

Pipeline Gas

By Methanation of Synthesis Gas over Raney Nickel Catalyst

Preparation, handling, and start-up procedures for fluid-bed Raney nickel methanation catalyst have been sufficiently improved to indicate economical use and successful scale-up

ONE method for the production of high-heating value (pipeline) gas from coal comprises gasification of the coal with steam and oxygen to a low-heating value synthesis gas, followed by catalytic conversion of the hydrogen and carbon monoxide content of the purified synthesis gas to methane (7, 17). In earlier studies of the methanation step the development of fixed-bed reactors has been stressed. Supported nickel catalysts were employed almost without exception.

Fluid-bed reactors are well suited for the methanation process because of the high rates of heat transfer obtainable with relatively simple heat exchange equipment. However, restriction of the possible range of operating conditions by the fluidization characteristics of the solids-gas system employed and catalyst attrition are major problems. Further, scale-up of fluid-bed reactors for synthesis operations is known to be difficult and was not fully demonstrated on a commercial scale until recently (7).

Attempts to utilize fluid-bed iron catalysts in small reactors have not been successful, and the performance of supported nickel catalysts has been difficult to reproduce (6). However, partially extracted Raney nickel has shown promise for fluid-bed operation (3, 4, 14).

This study demonstrated that the performance of Raney nickel as a fluid-bed methanation catalyst depends largely on the extent of aluminum conversion during caustic treatment; 65% aluminum conversion, mostly to alumina trihydrate, resulted in a final preparation of high activity. Rapid mechanical deterioration was overcome by pre-drying the catalyst and by slow start-up in hydrogen. A total methane yield of about 20,000 standard cubic feet (SCF) per pound of original Raney alloy

was repeatedly attained in laboratory operation with synthesis gases containing less than 0.01 grain of sulfur per 100 SCF.

In a 6-inch diameter pilot unit, the total methane yield was considerably lower because of more rapid decrease in catalyst activity. However, operation with a catalyst charge prepared from 0.5 cubic foot of alloy was satisfactory for about 500 hours, and catalyst loss was small. Improved catalyst preparation methods and fluid-bed reactor design should permit approach of laboratory results, thereby reducing catalyst cost to about 5 cents per thousand standard cubic feet of methane.

Experimental

Equipment and Procedure. In the work reported here, the catalysts were prepared by caustic leaching of 40- to 200-mesh Raney alloy, with a nominal composition of 42% (weight) nickel and 58 % (weight) aluminum (13). Synthesis gas was usually produced by catalytic steam reforming of natural gas in a tube furnace (9), and, in some instances, by suspension gasification of coal with steam and oxygen in a slagging downflow pressure reactor (15). Facilities were available to increase the hydrogen to carbon monoxide ratio of synthesis gas produced from coal from the usual 1 to 1 up to 1.5 to 1 range to about 3 to 1 by catalytic conversion of carbon monoxide and added steam to hydrogen and carbon dioxide. However, it was preferred to simulate the composition of synthesis gas from coal after carbon monoxide shift and before carbon dioxide removal by adding carbon dioxide from bottle storage to 3 to 1 hydrogen to carbon monoxide ratio reformed natural gas.

Except for a limited number of tests of sulfur tolerance, synthesis gas was purified, by passage through fixed beds of iron oxide and activated carbon, to a sulfur content of less than 0.01 grain per 100 standard cubic feet (SCF, at 60° F., 30 inches of mercury, and saturated with water vapor); generally the sulfur content was about 0.001 grain per 100 SCF. Analytical procedures for sulfur compounds in synthesis gas have been presented elsewhere (10).

Catalyst evaluation tests and process variable studies were made in a battery of 1.049-inch inside diameter, Dowtherm-jacketed reactors similar to those described by Greyson and others (6, 14). The effect of catalyst preparation on initial activity and total methane production capacity was determined with purified synthesis gases of approximately 3 to 1 hydrogen to carbon monoxide ratio and either negligible or 30 mole % average carbon dioxide content.

Nominal test conditions were: space velocity, 10,000 SCF per cubic foot of catalyst volume per hour; reactor pressure, 75, 150, and 300 p.s.i.g.; and initial alloy volume, 100 cc. (Space velocities are based on the initial dry alloy volume.) A systematic study was also made of the variables of feed gas composition (hydrogen to carbon monoxide ratio, carbon dioxide, and organic sulfur content), feed gas space and superficial velocity, and operating pressure. Catalyst bed temperature was controlled by adjusting pressure in the Dowtherm jacket and reflux condenser, with the Dowtherm maintained at the boiling point by an electric heater surrounding the jacket. Temperatures, although difficult to maintain constant throughout the bed because of the high exothermicity of the reaction, were normally in the 700° to 800° F. range.

A pilot unit of 3000 SCF per hour nominal synthesis gas capacity was also operated with catalyst charges prepared from 0.5 cubic foot of alloy to establish the feasibility of scale-up. The reaction zone was constructed of 6-inch, Schedule 40 pipe. It was 8.5 feet high, jacketed with 8-inch pipe, and contained six bayonet heat exchangers fabricated from 0.75-inch, Schedule 40 pipe. An enlarged disengaging section at the top contained four sintered stainless steel filters, 18 inches long and 3 inches in diameter. Hot product gas was passed through these filters (0.0008- to 0.0015-inch mean pore size) to prevent catalyst carryover.

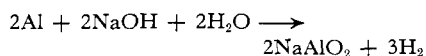
Dowtherm A circulating through the jacket and the six bayonets heated the catalyst to reaction temperature at the start of operation and, as increasing quantities of exothermic heat of reaction were released, removed heat from the catalyst bed. This was accomplished by controlling the Dowtherm temperature between the limits of 750° F. (corresponding to a vapor pressure of 144 p.s.i.g.) and 496° F. (the atmospheric boiling point) with a gas-fired heater upstream from the reactor and a flash chamber and reflux condenser downstream from the reactor. The flash temperature was controlled with a nitrogen back-pressure system. The high circulation rate (30 gallons per minute) allowed most of the Dowtherm to remain in liquid form.

Catalyst Preparation and Handling.

The crushed 42% (weight) nickel-58% (weight) aluminum alloy was supplied by the Raney Catalyst Co., Chattanooga, Tenn. Metallographic examination showed that the catalyst particles were highly fractured and consisted of regions of Ni_2Al_3 (gamma) phase surrounded by NiAl_3 (beta) phase, separated by regions of a fine-grained eutectic mixture consisting of alpha phase [less than 0.05% (weight) nickel] and beta phase. The gamma phase was more resistant to caustic attack than the other two phases, although x-ray analyses of caustic-treated alloy indicated the presence of all three original phases even when the aluminum content had been reduced to 5% (weight) or less. The major crystalline product of caustic leaching in the catalyst was identified by x-ray as β -alumina trihydrate, and the presence of small crystallites of metallic nickel was also indicated when the aluminum conversion by caustic leaching was substantial.

Originally, the activation procedure was based on published information indicating that an active catalyst could be prepared by extraction with dilute caustic of a small portion of the aluminum content and that this procedure could be repeated a number of times to

restore activity (14). This assumed that aluminum removal was determined stoichiometrically (13):



Thus, catalysts were first prepared by leaching with sufficient sodium hydroxide to remove 5% of the aluminum content in accordance with this reaction. Dilute caustic was added slowly to a water suspension of the alloy at a maximum temperature of 120° to 130° F. After 4 to 6 hours, vigorous hydrogen evolution stopped, and the catalyst was washed until neutral to litmus and stored in water. These preparations were very active but could not be regenerated by further caustic treatment. The first two pilot unit batches also showed poor attrition resistance.

After development of the necessary analytical techniques, it was found that at least 20% of the aluminum had to be converted before significant activity for the methanation reaction was obtained, and considerably higher conversions were required to produce a long-lived catalyst. Further, the presence of large amounts of alumina trihydrate in the caustic-treated alloy confirmed that much of the aluminum is converted by hydrolysis reactions (13) and not by extraction as the stoichiometric amount of aluminate. Efforts to reduce aluminum oxide formation under conditions allowing only partial aluminum conversion were not successful.

As 3 moles of hydrogen are evolved per 2 moles of aluminum converted to either aluminate or alumina, it was possible to follow the progress of catalyst activation by measurement of hydrogen evolution. In the standard procedure for preparing laboratory batches of catalyst, 100 cc. (162 grams) of alloy and 280 ml. of water were placed in a 2-liter three-necked flask. One neck of the flask held a mercury thermometer, the center neck held a reflux condenser, and the third neck held a buret for caustic or quench water addition. A wet-test meter was connected to the reflux condenser to measure the evolved hydrogen. A magnetic stirrer was used to agitate the alloy slightly.

Then 15 ml. of a 26% (weight) sodium hydroxide solution was added causing hydrogen evolution to begin, accompanied by a large heat release. When the temperature reached the boiling point after about 8 to 12 minutes, enough water was added to prevent flash vaporization but not enough to reduce the temperature below the boiling point. The reaction was permitted to proceed at the boiling point until either an apparent 30, 65, or 85% of aluminum conversion had occurred. For example, the 2.88 SCF of hydrogen corresponding to 65% apparent aluminum conversion of 162 grams of

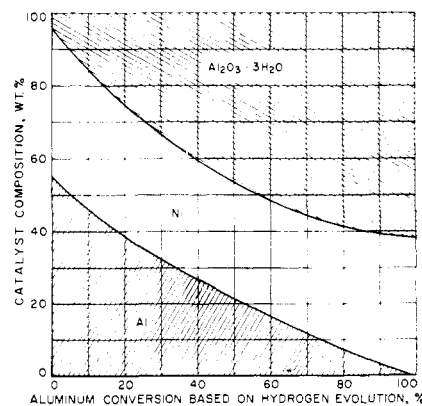
alloy was evolved in 34 to 42 minutes. As the desired point, the reaction was quenched by the addition of large amounts of cold water, and the liquid was decanted. The catalyst was washed until neutral to litmus and stored in methyl alcohol.

After development of the above laboratory procedure, it was adapted without significant changes for preparation of pilot unit catalyst charges. The required 0.5 cubic foot (55 pounds) of alloy was activated in two batches of equal weight in a 16-inch-diameter, stirred, water-jacketed autoclave having a volume of 4.8 cubic feet. The autoclave was equipped with a reflux condenser, a metering system for evolved hydrogen, a caustic feed inlet, a quench and wash water inlet, an overflow, and a drain. For each batch, 1400 ml. of a 26% (weight) sodium hydroxide solution was added to a water slurry of the alloy. Maximum activation temperature was controlled at 190° to 200° F. An apparent aluminum conversion of 65% was used for all batches prepared in accordance with this procedure. Activation time varied from about 2 to 4 hours because of variations in the initial slurry temperature and in the temperature and amount of quench water.

The particle size distribution of the alloy used for laboratory and pilot unit catalysts was standardized by combining individual U. S. standard sieve fractions in the following fixed proportions:

Mesh	Wt. %
40-60	15
60-80	15
80-100	10
100-140	35
140-200	25

The bulk density of the fluidized catalyst in the pilot unit was about 100 pounds per cubic foot.



Composition of Raney nickel catalysts was controlled by the amount of hydrogen evolved during caustic leaching

The chemical composition of catalysts prepared by the standard procedures (see figure) was determined by the following technique developed from conventional methods: A sample was dried by heating in a stream of dry hydrogen. Dry hydrogen chloride was then passed over it to volatilize the aluminum metal as aluminum chloride. The aluminum chloride was recovered, precipitated with ammonia, and ignited to the oxide. The residue from the hydrogen chloride treatment was boiled with nitric acid and filtered. The residue from the filtration was ignited to obtain the quantity of alumina not dissolved by this treatment. The filtrate was diluted to volume; on one aliquot, alumina was determined by double precipitation with benzoate and ignition to the oxide; on another aliquot, nickel was determined with dimethylglyoxime.

Initially, standard catalyst preparations were charged as a methyl alcohol slurry under a nitrogen blanket and dried in a stream of nitrogen at a temperature not exceeding 650° F. before introduction of synthesis gas. During shutdowns the catalyst was stored in the reactor under nitrogen. In case of extended laboratory tests which were interrupted by scheduled temporary shutdowns, the catalyst temperature was maintained at 400° to 500° F.

In catalyst life tests, the above charging and start-up procedures gave exceedingly poor reproducibility of results. Rapid catalyst loss occurred in many attempts to make an extended run; any particles escaping from the reactor through the porous stainless steel filters had to be very small, so that only a minor portion could be recovered. A common occurrence which preceded an abrupt reduction in conversion capacity was lifting of the bed into the disengaging zone and deposit on the filters requiring blow-back to reduce pressure;

this frequently took place after a weekend shutdown. No specific cause for this type of failure could be established, but the following revisions in procedures greatly improved the consistency of the catalyst performance data:

Store in methyl alcohol for not longer than 24 hours.

Predry in nitrogen at 250° F. for 2 hours to obtain free-flowing material.

Charge to unit under nitrogen blanket.

Start up slowly with hydrogen as fluidizing medium at approximately 1 foot per second superficial velocity and gradually replace hydrogen with synthesis gas after attainment of the desired temperature and pressure.

During interruption of an extended test, shut down in nitrogen at 450° F. and atmospheric pressure and start up with hydrogen as above.

A similar catalyst heating and start-up procedure was adopted for pilot unit operation after rapid failure of the first charge made by the standard activation procedure. Because of its bulk, the catalyst was predried in four batches using 4-inch-diameter glass tubes at furnace temperatures up to 490° F.

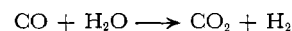
Process Variables

A number of thermodynamic analyses of the methanation reaction system have been made (2, 5, 6, 11) to evaluate the influence of the major operating variables—pressure, temperature, and hydrogen to carbon monoxide ratio—on the equilibrium conversion of the feed gas to methane, water vapor, carbon dioxide, and carbon. These analyses show that, in the absence of carbon formation, nearly stoichiometric conversion of 1 to 1 to 3 to 1 hydrogen to carbon monoxide ratio synthesis gases to methane can be attained at 650° F. and 25 atm. (353 p.s.i.g.); equilibrium methane yields decrease with increases in temperature and decreases in pressure but remain

reasonably high below 900° F. at pressures from 1 to 25 atm.

The calculation of equilibrium carbon yields is complicated by lack of information on thermodynamic properties of the carbon deposited on methanation catalysts. Carbon deposition boundary data based on equilibrium constants obtained from actual methanation reaction systems catalyzed by precipitated nickel (5) show substantially lower limiting feed gas hydrogen to carbon monoxide ratios than data based on beta graphite (6). For example, at 600° to 900° F. and 1 to 25 atm., the minimum hydrogen to carbon monoxide ratios calculated from the experimental equilibrium data range from 1 to 1 to 1.75 to 1; when beta graphite is used as the form of carbon, the minimum ratios range from 2.6 to 1 to 3.25 to 1. Addition of steam or carbon dioxide lowers the limiting hydrogen to carbon monoxide ratios.

The presence of carbon dioxide in the feed also has the desirable tendency to suppress carbon monoxide shift:



which causes hydrogen breakthrough accompanied by decreased methane yield. For example, if only the stoichiometric relationships are considered, a 3 to 1 hydrogen to carbon monoxide ratio feed gas could give methane yields ranging from 0.125 to 0.25 mole per mole of hydrogen plus carbon monoxide, while complete carbon monoxide conversion is maintained.

To establish the range of suitable fluid-bed operating conditions with Raney nickel catalysts, exploratory tests were made in the laboratory reactors. Synthesis gases of about 1.5 to 1 and 3 to 1 hydrogen to carbon monoxide ratio and two carbon dioxide contents were methanated over catalyst charges prepared by leaching of 100 cc. of alloy with

Table I. Fluid-Bed Raney Nickel Catalyst Gives Nearly Complete Conversion of Various Synthesis Gases to Methane over a Wide Range of Space Velocities

	H ₂ -CO Feed Gas Ratio											
	1.5-1			CO ₂ -free			3-1			CO ₂ -containing		
	CO ₂ -containing	CO ₂ -free	CO ₂ -containing	CO ₂ -free	CO ₂ -free	CO ₂ -free	CO ₂ -free	CO ₂ -free	CO ₂ -free	CO ₂ -containing	CO ₂ -containing	CO ₂ -containing
Pressure, p.s.i.g.	27	75	150	27	75	150	75	150	300	75	150	300
Space velocity, SCF/cu. ft. cat.-hr. ^a	1200-2200	2300-4400	3000-8000	1000-9500	1000-15,000	1000-15,000	8000-23,000	7000-21,000	7000-17,000	8000-23,000	7000-21,000	7000-17,000
Superficial feed gas velocity, ft./sec.	0.4-0.8	0.4-0.7	0.3-0.7	0.3-3.3	0.2-2.5	0.1-1.3	0.8-2.4	0.4-1.2	0.2-0.5	0.8-2.4	0.4-1.2	0.2-0.5
Moles product gas/mole feed	0.56	0.56	0.55	0.30	0.30	0.27	0.45	0.45	0.43	0.45	0.45	0.43
Moles H ₂ O formed/mole feed	0.07	0.07	0.07	0.23	0.23	0.24	0.20	0.20	0.21	0.20	0.20	0.21
Gas composition, mole %												
	Feed			Feed			Feed			Feed		
CO ₂	16	51	16	52	53	1	6	6	5	27	56	59-56
CO	31	...	32	24	16	...	17
H ₂	47	4	46	2	1	74	11-14	11	8	56	5	2-5
CH ₄	1	35	1	36	36	0	78-75	78	82	0	36	36
N ₂ ^b	5	10	5	10	10	1	5	5	5	1	3	3

^a Space velocities outside this range gave either less than 90% carbon recovery in the product gas or substantial carbon monoxide breakthrough.

^b Reported nitrogen content of product gases may include small percentage of carbon monoxide.

dilute caustic for more than 4 hours. The range of pressure levels investigated permitted up to fourfold variations in space velocity at constant superficial feed gas velocity. Table I gives a summary of average yield data.

With the low hydrogen to carbon monoxide ratio, high carbon dioxide content feed gas (produced by steam-oxygen gasification of coal), the range of space and superficial velocities was relatively narrow. Below superficial velocities of 0.3 to 0.4 foot per second, carbon recovery in the product gas tended to be low, possibly as a result of carbon deposition on overheated, incompletely fluidized catalyst. Above about 0.7 foot per second, carbon monoxide breakthrough was excessive. With the 3 to 1 hydrogen to carbon monoxide feed gases, operation was satisfactory over the entire range of flow rates studied, except for one instance of apparent low carbon recovery in the product gas from the low carbon dioxide content feed gas at 150 p.s.i.g. and 0.1 foot per second.

In the first two series of tests in Table I, a thermowell of 0.840-inch diameter was used instead of the 0.675-inch diameter well used in all subsequent tests with the 1.049-inch inside diameter laboratory reactors. As a result, catalyst bed depths and superficial gas velocities at equivalent operating conditions were about 60% higher. This was probably responsible for the 650° to 750° F. catalyst bed temperature level in the first two series of tests, compared to 690° to 790° F. in the third, under conditions giving essentially complete carbon monoxide conversion.

The data of Table I show the expected trends: more water formation at the higher feed gas hydrogen to carbon monoxide ratio; higher product gas methane content, and lower hydrogen content, at the higher pressures. At 75 p.s.i.g., the carbon dioxide content of the 3 to 1 hydrogen to carbon monoxide ratio feed gas had little effect on hydrogen breakthrough. However, at 150 p.s.i.g., hydrogen breakthrough was reduced at the lower space velocities. At 300 p.s.i.g., the combined effect of high pressure and presence of carbon dioxide in the feed gas almost completely suppressed hydrogen breakthrough except at the very high space velocities. The tendency toward increases in hydrogen breakthrough with increases in space velocity for the high hydrogen to carbon monoxide ratio synthesis gases was not clearly defined at all pressure levels, possibly because of variations in feed gas composition. In the tests with the high carbon dioxide content, 3 to 1 hydrogen to carbon monoxide ratio gas, there was a slight reduction in the quantity of carbon dioxide leaving the reactor compared to the quantity entering.

Although only some of the product gases had carbon monoxide concentrations readily detectable by the analytical procedures employed (mass spectrometer supplemented by infrared analysis), the carbon monoxide shift reaction closely approached equilibrium in all tests, as carbon monoxide concentrations of less than 1 mole %, and normally as low as 0.1 to 0.5 mole %, would give experimental equilibrium constants consistent with the theoretical values.

Catalyst Performance

The important catalyst performance variables are activity and total conversion capacity. In this study, activity is defined in terms of the percentage of the synthesis gas hydrogen plus carbon monoxide content converted to methane or methane equivalent:

% H₂ - CO conversion =

$$100 \frac{4 \left[\left(\frac{\text{Moles dry prod. gas}}{\text{Mole dry feed gas}} \right) \left(\frac{\text{Mole \% CH}_4\text{-equiv. in dry prod. gas}}{\text{Mole \% H}_2 + \text{CO in dry feed gas}} \right) - \left(\frac{\text{Mole \% CH}_4\text{-equiv. in dry feed gas}}{\text{Mole \% H}_2 + \text{CO in dry feed gas}} \right) \right]}{100}$$

where the methane equivalent is the sum of mole percentage multiplied by carbon number for each gaseous hydrocarbon. At complete conversion to methane of any synthesis gas in the 1 to 1 to 3 to 1 hydrogen to carbon monoxide ratio range, a value of 100% would be obtained. If ethane is also produced, the hydrogen to carbon monoxide conversion based on the above definition could slightly exceed 100%; however, the maximum value at complete conversion of 0.75 to 1 to 2.5 to 1 hydrogen to carbon monoxide ratio synthesis gases to ethane would be only 114%. The total conversion capacity of the catalyst is defined as the weight of net methane equivalent per unit weight of original alloy nickel content, or the volume of net methane equivalent per unit weight of original alloy, produced by the catalyst during the period in which it maintains 70% hydrogen to carbon monoxide conversion or more.

Laboratory Tests. Sulfur tolerance limits of standard fluid-bed Raney nickel catalysts prepared by 65 to 85% aluminum conversion were determined to establish synthesis gas purification requirements. In these tests, carbon dioxide-containing 3 to 1 hydrogen to carbon monoxide ratio synthesis gases having organic sulfur contents (mainly in the form of carbonyl sulfide) of 0.5 to 4 grains per 100 SCF were methanated at space velocities of 5000 to 13,000 SCF per cubic foot of catalyst per hour and 75 p.s.i.g. Each test, made with a fresh batch of catalyst, continued until most of the activity had been lost.

The catalyst activity dropped rapidly to less than 70 to 80% hydrogen to carbon monoxide conversion when the total

sulfur exposure reached approximately 0.5 pound per 100 pounds of nickel. This agrees quite well with similar sulfur poisoning test results obtained in studies with supported nickel catalysts (16). Measurement of hydrogen sulfide and organic sulfur liberated from a poisoned catalyst by acid treatment showed that essentially all of the organic sulfur introduced in a test was removed by the catalyst. From a linear extrapolation of these results, adequate catalyst activity could be expected for about 1500 hours when gas containing 0.01 grain of sulfur per 100 SCF is fed at 10,000 SCF per cubic foot of catalyst per hour.

Typical results of a catalyst life test with purified synthesis gas are given in Table II. The carbon dioxide-free heating values are lower than would be desirable for use of the process as a source of a natural gas supplement.

However, gas of approximately 900 B.t.u. per SCF of carbon dioxide-free heating value was produced for about 500 hours in a similar test at 150 p.s.i.g. By adjustment of the hydrogen to carbon monoxide ratio to minimize hydrogen breakthrough and reduction of the nitrogen content of the synthesis gas, it is also possible to produce 900 B.t.u. per SCF gas at 75 p.s.i.g. and 10,000 SCF per cubic foot of catalyst per hour space velocity for limited periods.

The reproducibility of catalyst life tests similar to Run 540 (Table II) was satisfactory after adoption of the predrying and slow start-up procedures. In four tests at 75 and 150 p.s.i.g. with charges prepared by 65% aluminum conversion, hydrogen-carbon monoxide conversions above 70% were maintained for 1180 to 1500 hours, interrupted by 10 to 19 shutdowns. Catalyst recoveries varied from 25 to 45% (volume) (under methyl alcohol), and there were no significant differences between fresh and recovered catalyst analyses. Some of the decrease in conversion capacity may, therefore, have been due to catalyst loss. Net equivalent methane yields were within a range of 1970 to 2270 pounds per pound of original alloy nickel content. This corresponds to yields of approximately 20,000 to 23,000 SCF of methane per pound of alloy.

Thus, at the currently quoted cost of 90 cents per pound for pulverized 42% (weight) nickel-58% (weight) aluminum Raney alloy in 25,000-pound lots (72), alloy costs per 1000 SCF of methane equivalent would be 4 to 5 cents, assuming no nickel credit for the spent catalyst. If these results could

be duplicated on a commercial scale, catalyst costs should not be a major factor in determining the final cost of producing pipeline gas from coal via the methanation process (8).

Pilot Plant Tests. A series of exploratory tests was made before catalyst preparation, analysis, handling, and start-up procedures had been fully developed, comprising 177 hours of steady-state operation (125 pounds of net equivalent methane yield per pound of original alloy nickel content). The reactor was then slightly modified to increase the heat transfer area and reduce the danger of filter plugging with catalyst fines, the cause for shutdown of the first series of runs.

In subsequent short runs, satisfactory operation at design capacity was achieved with low carbon dioxide-content, 3 to 1 hydrogen to carbon monoxide ratio synthesis gas produced by reforming of natural gas. Integrated operation of the carbon monoxide shift, purification, and methanation sections of the pilot plant, with synthesis gas produced from coal, demonstrated the feasibility of continuously supplying a feed gas of acceptable purity, 3 to 1 hydrogen to carbon monoxide ratio, and about 30 mole % carbon dioxide content from this source. However, with feed gases of this composition, which had caused no operating problems in the laboratory

tests, the catalyst bed lifted into the disengaging and filter zone of the pilot unit reactor and overheated severely. Although this may have been due in part to the lack of control over catalyst properties before standardization of procedures, later pilot unit tests confirmed that similar synthesis gases tended to lift the bed at 3000 SCF per hour feed rate when the reactor pressure was below 150 p.s.i.g.

Table III summarizes the results of the most successful pilot unit run to date, comprising 505 hours of operation, and two temporary shutdowns, with a standard, predried catalyst charge prepared from 55 pounds of alloy. The predried catalyst weighed 49.93 pounds and had a volume of 0.394 cubic foot. In addition to the operation with low carbon dioxide content reformed natural gas shown in Table III, there were two periods of operation with 30 mole % carbon dioxide content feed gas following the two temporary shutdowns. On start-up with these gases, severe upsets occurred because of lifting of the catalyst bed, which may have damaged the catalyst. About 70% (weight) of the predried catalyst was recovered, most of it in a free-flowing condition; volume recovery was nearly 100%. If any direct loss of catalyst occurred, it was probably in the form of fines smaller than 0.1 micron; only a negligible amount of fines was

recovered on an absolute glass filter placed in the hot product gas line.

On the basis of the catalyst analysis procedure employed, there was no selective loss of nickel, aluminum, or alumina. However, as the catalyst analyses are not based on a weighed sample, and arbitrarily report alumina as the trihydrate, a considerable portion of the apparent weight loss may have been due to dehydration of alumina. This is confirmed by x-ray analyses which show nearly complete disappearance of hydrated forms of alumina in spent catalysts.

The net equivalent methane yield for Run P-25 was 471 pounds per pound of original alloy nickel content, which is only about one fourth of the yield obtained in laboratory operation. However, subsequent laboratory tests on the spent catalyst for Run P-25 showed substantial additional conversion capacity, so that pilot unit design could have contributed to the poorer performance.

From the temperatures reported in Table III, the expanded catalyst bed height appears to be less than 45 inches and probably nearer 36 inches. This is confirmed by differential pressure drop measurements. The unexpanded bed height based on the initial dried catalyst charge volume would be 28.9 inches. Assuming an effective bed height of 3 feet, corresponding to a heat transfer area of 9.7 square feet, the over-all

Table II. With Purified Synthesis Gas, the Standard Fluid-Bed Raney Nickel Catalyst Maintains High Conversion Capacity for Long Periods

Run No. 540, catalyst No. 82 prepared by 65% aluminum conversion of 100 cc. (162 grams) of 40-200 mesh, 42 wt. % nickel-58 wt. % aluminum alloy. Methyl alcohol slurry of catalyst predried in nitrogen at 250° F.

	Duration of Test, Hr.							
	100	500	920	1300	100	500	920	1300
Pressure, p.s.i.g.	75	75	75	75	75	75	75	75
Temp., ° F.								
Bottom of reactor	750	755	755	765	750	755	755	765
9 in. from bottom	755	755	745	750	755	755	745	750
18 in. from bottom	760	730	730	745	760	730	730	745
27 in. from bottom	765	745	745	730	765	745	745	730
Feed gas								
Space velocity, SCF/cu. ft. cat.-hr.	10,220	10,140	10,360	10,270	10,220	10,140	10,360	10,270
Superficial inlet velocity, ft./sec.	1.09	1.08	1.11	1.10	1.09	1.08	1.11	1.10
Product gas ^a								
SCF/SCF feed	0.474	0.473	0.490	0.549	0.474	0.473	0.490	0.549
C recovery, %	98	100	101	103	98	100	101	103
H recovery, %	68	67	66	69	68	67	66	69
O recovery, %	74	75	78	82	74	75	78	82
Composition, mole %								
	Feed	Feed	Feed	Feed	Feed	Feed	Feed	Feed
CO ₂	25.5	52.6	24.2	51.4	25.2	52.7	26.1	48.0
CO	16.9	0.6	17.5	1.2	16.9	1.7	15.9	5.7
H ₂	53.9	6.6	56.9	9.5	56.2	10.8	56.8	20.0
CH ₄	0.9	36.8	0.1	35.7	0.4	32.7	0.4	26.0 ^b
N ₂	2.8	3.4	1.3	2.2	1.3	2.1	0.8	0.3
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
CO ₂ -free sp. gr. (air = 1.000)		0.522		0.489		0.477		0.416
CO ₂ -free heating value, B.t.u./SCF		820		803		773		658
Water formation, moles/mole feed gas								
By H balance		0.18		0.19		0.20		0.18
By O balance		0.18		0.17		0.15		0.12
H ₂ -CO conversion, %		93		87		86		77

^a Excluding water formed by methanation reactions. ^b Includes 0.1 mole % ethane.

Table III. Fluid-Bed Methanation with Raney Nickel Catalyst Was Scaled Up to a 6-Inch-Diameter Pilot Unit

Run No. P-25, catalyst No. 83-84 prepared by 65% aluminum conversion of 0.5 cu. ft. (55 lb.) of 40-200 mesh 42 wt. % nickel-58 wt. % aluminum alloy. Methyl alcohol slurry of catalyst predried in nitrogen at 490° F. maximum furnace temperature

	Duration of Test, Hr.											
	105	245	358.5	373	418	505						
Pressure, p.s.i.g.	105	103	104	158	150	152						
Temp., ° F.												
Bottom of reactor	850	845	850	865	830	820						
9 in. from bottom	850	845	850	865	830	820						
18 in. from bottom	850	840	830	845	830	795						
27 in. from bottom	850	840	830	845	830	795						
36 in. from bottom	835	850	850	835	825	815						
45 in. from bottom	765	800	805	775	780	790						
54 in. from bottom	740	770	760	725	745	770						
72 in. from bottom	710	740	735	700	720	760						
90 in. from bottom	505	670	685	660	705	...						
154 in. from bottom	620	660	695	670	700	825						
Dowtherm temp., ° F.												
Inlet to jacket, bayonets	590	630	635	610	645	725						
Exit												
Jacket	600	630	635	610	645	725						
Bayonets	625	635	650	620	645	725						
Feed gas												
Space velocity, SCF/cu. ft. cat.-hr. ^a	5160	6400	5880	6020	6320	6090						
Superficial inlet velocity, ft./sec. ^b	1.47	1.70	1.64	1.20	1.30	1.21						
Product gas ^c												
SCF/SCF feed	0.282	0.295	0.303	0.306	0.335	0.444						
C recovery, %	99	94	98	100	100	101						
H recovery, %	64	64	61	64	66	72						
O recovery, %	19	22	25	22	30	42						
Composition, mole %												
	Feed	Feed	Feed	Feed	Feed	Feed						
CO ₂	1.6	9.1	2.7	10.4	2.7	10.6	1.9	8.9	2.4	11.3	1.7	9.0
CO	23.6	0	23.3	0.3	21.0	0.9	21.8	0.6	22.1	1.3	21.7	5.8
H ₂	73.8	8.4	73.2	14.1	74.9	19.9	74.6	18.1	74.1	24.1	74.8	43.8
CH ₄		79.5	0.1	72.7	0.5	66.8	0.7	70.0	0.4	61.3	0.9	40.3
N ₂	1.0	3.0	0.7	2.5	0.9	1.8	1.0	2.4	1.0	2.0	0.9	1.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
CO ₂ -free sp. gr. (air = 1.000)		0.523	0.491		0.459		0.472		0.438		0.353	
CO ₂ -free heating value, B.t.u./SCF	902	861	819	831	780	615						
Water formation, mole/mole feed gas												
By H balance	0.27	0.26	0.29	0.28	0.26	0.21						
By O balance	0.22	0.22	0.20	0.20	0.19	0.15						
By condensate measurement	0.24	0.23	0.21	0.22	0.20	0.16						
H ₂ -CO conversion, %	92	88	82	86	84	70						

^a Based on 0.5 cu. ft. original alloy volume. ^b All feed gas introduced at bottom of reactor. ^c Excluding water formed by methanation reactions and carbon dioxide introduced through pressure taps.

heat transfer coefficient between the catalyst bed and the circulating Dowtherm was on the order of 50 B.t.u. per hour per square foot per ° F.

Acknowledgment

The members of the Project Supervising Committee of the American Gas Association gave valuable technical assistance. D. McA. Mason was responsible for the development of catalyst analysis procedures. J. R. Dvorak of the Armour Research Foundation carried out the metallographic work.

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RECEIVED for review July 17, 1959
ACCEPTED March 25, 1960

Division of Gas and Fuel Chemistry, 136th Meeting, ACS, Atlantic City, N. J., September 1959. Study supported by the Promotion-Advertising-Research Plan of the American Gas Association under sponsorship of its Gas Operations Research Committee.