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PRODUCTION OF PIPELINE GAS BY METHANATION OF
SYNTHESIS GAS OVER RANEY NICKEL CATALYSTS

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The technically most advanced method for the production of a 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.^{1,2,3} The major effort has been expended on the gasification step because of its wide applicability. Fixed-bed and suspension gasification processes have been developed to a pilot plant scale,^{7,11,33,34} and some have been operated successfully on a commercial scale.^{15,17,21,36}

The methanation step has also been studied extensively, but much of the work has been concerned with catalyst development and, therefore, has involved small-scale experiments. In studies by the British Fuel Research and Gas Research Boards^{3,8-10} the development of fixed- and moving-bed reactors has been stressed. Initially, studies by the U.S. Bureau of Mines^{7,35} and the Institute of Gas Technology^{2,3} were also conducted in relatively small fixed-bed reactors. In these investigations, supported nickel catalysts were employed nearly without exception.

The largest-scale fixed-bed methanation data for the production of high-heating-value fuel gas were reported by Dent and Hebden,⁸ who achieved near-equilibrium conversion of 3.6:1 H₂/CO ratio synthesis gas for 3500 hours in a 9.5-inch diameter by 10-inch deep catalyst bed at 20 atmospheres, 2000 std. cu. ft./cu.ft. catalyst-hr. fresh feed gas space velocity, and 6:1 recycle ratio. A coimpregnated nickel-alumina-china clay catalyst was employed.

The design of large-scale fixed-bed reactors for essentially complete conversion of hydrogen and carbon monoxide to methane at high throughputs presents difficult engineering problems. Large quantities of exothermic heat of reaction must be removed without causing excessive temperature gradients to occur in the catalyst bed. This requires either complex heat exchange equipment in the catalyst bed when a fluid coolant is used, or the use of high product gas recycle rates. In both instances, the investment and operating costs are high.

Fluid-bed reactors appeared to be better suited for the methanation process because of the high rates of heat transfer obtainable with relatively simple heat exchange equipment. The ease of addition and withdrawal of catalyst also seemed to be a significant advantage. However, restriction of the possible range of operating conditions by the fluidization characteristics of the solids-gas system employed, and catalyst attrition, were recognized as major problems. Further, scale-up of fluid-bed reactors for synthesis operations was known to be difficult^{1,6} and was not fully demonstrated on a commercial scale until recently.^{17,21}

In 1954, the U.S. Bureau of Mines achieved satisfactory fluid-bed operation in a 1-inch diameter reactor with a partially extracted Raney nickel catalyst;³¹ attempts to utilize fluid-bed iron catalysts

were not successful, and the performance of supported nickel catalysts was found to be difficult to reproduce.¹⁴ Russian investigators have also reported high conversion capacities of partially extracted Raney nickel catalysts in fluid-bed operation.^{4,5} A systematic study of this methanation technique was, therefore, initiated by the Institute of Gas Technology as part of its pipeline-gas-from-coal research program.

EXPERIMENTAL

In all of the work reported here, the catalysts were prepared by caustic leaching of 40-200 mesh Raney alloy with a nominal composition of 42 wt. % nickel and 58 wt. % aluminum.^{24,25} Synthesis gas was produced by catalytic steam reforming of natural gas in a tube furnace,²⁰ or by suspension gasification of coal with steam and oxygen in a slagging downflow pressure reactor.³⁴ Facilities were also available to increase the H₂/CO ratio of synthesis gas produced from coal from the usual 1:1-1.5:1 range to 3:1 by catalytic conversion of CO with steam to form H₂ and CO₂. In some instances, CO₂ from bottle storage was added to the 3:1 H₂/CO ratio reformed natural gas to simulate the composition of synthesis gas from coal after CO shift and before CO₂ removal.

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 SCF (standard cubic foot at 60°F., 30 inches of mercury and saturated with water vapor), and generally to about 0.001 grain per 100 SCF. Details of the analytical procedures for determination and identification of sulfur compounds in synthesis gas have been presented elsewhere.^{22,23,32}

Three major methods of operation were employed in the study of fluid-bed methanation of synthesis gas over Raney nickel catalysts:

1. Catalyst evaluation tests and process variable studies in a battery of approximately 1-inch inside diameter Dowtherm-jacketed reactors (Figure 1). The effect of catalyst preparation on initial activity and total methane production capacity was determined with purified synthesis gases of approximately 3:1 H₂/CO ratio, and either negligible or 30 mole % average CO₂ content. Nominal test conditions were: 10,000 SCF/cu.ft. catalyst-hr. space velocity, 75, 150 and 300 p.s.i.g. reactor pressure, and 100 cc. initial alloy volume. (Space velocities are based on the initial dry alloy volume). A systematic study was also made of the variables of synthesis gas H₂/CO ratio, synthesis gas CO₂ and organic sulfur content, space velocity and operating pressure. Catalyst bed temperature was controlled by adjustment of 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 within 700°-800°F.

2. Capacity tests of a 6-inch inside diameter pilot plant reactor (Figure 2). Dowtherm "A" circulating through an external jacket and through six internal bayonets was used to heat the catalyst to reaction temperature at the start of operation, and then, as increasing quantities of exothermic heat of reaction were released, to remove 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 gal./min.) allowed most of the Dowtherm to remain in liquid form. Purified synthesis gas produced by catalytic steam

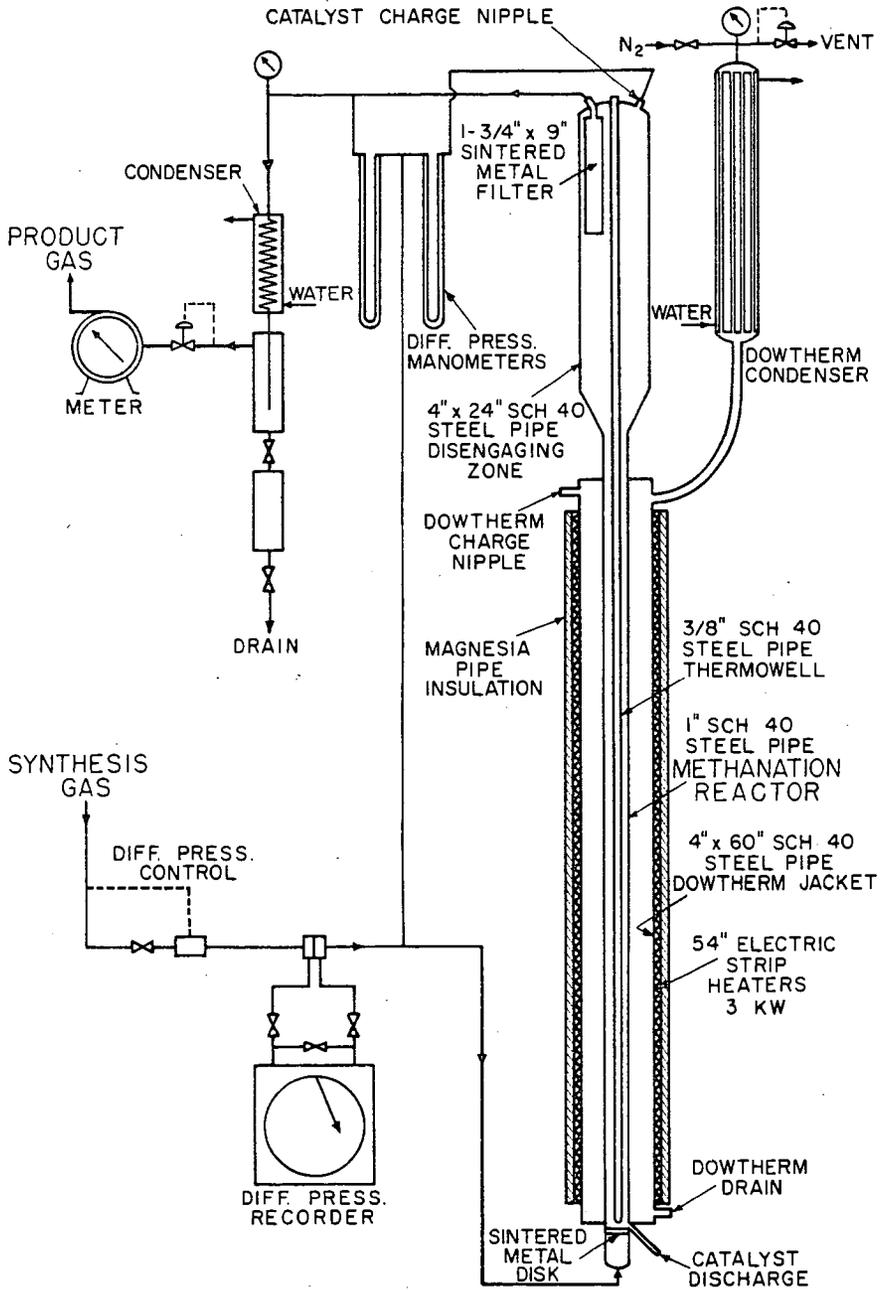


Fig. 1.-LABORATORY FLUID-BED METHANATION UNIT

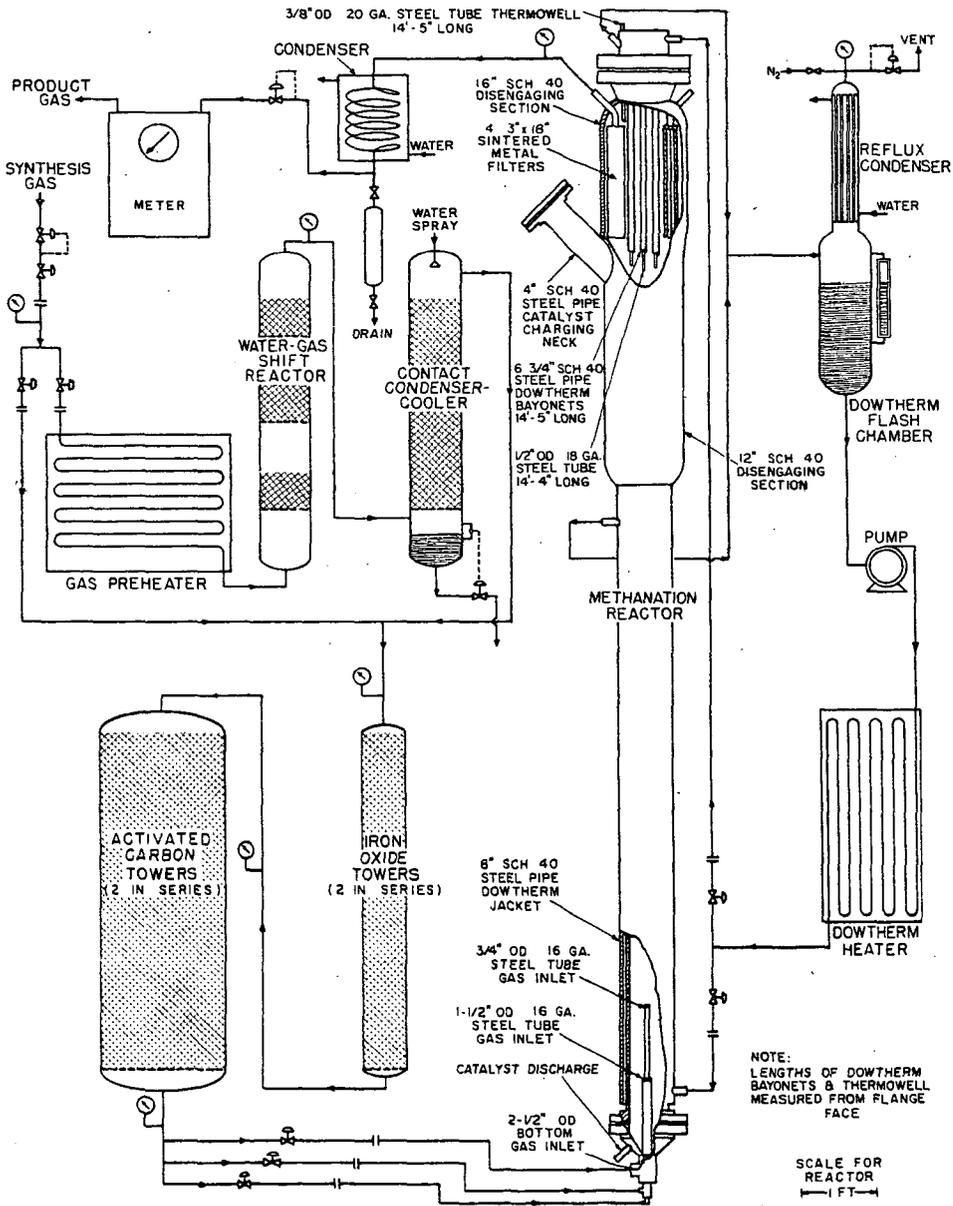


Fig. 2.-FLUID-BED METHANATION PILOT UNIT

reforming of natural gas was used as feed at pressures up to 190 p.s.i.g. After a series of short tests, comprising 177 hours of steady-state operation with a batch of catalyst prepared from 0.343 cu.ft. of alloy, the reactor was slightly modified to the design depicted in Figure 2 to permit attainment of a synthesis gas capacity of 3000 SCF/hr. with a 0.5 cu. ft. catalyst charge; initially, the cooling bayonets were constructed of 1/2-inch Schedule 40 pipe, the disengaging section was smaller, and the porous stainless steel gas filters were also smaller and located in a side offtake.

3. Exploratory pilot plant tests of simulated integrated pipe-line-gas-from-coal operation involving the process steps of a) suspension gasification of coal with steam and oxygen to produce synthesis gas at a nominal rate of 20,000 SCF/hr., b) preliminary purification with iron oxide for bulk removal of hydrogen sulfide, c) temporary pressure storage and withdrawal at 3000 SCF/hr., d) adjustment of synthesis gas composition by partial carbon monoxide shift of a portion of the synthesis gas, e) final purification with iron oxide and activated charcoal to less than 0.01 grain of sulfur per 100 SCF, and f) methanation over fluidized Raney nickel catalyst in the reactor depicted in Figure 2.

CATALYST PREPARATION AND HANDLING

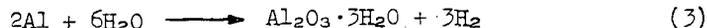
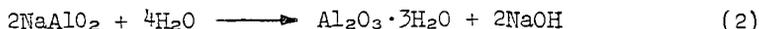
The 42 wt. % nickel-58 wt. % aluminum alloy was supplied by the Raney Catalyst Company. The structure of the crushed alloy is shown in Figure 3. The highly fractured condition of the catalyst particle is typical of the material used in the test program. The dark homogeneous regions are Ni_2Al_3 (gamma) phase, the light homogeneous regions are $NiAl_3$ (beta) phase, and the elongated mottled regions are a fine-grained eutectic mixture consisting of alpha phase (less than 0.05 wt. % nickel) and beta phase. Metallographic studies of caustic-etched particles showed that the gamma phase is more resistant to attack than are the other two phases, although x-ray analyses of caustic-treated alloy indicated the presence of all of the three original phases even when the aluminum content had been reduced to 5 wt. % or less. The major product of caustic leaching recovered in the catalyst was identified by x-ray as beta-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 reported by the U. S. Bureau of Mines was employed.³¹ This procedure was based on the assumption that an active catalyst could be prepared by extraction, with dilute caustic, of only 3-5 % of the aluminum content, and that the amount of aluminum removed was determined by a stoichiometric relationship such as:²⁵



It was further assumed that this procedure could be repeated a number of times to restore the activity of the catalyst.

After development of the necessary analytical techniques, it was shown in this study that at least 20% of the aluminum had to be converted before significant activity for the methanation reaction was obtained, and that considerably higher conversions were required to produce a long-lived catalyst. Further, the presence of large amounts of $Al_2O_3 \cdot 3H_2O$ in the extracted alloy confirmed that in addition to Reaction (1), sodium aluminate or direct aluminum hydrolysis reactions occur:²⁵



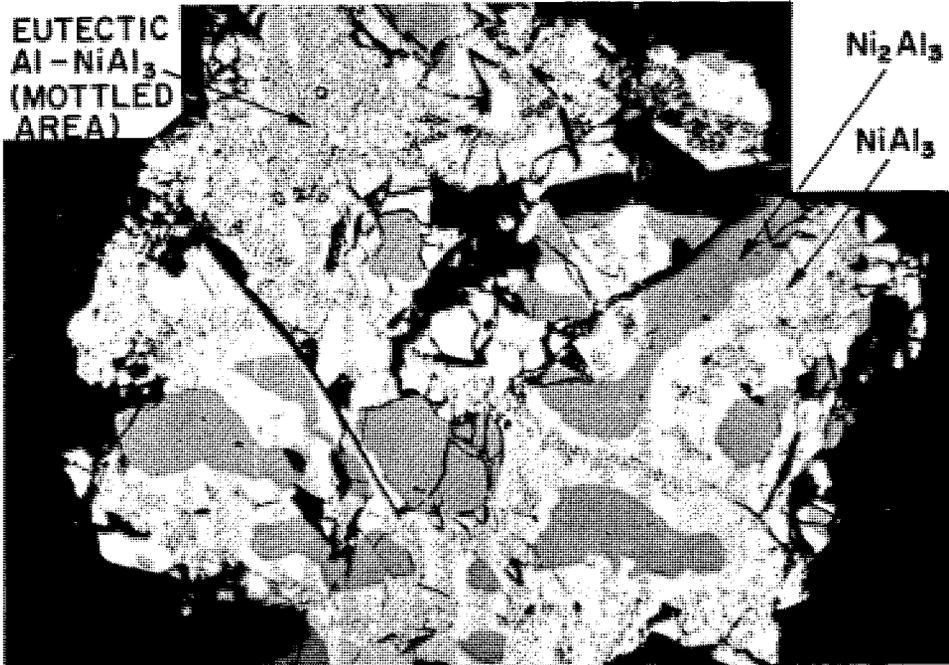


Fig. 3.-MICROSTRUCTURE OF 42 WT.% NICKEL - 58 WT.% ALUMINUM ALLOY (X 500)

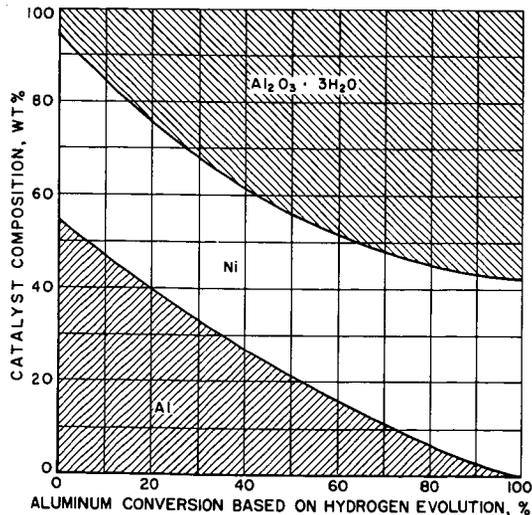


Fig. 4.-COMPOSITION OF RANEY NICKEL CATALYSTS PREPARED BY CAUSTIC LEACHING AT CONTROLLED RATE AND AMOUNT OF HYDROGEN EVOLUTION

Efforts to reduce aluminum oxide formation under conditions allowing only partial aluminum conversion were not successful. (In commercial Raney nickel catalyst preparation,²⁵ the alloy is added to an excess of concentrated caustic which apparently favors aluminum removal as aluminate.)

Since 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 g.) of 42 wt. % nickel-58 wt. % aluminum alloy and 280 cc. of water were placed in a 2-liter three-neck 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 slightly agitate the alloy. Fifteen cc. of a 26 wt. % 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% of apparent aluminum conversion of 162 g. of alloy was evolved in 34 to 42 minutes. At the desired point, the reaction was quenched by the addition of large amounts of cold water and the caustic liquid decanted from the wet catalyst. The catalyst was washed neutral to litmus and stored in methanol.

Figure 4 shows the relationship between chemical analysis of the catalysts prepared in accordance with the standard procedure, and the percent of aluminum conversion indicated by hydrogen evolution. It was necessary to further develop conventional procedures^{9,18} to make these analyses. The most reliable technique consisted of drying the sample by heating in a stream of dry hydrogen, and passing dry hydrogen chloride 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 by dimethylglyoxime.

Batches of pilot plant catalysts were prepared only by the original activation method, which consisted of leaching a suspension of the alloy in water at a maximum temperature of 120°-130°F. by slow addition of sufficient dilute sodium hydroxide solution to convert 5% of the aluminum content in accordance with Reaction (1). After 4 to 6 hours, vigorous hydrogen evolution stopped, and the catalyst was washed neutral to litmus and stored in water. No reliable analyses of pilot plant catalysts are available, since the analytical technique had not been fully developed at that time.

The particle size distribution of the alloy used in the preparation of laboratory batches was standardized by combining individual screen fractions in the fixed proportions shown below; the screen analysis of the 0.343 cu. ft. of alloy for the original pilot plant batch is also given:

U.S.S. Sieve	Alloy Size Distribution, Wt. %	
	Standard Laboratory Charge	Pilot Plant Charge
+40	0	1.2
-40 + 60	15	15.8
-60 + 80	15	10.1
-80 + 100	10	9.7
-100 + 140	35	34.7
-140 + 200	25	28.3
-200	0	0.2

In the pilot plant study, the prepared catalyst was charged as a water slurry and, in the majority of the laboratory tests, as a methanol slurry. Charging was done under a nitrogen blanket. Transfer as a slurry was used to avoid the possibility of catalyst oxidation, which could result in catalyst deactivation. After the slurry had been charged into the reactor, it was dried in a stream of nitrogen before introduction of synthesis gas. The catalyst temperature was raised to a level not exceeding 650°F., which was sufficient to initiate reaction of the synthesis gas, causing further temperature rise which had to be controlled by adjustment of the Dowtherm temperature level. Since the reactors were shut down repeatedly without change of the catalyst charge, it was necessary to store the catalyst in the reactor under nitrogen. In case of extended tests which were interrupted only temporarily, such as by scheduled weekend shutdowns, the catalyst temperature was maintained at 400°-500°F.

In catalyst life tests, the above charging and startup procedures gave exceedingly poor reproducibility of results. Rapid loss of catalyst through the porous stainless steel filters occurred in many attempts to make an extended run; the particles escaping from the reactor were very small and 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 it was found that by making the following revisions in these procedures it was possible to greatly improve the consistency of the catalyst performance data:

1. Store in methanol for not longer than 24 hours.
2. Predry in nitrogen at 250°F. for 2 hours to obtain free-flowing material.
3. Charge to unit under nitrogen blanket.
4. Start up slowly with hydrogen as fluidizing medium at approximately 1 ft./sec. superficial velocity, and gradually replace hydrogen with synthesis gas after attainment of the desired temperature and pressure.
5. During interruption of an extended test, shut down in nitrogen at 450°F. and atmospheric pressure and start up with hydrogen as above.

PROCESS VARIABLES

A number of thermodynamic analyses of the methanation reaction system have been made^{3,9,14,23} in an effort to evaluate the influence of the major operating variables: pressure, temperature and H₂/CO ratio,

on the equilibrium conversion of the feed gas to methane, water vapor, carbon dioxide and carbon. In these analyses the chemical reactions:



were employed as the basis of the equilibrium product distribution calculations. Under conditions of chemical equilibrium in the absence of carbon formation, any two of the first three reactions will define the system. When equilibrium carbon formation is to be included, one of the three carbon-forming Reactions (7), (8) and (9) must also be considered. The results of the various thermodynamic studies show that in the absence of carbon formation, nearly stoichiometric conversion of 1:1 to 3:1 H₂/CO ratio synthesis gases to methane can be attained at 650°F. and 25 atmospheres (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 atmospheres.

The calculation of equilibrium carbon yields is complicated by lack of information on the nature of the carbon deposited on methanation catalysts. Standard thermodynamic data are normally based on carbon in the form of beta-graphite²⁷, whereas under actual experimental conditions the deposited carbon may be in different forms, and, therefore, have different thermodynamic properties. For example, removal of excessive carbon from the system may involve carbide formation with the metallic catalyst component.

Carbon deposition boundary data based on equilibrium constants obtained from actual methanation reaction systems catalyzed by precipitated nickel⁹ show substantially lower limiting feed gas H₂/CO ratios than data based on beta-graphite.¹⁴ For example, at 900°F., the minimum H₂/CO ratios calculated from the experimental equilibrium data are 1.75:1 at one atmosphere, and 1.5:1 at 25 atmospheres. In comparison, when beta-graphite is used as the form of carbon, the minimum H₂/CO ratios at 900°F. are 3.25:1 at one atmosphere, and 2.6:1 at 25 atmospheres. For the calculations based on experimental results, the limiting H₂/CO ratio drops to 1:1 at 600°F., whereas for the beta-graphite data, freedom from carbon formation is not indicated anywhere in the low-temperature range below H₂/CO ratios of 2.6:1. Addition of steam or CO₂ to the feed gas lowers the limiting H₂/CO ratios.

The presence of CO₂ in the feed also has the desirable tendency to suppress hydrogen breakthrough. For example, if only the stoichiometric relationships are considered, a 3:1 H₂/CO ratio feed gas could give methane yields ranging from 0.125 moles to 0.25 moles/mole H₂ + CO, while complete CO conversion is maintained. Thus, unless CO conversion via the CO₂-forming Reactions (5) or (6) is limited by equilibrium hindrance, the actual methane yield may be substantially below the theoretically attainable level.

To establish the range of suitable fluid-bed operating conditions with Raney nickel catalysts, a series of exploratory tests was made in the laboratory reactors. Synthesis gases of about 1.5:1 and 3:1 H₂/CO ratio and various CO₂ contents were methanated over catalyst charges prepared by leaching of 100 cc. of alloy with dilute caustic for more than 4 hours. Pressure levels of 27, 75 and 150 p.s.i.g. were investigated, which permitted up to fourfold variations in space velocity at constant superficial feed gas velocity. With purified synthesis gas produced by steam-oxygen gasification of coal (42-47 mole % H₂, 31-32 mole % CO, 15-19 mole % CO₂, 1-2 mole % CH₄, 4-5 mole % N₂) complete CO and nearly complete

H₂ conversions were obtained at superficial feed gas velocities up to approximately 0.7 ft./sec. This corresponds to a space velocity of 8000 SCF/cu. ft. catalyst-hr. at 150 p.s.i.g. At superficial velocities below 0.3 ft./sec., carbon recoveries in the product gas tended to be low, possibly as a result of carbon deposition on overheated, incompletely fluidized catalyst.

In a series of parallel tests with 2.8-3.4:1 H₂/CO ratio synthesis gases containing only small amounts of CO₂, CH₄ and N₂, no significant CO breakthrough was observed at space velocities as high as 9000 SCF/cu. ft. catalyst-hr. at 27 p.s.i.g., and 15,000 SCF/cu. ft. catalyst-hr. at 75 and 150 p.s.i.g. Satisfactory operation in all other respects was also obtained over a superficial feed gas velocity range of 0.1-3.3 ft./sec., except for one instance of apparent low carbon recovery in the product gas at 0.1 ft./sec. and 150 p.s.i.g.

In an additional series of tests, the effect of 20-30 mole % CO₂ dilution of 3.2-3.8:1 H₂/CO synthesis gas was investigated at pressures of 75, 150 and 300 p.s.i.g. At gas feed rates corresponding to space velocities of 7000-23,000 SCF/cu. ft. catalyst-hr. and superficial velocities of 0.2-2.4 ft./sec., no significant CO breakthrough was observed, and carbon recoveries in the product gas were approximately 100%.

The 1.049-inch inside diameter reactors used in the last series and in subsequent tests had approximately 60% more annular space than the reactors used initially, since the diameter of the thermowell had been decreased from 0.840 inches to 0.675 inches. As a result, catalyst bed depths and superficial gas velocities at equivalent operating conditions were about 60% of the values with the original reactor design. This was probably responsible for an increase in the maximum temperature level of the catalyst bed from 650°-750°F. to 690°-790°F. under conditions giving essentially complete CO conversion.

A summary of the average yield data for these three series of tests is presented in Table 1. The data show the expected trend of increase in methane content, and decrease in hydrogen content, of the product gas as pressure is increased. At 75 p.s.i.g., there was little suppression of hydrogen breakthrough due to the effects of feed gas CO₂ content. However, at 150 p.s.i.g., substantial reduction in hydrogen breakthrough was observed at the lower space velocities. At 300 p.s.i.g., the combined effect of high pressure and presence of CO₂ in the feed gas resulted in nearly complete suppression of hydrogen breakthrough except at the very high space velocities. The tendency toward increases in hydrogen breakthrough with increases in space velocity for the high H₂/CO ratio synthesis gases was not clearly defined at all pressure levels, possibly due to variations in feed gas composition. In the tests with the high CO₂-content 3:1 H₂/CO ratio gases there was a slight reduction in the quantity of CO₂ leaving the reactor compared to the quantity entering.

Although only some of the product gases had CO concentrations readily detectable by the analytical procedures employed (mass spectrometer supplemented by infrared analysis), it appears that the carbon monoxide shift reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ closely approached equilibrium in all tests, since CO concentrations of less than 1 mole %, and normally as low as 0.1-0.5 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 H₂ + CO content that is converted to methane

Table 1.-EFFECT OF OPERATING CONDITIONS ON FLUID-BED METHANATION YIELDS WITH RANEY NICKEL CATALYST

CO₂-Containing 1.5:1 H₂/CO Ratio Feed Gas

Pressure, p.s.i.g.		27		75		150
Space velocity, SCF/cu. ft. cat.-hr. ^a		1200-		2300-		3000-
		2200		4400		8000
Moles product gas/mole feed		0.56		0.56		0.55
Moles water formed/mole feed		0.07		0.07		0.07
Gas composition, mole %		<u>Feed</u>		<u>Feed</u>		
CO ₂		16	51	16	52	53
CO		31	--	32	--	--
H ₂		47	4	46	2	1
CH ₄		1	35	1	36	36
N ₂ ^b		5	10	5	10	10

Essentially CO₂-Free 3:1 H₂/CO Ratio Feed Gas

Pressure, p.s.i.g.		27		75		150
Space velocity, SCF/cu. ft. cat.-hr		1000-		1000-		1000-
		9000		15,000		15,000
Moles product gas/mole feed		0.30		0.30		0.27
Moles water formed/mole feed		0.23		0.23		0.24
Gas composition, mole %		<u>Feed</u>				
CO ₂		1	6		6	5
CO		24	--		--	--
H ₂		74	11-14		11	8
CH ₄		0	78-75		78	82
N ₂ ^b		1	5		5	5

CO₂-Containing 3:1 H₂/CO Ratio Feed Gas

Pressure, p.s.i.g.		75		150		300
Space velocity, SCF/cu. ft. cat.-hr		8000-		7000-		7000-
		23,000		21,000		17,000
Moles product gas/mole feed		0.45		0.45		0.43
Moles water formed/mole feed		0.20		0.20		0.21
Gas composition, mole %		<u>Feed</u>				<u>Feed</u>
CO ₂		27	56	59-56		25
CO		16	--	--		17
H ₂		56	5	2-5		57
CH ₄		0	36	36		0
N ₂ ^b		1	3	3		1
						54-52
						--
						1-3
						42
						3

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

^bReported N₂ content of product gases may include small percentage of CO.

or methane equivalent: % H₂-CO Conversion =

$$100 \frac{4 \left[\frac{(\text{Moles Dry Prod. Gas})}{(\text{Moles Dry Feed Gas})} (\text{Mole \% CH}_4\text{-Equiv. in Dry Prod. Gas}) - (\text{Mole \% CH}_4\text{-Equiv. in Dry Feed Gas}) \right]}{\text{Mole \% H}_2 + \text{CO in Dry Feed Gas}}$$

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 1:1-3:1 H₂/CO ratio range by the necessary combination of Reactions (4) and (5), or (4) and (6), a value of 100% would be obtained. If ethane is also produced, the H₂-CO conversion based on the above definition could slightly exceed 100%; however, the maximum value at complete conversion of 0.75:1-2.5:1 H₂/CO 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% H₂-CO conversion or more.

Sulfur tolerance limits of standard fluid-bed Raney nickel catalysts prepared by 65 and 85% aluminum conversion were determined to establish synthesis gas purification requirements. In these tests, CO₂-containing, 3:1 H₂/CO ratio synthesis gases having organic sulfur contents (mainly in the form of COS) of 0.5 to 4 grains per 100 SCF were methanated at space velocities of 5000 to 15,000 SCF/cu.ft. catalyst-hr. and 75 p.s.i.g. Each test was made with a fresh batch of catalyst, and continued until most of the catalyst activity had been lost. It was observed that the catalyst activity dropped rapidly to less than 70 to 80% H₂-CO conversion when the total sulfur exposure attained a level of approximately 0.5 lb./100 lb. of nickel. This agrees quite well with similar sulfur poisoning test results obtained in studies with supported nickel catalysts.³⁵ It was determined by measurement of H₂S and organic sulfur liberated from a poisoned catalyst by acid treatment that essentially all of the organic sulfur introduced in the course of 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 a gas containing 0.01 grain of sulfur per 100 SCF is fed at a rate of 10,000 SCF/cu.ft. catalyst-hr.

Typical results of a catalyst life test with purified synthesis gas are given in Table 2. In this test, H₂-CO conversion dropped to approximately 80% in 1010 hours of operation at 75 p.s.i.g.; at that time, the pressure level was increased to 150 p.s.i.g., which resulted in an increase in H₂-CO conversion to a level of about 90%. However, after 1300 hours of operation, the H₂-CO conversion dropped to 70% and the run was terminated. Only 45% of the original catalyst volume (measured under methanol) was recovered, so the decrease of conversion capacity cannot be ascribed solely to activity loss.

The CO₂-free heating values shown in Table 2 are lower than would be desirable for use of the process as a source of a natural gas supplement. This is typical of operation at relatively low pressure and high space velocity with a high H₂/CO ratio synthesis gas. However, gas of approximately 900 B.t.u./SCF CO₂-free heating value was produced for about 500 hours in a similar run in which the pressure was maintained at 150 p.s.i.g. through the entire operating period. By adjustment of the H₂/CO 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./SCF CO₂-free gas at 75 p.s.i.g. and 10,000 SCF/cu.ft. catalyst-hr. space velocity for limited periods.

Table 2.-TYPICAL PERFORMANCE DATA FOR STANDARD FLUID-BED RANEY NICKEL CATALYST^a

Duration of test, hr.	300	500	720	970	1070	1300
Feed gas	2.98	3.12	3.22	3.28	3.05	3.65
H ₂ /CO ratio	0.0010	0.0004	0.0005	0.0007	0.0005	0.0008
Sulfur, grains/100 SCF	75	75	75	75	150	150
Pressure, p.s.i.g.	790	725	735	710	750	685
Temperature, °F.	795	770	775	775	800	755
Bottom of reactor	785	780	780	795	795	800
9 inches from bottom	785	780	780	795	790	790
18 inches from bottom						
27 inches from bottom						
Feed gas						
Space velocity, SCF/cu.ft. cat.-hr	11,578	11,556	12,248	11,981	10,210	10,584
Superficial inlet velocity, ft./sec.	1.27	1.20	1.29	1.20	0.59	0.58
Product gas ^b						
SCF/SCF feed	0.495	0.506	0.499	0.522	0.488	0.573
Carbon recovery, %	100	98	100	98	100	100
Hydrogen recovery, %	66	68	71	68	69	69
Oxygen recovery, %	80	79	76	79	77	82
Composition, mole %						
CO ₂	Feed 28.1	Feed 26.9	Feed 47.0	Feed 23.5	Feed 25.2	Feed 44.7
CO	17.7	0.6	1.1	16.9	17.6	22.2
H ₂	52.7	50.9	11.8	55.5	52.7	15.6
CH ₄	0.3	3.6	37.0	0.9	0.6	56.9
C ₂ H ₆	--	0.1	0.3	0.2	0.2	22.2
N ₂	1.2	2.1	2.8	1.2	1.1	0.4
Total	100.0	100.0	100.0	100.0	100.0	100.0
CO ₂ -free specific gravity, air = 1.000	0.528	0.505	0.484	0.442	0.514	0.407
CO ₂ -free heating value, B.t.u./SCF	856	840	784	701	863	584
Water formation, moles/mole feed gas						
By hydrogen balance	0.1821	0.1852	0.1796	0.1875	0.1736	0.1820
By oxygen balance	0.1486	0.1470	0.1487	0.1441	0.1651	0.1230
H ₂ -CO conversion, %	92	86	87	78	94	68

^a Run No. 498, Catalyst No. 59B prepared by 65% aluminum conversion of 100 cc. (162g.) of 40-200 mesh 42 wt. % nickel-58 wt. % aluminum alloy.

^b Excluding water formed by methanation reactions.

Table 3 summarizes the test results for five extended runs in which more than 1000 lb. net CH₄-equivalent/lb. Ni was produced. Included are results of an early test with a catalyst which was activated by three successive caustic extractions (No. 25C). It can be seen that the conversion capacities obtained after the first two extractions were very small. Extended operation was possible only after most of the aluminum had been extracted. This run was discontinued voluntarily before the H₂-CO conversion had decreased to the minimum acceptable level. In a test with another early catalyst preparation (No. 33A) it was possible to obtain a total conversion capacity of 2770 lb. net CH₄-equivalent/lb. Ni by successive pressure increases from 75 to about 300 p.s.i.g. The attrition rate in this test was the lowest of any completed so far; unfortunately, the analytical data for Catalyst 33A are not reliable, since they were obtained at a time when the procedures were still under development. For example, the significant difference in the composition of fresh and recovered catalyst was not observed in the three most recent tests (Catalysts 66B, 59B and 59A2). It has also not been possible to reproduce the composition of fresh Catalyst 33A, which shows an unusually high nickel and low alumina content.

On the basis of the data of Table 3, at the currently quoted cost of 90 cents per lb. for pulverized 42 wt. % nickel-58 wt. % aluminum Raney alloy in 25,000 lb. lots,²⁸ alloy costs per 1000 SCF of methane-equivalent would be in the range of 3 to 6 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.^{1a}

PILOT PLANT TESTS

The fluid-bed pilot unit was operated intermittently over a period of ten months with the original 0.343 cu. ft. charge of caustic-extracted 42 wt. % nickel-58 wt. % aluminum Raney catalyst. Nine runs with steady-state periods ranging from 7 to 47-1/2 hours were made with a cumulative steady-state operating period of 177 hours. During this time, approximately 47,000 SCF of net methane-equivalent, corresponding to 125 lb./lb. Ni, were produced. Typical operating data from this series of runs are given in Table 4.

The alloy used in the preparation of the pilot plant catalyst had a bulk density of approximately 110 lb./cu. ft. Assuming no volume change during extraction, the static bed height in the reactor would have been approximately 2 feet. It appears from the temperature patterns observed in the reactor at the higher feed rates that the actual bed height during operation was approximately 3 feet.

The feed gas was introduced through the two lower inlets, with 2/3 or more fed at the bottom of the reactor, and the remainder at the 18-inch level. Pressure levels in the reactor were generally increased with increases in feed rate, so that the superficial bottom feed gas velocity was maintained in the 0.2-0.6 ft./sec. range (calculated on the basis of inlet temperature, reactor pressure and cross-sectional area of the empty reactor). To maintain product gas quality as throughput rate and pressure were increased, it was necessary to increase the catalyst bed temperature from approximately 700°F. at space velocities of less than 1000 SCF/cu. ft. catalyst-hr. to 900°F. at space velocities of 5000 to 6000 SCF/cu. ft. catalyst-hr.

Table 3.-SUMMARY OF CATALYST LIFE TEST RESULTS

Catalyst No.	407	409	25c	411	66B	59B	59A2	33A
Run No.	160	174		180	516	498	511	444
Catalyst preparation								
Maximum temperature, °F	25	32		48	205	204	206	208
Activation duration, min	24	24		23	22	74 ^a	74 ^a	More than
Aluminum conversion, %	No	No		No	2 hr. at	65	65	4 hr.
Predrying in N ₂					250°F.	No	250°F.	85
Catalyst composition, wt. % ^c								No
Aluminum	29.8	18.7		5.4	16.2 (16.8)	14.9 (11.4)	15.8 (15.4)	11.4 (0)
Nickel	32.5	30.3		31.7	32.6 (32.3)	29.6 (31.9)	32.6 (31.4)	49.1 (20.1)
Al ₂ O ₃ ·3H ₂ O	37.7	51.0		62.9	51.2 (51.0)	55.5 (52.5)	51.6 (53.2)	39.5 (79.9)
Operating conditions								
Run duration, hr	48	40	300	310	1180	1010	1500	850 ^d
Number of shut downs	75	75	11	25	10	16	19	44
Pressure, p.s.i.-g.			75-	150-	150	75	75-	122-
Maximum temperature, °F.	760-	770-	775-	800-	690-	750-	720-	755-
	835	785	805	885	805	815	830	875
Feed gas								
H ₂ /CO ratio	3.7-	3.6-	3.2-	3.0-	2.5-	2.2-	2.5-	2.6-
	4.2	3.8	4.2	3.2	3.7	4.6	3.8	3.9
CO ₂ content, mole %	1	1	0-	0-	0	11-	0-	21-
Superficial velocity, ft./sec.	1.0-	1.1-	1.0-	0.5-	0.3	1.7	3.2	3.1
Space velocity, SCF/cu.ft. cat.-hr	1.2	1.2	1.2	0.6	1.0	1.5	0.9-	1.0-
Net equivalent methane yield	9,400-	9,700-	9,200-	8,500-	9,200-	9,500-	8,000-	7,400-
lb./lb. nickel	10,800	10,600	11,900	10,400	16,500	15,700	14,800	10,700
1000 SCF/lb. alloy				9,700		10,600	12,300	12,000
Catalyst recovery, vol.%			14.0		19.70	21.00	22.70	27.0 ^d
			14.5		19.9	21.3	22.9	27.9
			--		25	45	40	70

a Double preparation (200 cc. of alloy)
 b Based on nominal 58 wt. % aluminum content of alloy.
 c Recovered catalyst analyses are given in parenthesis.
 d Includes a number of short tests at a variety of operating conditions.

Table 4.-TYPICAL FLUID-BED PILOT UNIT METHANATION TEST RESULTS WITH RANEY NICKEL CATALYST AND PURIFIED 3:1 H₂/CO RATIO SYNTHESIS GAS

Run No.	0.245 cu.ft. of original alloy			0.5 cu.ft. of catalyst		
	P-7	P-11	P-15	P-19	P-20	P-21
Total steady state duration, hr	6	84	131.5	166	19.75	37.75
Pressure, p.s.i.g.	11	143	190	167	110	103
Temperature, °F						
Bottom of Reactor	705	810	800	890	750	860
9 inches from bottom					805	925
18 inches from bottom	695	815	805	900	820	925
27 inches from bottom	690	735	665	745	785	830
36 inches from bottom	710	680	650	650	---	730
54 inches from bottom	710	640	590	590	---	---
72 inches from bottom	700	585	670	640	---	---
90 inches from bottom					---	---
Dowtherm inlet temperature, °F	700	695	665	595	720	605
Jacket	700	685	650	600	720	605
Bayonets						
Feed Gas						
Space velocity, SCF/cu.ft. cat.-hr.	712	3491	5708	5923	4410	5761
Total gas rate, SCF/hr.	244	1198	1928	2031	2205	2881
Gas rate, bottom reactor, %	68	82	80	82	78	89
Gas rate, 12 inches from bottom, %						
Gas rate, 18 inches from bottom, %						
Superficial bottom inlet velocity ft./sec.						
Product gas						
SCF/SCF feed	0.302	0.339	0.304	0.293	0.282	0.297
Carbon recovery, %	100	77	102	98	100	105
Hydrogen recovery, %	64	18	70	64	67	67
Oxygen recovery, %						
Composition, mole %						
CO ₂	2.4	7.4	2.9	6.5	5.6	8.8
CO	20.3	24.6	23.3	22.3	23.1	22.0
H ₂	77.3	69.1	73.8	75.1	73.2	73.7
CH ₄	69.5	20.1	13.9	16.4	6.1	5.4
N ₂	1.0	3.1	3.4	3.3	84.4	82.1
N ₂ Total	100.0	100.0	100.0	100.0	100.0	100.0
CO ₂ -free specific gravity, air = 1.000	0.445	0.463	0.500	0.484	0.540	0.543
CO ₂ -free heating value, B.t.u./SCF	791	818	865	843	912	916
Water formation, moles/mole feed gas						
By hydrogen balance	0.2818	0.1931	0.2287	0.2742	0.2461	0.2481
By oxygen balance	0.2125	0.2354	0.2231	0.2149	0.2374	0.2217
By condensate measurement	0.2158	0.2315	0.2288	0.2013	0.2335	0.2489
H ₂ -CO conversion, %	85	96	97	88	97	98

*Excluding water formed by methanation reactions. †Includes small amount of C₂H₆.

‡May include some CO not distinguishable from N₂ by mass spectrometer analysis when present in small concentrations.

Complete CO conversion was obtained over the entire range of space velocities investigated, and H₂-CO conversions were normally above 90%. Some of the variation in the H₂-CO conversions was the result of small changes in feed gas H₂/CO ratio. The product distribution was very close to equilibrium values^{9,14} calculated on the basis of Reactions (4) and (6), except when catalyst activity limited H₂-CO conversion at high space velocities and relatively low temperatures. Reduction in temperature of approximately 70°F. below the level necessary to maintain equilibrium conversions resulted in a significant increase in H₂ breakthrough, CO₂ formation, and total dry product gas volume, accompanied by a decrease in CH₄ concentration (compare the two test periods reported for Runs P-11 and P-15). The increased amounts of combined oxygen (CO₂) and free hydrogen in the product gas were balanced by decreased water formation. At temperatures high enough to maintain adequate catalyst activity there was little net carbon dioxide formation.

The catalyst bed temperature increase with increases in throughput rate was accompanied by a decrease in Dowtherm inlet temperature from approximately 700°F. to 600°F. This indicates that it was possible to remove the exothermic heat of reaction at the lower space velocities under essentially isothermal conditions, whereas at the high throughput rates a temperature difference of approximately 300°F. between the catalyst bed and the Dowtherm was required. For a heat of reaction of approximately 100,000 B.t.u./pound-mole of methane (equivalent to approximately 65 B.t.u./SCF of H₂ + CO converted), and assuming an actual catalyst bed height of 3 feet equivalent to a heat transfer area of 8.7 sq. ft., the overall heat transfer coefficient between the catalyst bed and the circulating Dowtherm was on the order of 50 B.t.u./hr.-sq. ft.-°F. It is estimated that the overall coefficient for the cooling bayonets was actually on the order of 100 B.t.u./hr.-sq. ft.-°F. because of the lower Dowtherm film resistance at the high flow rates in the bayonets as compared to the jacket.

The test program with the original charge of catalyst was discontinued because of excessive pressure drops through the reactor. Inspection of the reactor offtake section showed that the four 1-1/2 x 9-inch porous stainless steel gas filters were clogged with a considerable quantity of catalyst fines. Since this condition was probably aggravated by the offtake design and inadequate filter area, these equipment components were modified by the addition of a 16-inch diameter x 2-foot section to the disengaging zone. This section housed four 3 x 18-inch porous stainless steel filters with a combined area three times as large as that of the original installation.

In addition, the 1/2-inch Schedule 40 cooling bayonets were enlarged to 3/4-inch Schedule 40 pipe to give an increase of approximately 25% in the cooling surface to catalyst volume ratio (17.0 sq. ft./cu. ft. to 21.4 sq. ft./cu. ft.). The gas inlet system was also enlarged to reduce the high pressure drop encountered at the higher gas rates. It was hoped that these changes would permit attainment of the nominal 3000 SCF/hr. synthesis gas capacity desired for integrated pilot plant operation.

The modified reactor was operated at approximately 100 p.s.i.g. with a catalyst charge consisting of approximately 1/3 recovered catalyst from the preceding test period, and 2/3 of catalyst prepared by the original procedure, which had been stored under water for nearly one year. The total catalyst volume, measured under water, was approximately 0.5 cu. ft. In two runs totalling 44 hours of steady-state operation with H₂/CO ratio synthesis gas produced by reforming of natural gas, feed gas rates ranging from 1400 to 3300 SCF/hr. were investigated. Gases of

about 900 B.t.u./SCF and 84 mole % CH₄ content were produced up to the highest feed rate, confirming that the desired capacity of the reactor could be attained. Typical run data for the modified reactor are given in the last two columns of Table 4. They indicate substantially lower hydrogen breakthrough, and somewhat higher H₂-CO conversion, than were obtained with the original catalyst charge and reactor design.

On the basis of these pilot plant test results, it appears that a practical full-scale, dense-phase fluid-bed methanation reactor can be designed for high-capacity, one-pass operation, although such a reactor will have a relatively shallow catalyst bed. For example, at typical operating conditions of 1 ft./sec. superficial feed gas velocity, 5000 SCF/cu.ft. catalyst-hr. feed gas space velocity, 300 p.s.i.g., 750°F. catalyst bed temperature, 550°F. coolant temperature and at a heat transfer coefficient of 100 Btu/hr.-sq.ft.-°F, a 10-foot diameter methanation reactor would require about 2500 1-inch tubes for heat removal, and would contain an unexpanded catalyst bed about 6.6 ft. deep, equivalent to an unexpanded catalyst volume of 360 cu.ft. Such a reactor would handle a methane production rate of about 1.8 million SCF/hr. corresponding to a methane production rate of about 450,000 SCF/hr., or over 10 million SCF/day. Lean-phase fluidization may give more flexibility of operation; each of the two reactors constructed by the M. W. Kellogg Company for SASOL in South Africa reportedly handles 9.5 million SCF/hr. of synthesis gas at 5000 tons/hr. catalyst circulation.¹⁷

INTEGRATED PIPELINE-GAS-FROM-COAL OPERATION

The process steps shown in Figure 5 were investigated in a number of exploratory runs. Although only short on-stream periods were possible because of rapid catalyst failure, the indicated operating conditions and results should be representative of those attainable in steady-state operation. The catalysts used in these runs were prepared before the activation, handling and startup procedures described in the preceding sections had been developed. Catalyst failure appeared to be the result of attrition or disintegration, which caused lifting of the bed into the disengaging and filter zone of the reactor, where severe overheating occurred.

The design and operation of the suspension coal gasifier have been fully described elsewhere.³⁴ However, the use of CO₂ instead of air to pressurize the coal feed tank was a departure from the previous procedure, necessitated by the requirement for a low N₂ content of the synthesis gas when a high-heating-value product gas is desired. Intermediate partially purified synthesis gas storage was provided, since the generating capacity under the preferred operating conditions is 20,000 SCF/hr. for limited on-stream periods, whereas the nominal capacity of the remainder of the plant is 3000 SCF/hr.

One of the major problems of integrated operation investigated in the exploratory pilot plant tests was synthesis gas purification. The use of fixed-bed iron oxide purification (9 lb. Fe₂O₃/bushel) for bulk H₂S removal, and of separate CO₂ removal from the methanated gas, is probably uneconomical in comparison to hot carbonate, ethanolamine or Rectisol scrubbing of the raw synthesis gas for combined H₂S, CO₂ and partial organic sulfur removal.^{2,12,17,21,29,37} However, the scheme employed here has the advantage of allowing CO₂ to remain in the purified synthesis gas, which is beneficial for two reasons: first, it inhibits hydrogen breakthrough and carbon formation, and second, it provides a diluent as a heat sink for some of the exothermic heat of reaction with-

out the use of gas recycle. Further, in relatively small-scale operation, the highly effective trouble-free and well known iron oxide purification technique appeared preferable from practical considerations.

The organic sulfur (COS and CS_2) concentration of 10 grains/100 SCF used in Figure 5 is only nominal, since it varied considerably with the sulfur content of the coal. In one test with a 4 wt. % sulfur content bituminous coal, the raw gas after bulk H_2S removal contained 26 grains of organic sulfur per 100 SCF; satisfactory operation of the purification system at 3200 SCF/hr. feed rate was still obtained. However, in view of the limited capacity of activated carbon for organic sulfur removal at high partial pressures of CO_2 ,³⁰ it would have been desirable to reduce the load on the carbon towers by the addition of another conventional purification step for selective catalytic conversion of COS and CS_2 to H_2S by hydrolysis and hydrogenation.¹³ With the scheme shown in Figure 5, the synthesis gas bypassing the CO shift reactor had the original organic sulfur content, although the remainder contained only a small amount, since COS and CS_2 conversion proceeds simultaneously with catalytic CO shift. The resulting reappearance of H_2S was easily handled by a second set of small iron oxide towers.

The final CO_2 removal step shown in Figure 5 had not yet been put into operation when the pilot plant program was interrupted to overcome catalyst problems. In practice, it is unlikely that monoethanolamine scrubbing would be competitive with other processes, such as hot carbonate, at the high CO_2 concentrations and pressures involved.^{2,12}

CONCLUSIONS

The technical feasibility of a pipeline-gas-from-coal process utilizing a fluid-bed, partially extracted Raney nickel alloy catalyst for the synthesis gas methanation step was demonstrated. However, rapid mechanical deterioration of this catalyst occurred frequently without a clear indication of the exact causes. This problem was overcome on a laboratory reactor scale by careful control of the caustic leaching step employed for activation of the alloy, by predrying of the catalyst to insure a free-flowing, readily fluidizable charge, and by slow startup in hydrogen. However, successful use of these techniques in the operation of a pilot-plant-scale reactor has yet to be demonstrated. In process variables studies, the use of CO_2 -containing, 3:1 H_2/CO synthesis gases was shown to have a beneficial effect on H_2 - CO conversion to methane under operating conditions where the catalyst activity was sufficient to permit close approach to equilibrium of the CH_4 - CO_2 - H_2O - CO - H_2 system. Organic sulfur tolerance of the catalyst at high contamination levels was approximately 0.5 lb./100 lb. of nickel, indicating the need for purifying synthesis gas to a sulfur content of less than 0.01 grain/100 SCF if active catalyst life is not to be limited below a practical economic level. The total catalyst conversion capacity with purified synthesis gas at 10,000 SCF/cu. ft. catalyst-hr. synthesis gas space velocity, and operating pressures of 75-150 p.s.i.g., was approximately 20,000 SCF of methane/lb. of original Raney alloy, or 2000 lb. of methane/lb. of nickel. This corresponded to an active catalyst life of 1000-1500 hours and an original alloy cost on the order of 5 cents/1000 SCF of methane. Since generally less than half of the catalyst was recovered at the end of a test of this duration, it appears that catalyst life was limited by attrition rather than by deactivation.

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