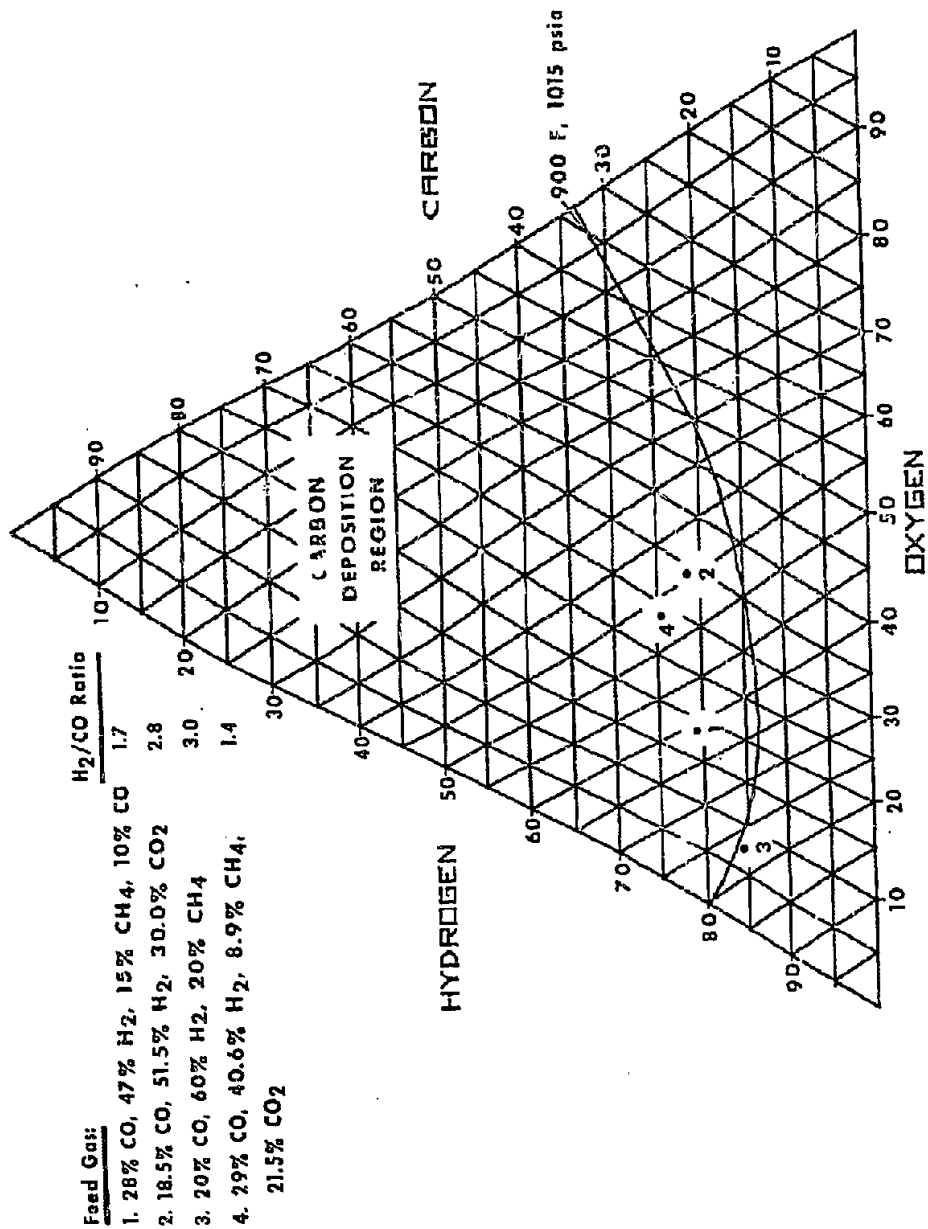
Among the four gas compositions shown on Figure 5, only the third one (i.e., "normal" synthesis gas) is below the carbon deposition boundary at 900 F and 1015 psia. Nevertheless, the PEDU fluid-bed methanator has been operated for extended periods of time with all the feed gases listed on Figure 5, and no serious carbon deposition problems were encountered. This simply indicates that the rates of competing reactions (i.e., methanation and shift) were great enough to prevent the carbon-forming reactions from approaching equilibrium.

On the other hand, a phenomenon has been encountered during several recent PEDU tests which did, in fact, result in some carbon buildup in the methanator. These upsets invariably occurred between steady-state operating periods, while changes were being made in reactor conditions and/or feed gas composition. In every instance, the upset was initiated by a drop in catalyst bed temperature to below 600 F (i.e., below the catalyst "light-off" temperature). It should be emphasized that these temperature losses resulted from difficulty in controlling reaction conditions as changes were being made to the system, rather than from prior carbon deposition on the catalyst.

After bed temperatures had dropped, most of the feed gas passed through the catalyst bed unreacted. Subsequently, localized hot spots developed in the disengaging zone of the reactor, notably at the catalyst filters, as the raw synthesis gas came into contact with catalyst fines collected on the filters. We are not certain as to what temperatures might have been reached. However, in one instance, sintered copper filters were being used which had been reinforced at the seams by silver soldering. At the conclusion of the test, the filters were examined, and it was found that the silver solder completely melted at some of the seams. Since silver solder melts at about 1300 F, it is evident that this temperature had been exceeded during the thermal upset.

Residues remaining on the catalyst filters were found to contain abnormally high carbon contents---up to nearly 70 percent in one case. In addition, carbon contents of the bulk spent catalyst samples were on the order of 2 to 3 percent. This is not exceedingly high, although it is about twice the amount normally observed in the spent catalyst.

Generally, there was at least a temporary decline in catalyst activity following these temperature upsets, although in most cases it was difficult to determine whether this was due to catalyst deactivation (coking) or the fact that the reactor was being operated under rather adverse conditions.



BCR 8040G236

Figure 5. Carbon Deposition Diagram for Total Equilibrium at 900F and 1015 psia

In situations where the upset was followed by a return to normal operating conditions, the catalyst appeared to return eventually to its original activity level.

Because the available evidence indicates that the formation of carbon is associated with the occurrence of hot spots near the reactor outlet (i.e., in the presence of high methane concentrations), there is a strong possibility that the carbon-forming reaction involves thermal decomposition of methane



rather than disproportionation of carbon monoxide



The equilibrium constants of reactions 1 and 2 at 1000 K (1340 F) are 10.3 and 0.6, respectively.⁸

COMBINED SHIFT AND METHANATION

As far as the BCR methanation research program is concerned, the possibility of simultaneously carrying out water-gas shift and methanation in a single reactor is certainly not a novel concept. Almost exactly 4 years ago, in October 1973, BCR filed a patent application* on a combined shift and methanation process based on the vapor-phase, fluid-bed catalytic reactor.⁹

Nearly all of our methanation PEDU tests to date have involved periods of operation at hydrogen/carbon monoxide ratios below 3, with synthesis gases simulating the feed to the shift converter in the BI-GAS process. Until recently, however, we were unable to operate below a hydrogen/carbon monoxide ratio of 1.6 because of design limitations on the natural gas reformer.

In the latest PEDU test with the Homer City methanation catalyst, arrangements were made to add supplemental carbon monoxide to the feed from compressed gas cylinders. Because of the limited capacity of the cylinders, operating time was restricted to one data period at a hydrogen/carbon monoxide ratio of 1.4 and a second, very short data period at a hydrogen/carbon monoxide ratio of 1.1. The first of these data periods (hydrogen/carbon monoxide = 1.4) was especially significant, since the synthesis gas exactly reproduced the feed to the BI-GAS shift converter on a dry, steam-free basis (41 percent hydrogen, 29 percent carbon monoxide, 21 percent carbon dioxide, 9 percent methane). Under these conditions, at an hourly gas space velocity of about 2500 and a catalyst bed temperature of 900 F, a useful conversion

*The patent was subsequently issued in September, 1975.

of 97 percent was obtained. Analysis of the material balance data showed that about 60 percent of the feed carbon monoxide was methanated and about 37 percent was shifted (of the balance, 1 percent was converted to ethane and 2 percent remained unreacted). Hydrogen generated via the shift reaction accounted for 20 percent of that consumed in methanation. No carbon deposition problems were apparent throughout a 4-hour, steady-state period of operation, even though the feed composition was well into the region of potential carbon formation (point 4, Figure 5).

In view of these encouraging preliminary results, we are planning to convert part of the present nitrogen storage facility to carbon monoxide storage, to enable us to conduct further, more extended tests on combined shift and methanation. So far, no tests have been conducted with the addition of steam to the feed gas. However, this capability also exists through the availability of a high pressure steam boiler at the PEDU site.

SUMMARY

During the past year, a valuable data base has been established for the methanation catalyst to be employed as the initial charge in the BI-GAS pilot-plant methanator. Five PEDU tests have resulted in a total of 30 days of operating experience with the catalyst. The behavior of the catalyst has been characterized both at normal design operating conditions and at sub-normal conditions that could be encountered during startup operations at Homer City.

Data have been obtained on catalyst attrition rates, heat transfer, and reaction patterns within the catalyst bed that should be useful in both operation and scale-up of the pilot-plant methanator.

In the coming year, bench- and PEDU-scale tests will be continued with the objective of finding other catalysts acceptable for use in the vapor-phase, fluidized-bed methanation process. Additional emphasis will be placed on studies of the combined shift/methanation process, as well as the sulfur tolerance of the more promising catalysts. With regard to the latter, BCR initiated a joint research program with Dr. Calvin Barrholomew of Brigham Young University in July, 1977. The objectives of this 9-month program will be to determine (1) the maximum hydrogen sulfide concentrations to which these catalysts can be exposed before undergoing irreversible deactivation, (2) the effects of reactor operating variables on the sulfur tolerance level, and (3) which catalyst types show the highest resistance to hydrogen sulfide poisoning. The BYU group has developed considerable expertise in this area as a result of over 2 year's involvement in a separate research program on the deactivation of nickel and ruthenium alloy catalysts.

ACKNOWLEDGMENT

The work described in this paper was conducted under the sponsorship of the U.S. Energy Research and Development Administration and the American Gas Association under ERDA Contract No. EF-77-C-01-1207.

REFERENCES

1. Graboski, M. S. and Diehl, E. K., "Design and operation of the BCR fluidized-bed methanation PEDU," Fifth Synthetic Pipeline Gas Symposium, Chicago, Ill., 1973. 17 pp.
2. Diehl, E. K., Stewart, D. L., and Streeter, R. C., "Progress in fluidized-bed methanation," Sixth Synthetic Pipeline Gas Symposium, Chicago, Ill., 1974. 19 pp.
3. Streeter, R. C., Anderson, D. A., and Cobb, J. T., Jr., "Status of the BI-GAS program, Part II - Evaluation of fluidized-bed methanation catalysts," Eighth Synthetic Pipeline Gas Symposium, Chicago, Ill., 1976. 43 pp.
4. Alcorn, W. R. and Cullo, L. A. (to Harshaw Chemical Co.), "Nickel-copper-molybdenum methanation catalyst," U.S. Pat. 3,962,140 (June 8, 1976). 8 pp.
5. Forsythe, W. L., Jr. and Hertwig, W. R., "Attrition characteristics of fluid cracking catalysts," Ind. Eng. Chem. 41 (6), 1200-1206 (1949).
6. Wender, L. and Cooper, G. T., "Heat transfer between fluidized-solids beds and boundary surfaces - correlation of data," A.I.Ch.E. Journal 4, 15-23 (1958).
7. White, G. A., Roszkowski, T. R., and Stanbridge, D. W., "Predict carbon formation," Hydrocarbon Process. 54 (7), 130-136 (1975).
8. Stull, D. R. and Prophet, H., "JANAF Thermochemical Tables, Second Edition," Vol. 37, Washington, D.C.: Nat. Bur. Stand., June 1971.
9. Graboski, M. S. and Donath, E. E. (to United States of America), "Combined shift and methanation reaction process for the gasification of carbonaceous materials," U.S. Pat. 3,904,386 (Sept. 9, 1975). 7 pp.