PRODUCTION OF HIGH-METHANE-CONTENT GAS BY STEAM REFORMING OF LIGHT DISTILLATES

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INTRODUCTION

A novel approach to gasification of light distillate oils, developed by the British Gas Council, was first reported in 1957[4,7,8] and was subsequently discussed in later publications.[6,9] The process entails reducing the sulfur content of the feed by a hydrodesulfurization step with subsequent steam reforming in the presence of a nickel catalyst. Because of the low temperature at which reforming is conducted – in the range of 400° to 550°C – the product gas contains 60 to 80 mole percent methane (dry basis). Data reported by the Gas Council[5,6] show product gas heating values of 626 to 704 Btu/SCF in operation over a pressure range of 1 to 25 atm. There was no carbon deposition at fairly low steam/hydrocarbon ratios, and the reaction was either thermally balanced or slightly exothermic. The catalyst is reported to be extremely sulfur-sensitive and is also subject to poisoning by olefins.

When a high-Btu gas is not the desired final product, the process includes a further stage in which the high-methane-content gas is further reformed to a low-Btu gas. This process is now used in Great Britain for baseload town gas production.[9]

A study of this process was begun under an IGT-supported basic research project. After a detailed study of the thermodynamics of the process, experiments were conducted with high-purity n-hexane, n-octane, and benzene, as well as commercial propane, naphtha, kerosene, and jet fuel.

The objectives of this study were to determine whether a catalyst could be developed that would be capable of reforming a variety of feedstocks that include paraffinic, olefinic, and aromatic materials with a wide range of molecular weights. Once a catalyst was developed, it was necessary to determine minimum steam/hydrocarbon ratios for operation without carbon deposition, the activity of the catalyst, and the effects of various operating variables on the gas yield and composition.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

A schematic diagram of the reaction system is shown in Fig. 1. Weighed amounts of the hydrocarbon feedstock (A) and water (B) flow through rotameters (C), and are charged by a duplex metering pump (D) to the feed vaporizer (F). The vaporized feeds are thoroughly mixed in a chamber above the vaporizer. The mixed feed flows down through the catalyst bed in the reactor (J). The product gas is cooled, and liquids are condensed in a cooler-condenser (K). Condensate is knocked out and drained from the system (L,M). The gas flows through filters (N) into a freezeout trap (R). After saturation with water vapor, the product gas (S) is metered by a wet-test meter (T) and sampled (U). The specific gravity is monitored by a recording gravitometer (5). The unit pressure is controlled by a dome-loaded back-

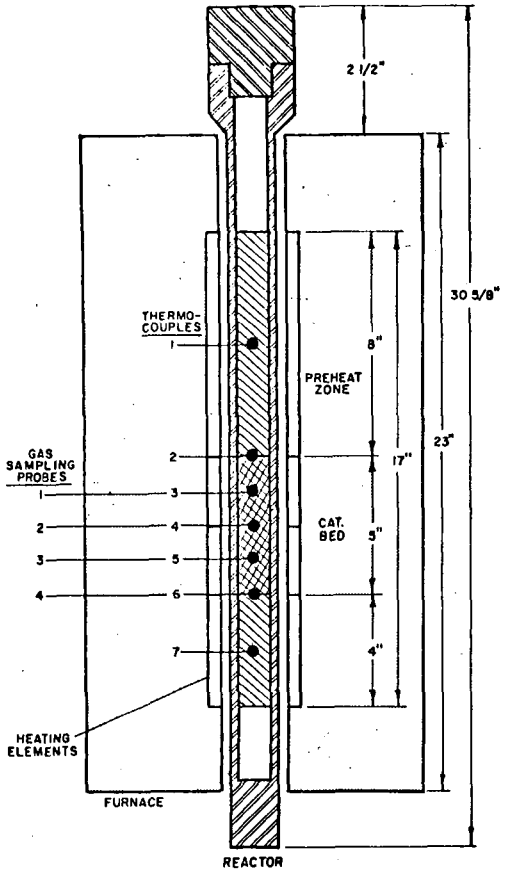

Fig. 3.-SECOND REACTOR AND FURNACE

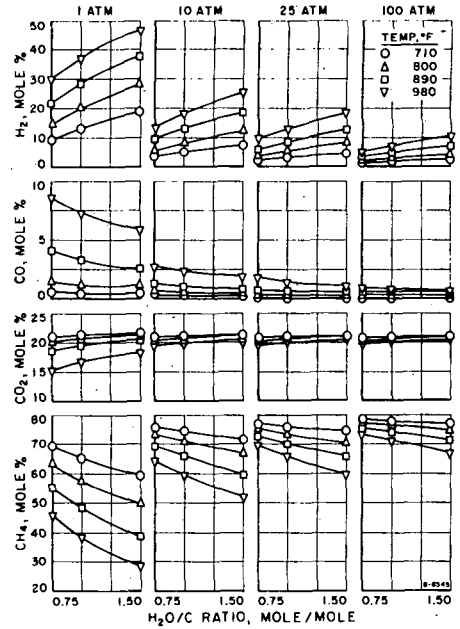

Fig. 4.-IDEAL GAS EQUILIBRIUM COMPOSITION (Water-Free) FOR STEAM REFORMING OF n-HEXANE

be produced from low molecular weight paraffins than from high molecular weight paraffins.

The reforming reaction can be either exothermic or endothermic depending on the temperature and pressure. Increases in pressure cause the reaction to become more exothermic, whereas increases in temperature cause the opposite effect. The reaction becomes progressively less exothermic as the feed steam/carbon ratio is increased. The degree of exothermicity increases with increases in molecular weight.

Reforming Studies with n-Hexane Feedstock

Space Velocity

Initial studies were made with pure grade n-hexane to determine the reaction stiochiometry, approach to equilibrium, and the catalyst behavior without complicating factors such as catalyst poisons. The feedstock space velocity was the first process variable studied to measure the maximum catalyst activity under the most ideal conditions. The effect of space velocity on product gas composition was also noted. At space-time yields over 50,000 SCF/cubic foot catalyst per hour, 98 percent of the hexane could be converted to gaseous products. When conversions dropped below 100 percent, the major effect of an increase in space velocity on gas composition was a decreased methane content and an increased hydrogen content of the product gas (Fig. 6). The carbon dioxide content of the gas remained essentially constant. Carbon monoxide remained negligible over the entire range of space velocity. Even at the highest space velocity used, the heating value of the product gas could be raised to about 850 Btu/SCF by simply scrubbing out carbon dioxide to a final content of 2 mole percent. This could be satisfactory for peakshaving.

Because the carbon monoxide content of the gas was so low, approaches to equilibrium could not be calculated accurately for runs at nearly complete conversion and low space velocity. One other factor that also makes it difficult to calculate approaches to equilibrium is the presence of a hot spot within the catalyst bed, which indicates that the reaction may occur in a very narrow zone. Temperature profiles were measured in three runs (Fig. 7). The gas compositions for these runs correspond to equilibrium at the temperatures measured near the bottom (exit) of the catalyst bed, which is what would be expected.

Steam/Hydrocarbon Ratio

The next series of tests was made to show the effect of the steam/hydrocarbon ratio on gas composition (Fig. 8) and to determine the minimum practical steam/hydrocarbon ratio. The trends shown are approximately the same as predicted by equilibrium calculations. The lack of complete temperature profile data makes it difficult to show how closely the trends agree with equilibrium predictions. Steam/hydrocarbon weight ratios as low as 1.6 (molar ratio of 7.7) were shown to be adequate to prevent carbon deposition. The product gas heating value at this low ratio was about 774 Btu/SCF. It could be raised to 957 Btu/SCF if the exit gas carbon dioxide were reduced to 2.0 mole percent by scrubbing.

Reforming of Various Feedstocks

When the catalyst developed proved to be capable of reforming pure n-hexane successfully at low steam/hydrocarbon ratios, we decided to test a variety of feedstocks having a wide range of molecular weight

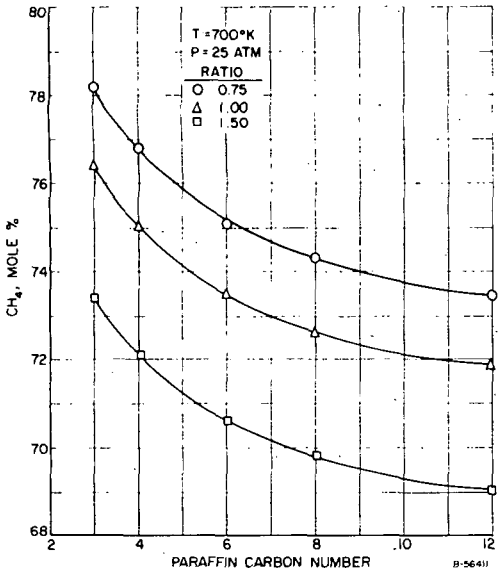

Fig. 5.-IDEAL GAS EQUILIBRIUM METHANE CONTENTS (Water-Free) FOR STEAM REFORMING OF VARIOUS PARAFFINIC HYDROCARBONS

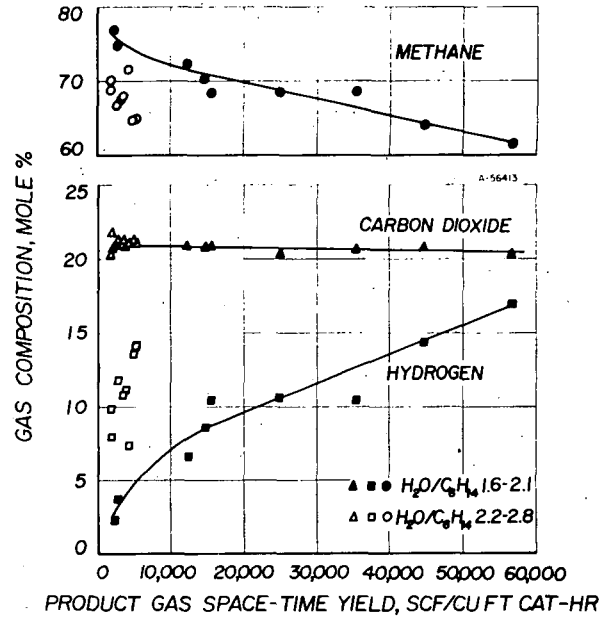

Fig. 6.-GAS COMPOSITION AS A FUNCTION OF SPACE-TIME YIELD AND STEAM/ HYDROCARBON RATIO

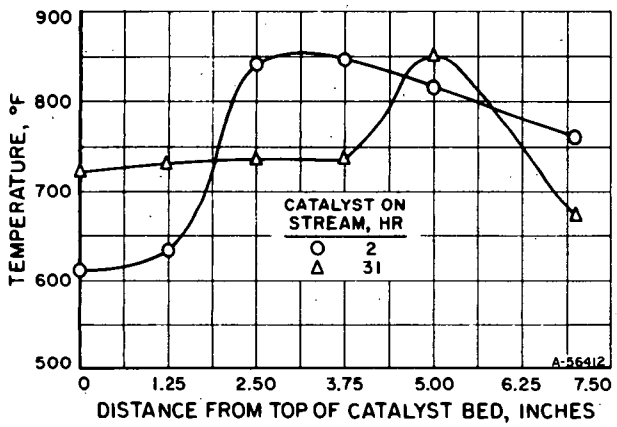

Fig. 7.-BED CATALYST TEMPERATURE PROFILES

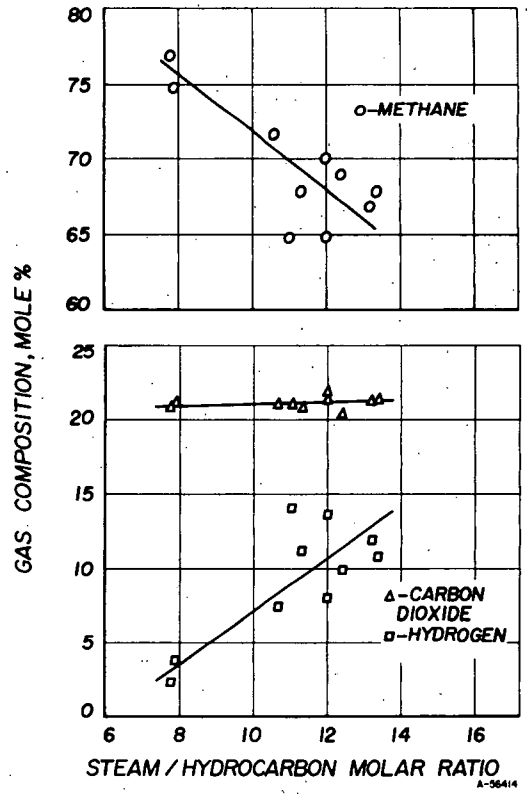

Fig. 8.-EFFECT OF STEAM/HYDROCARBON RATIO ON GAS COMPOSITION

and various types of hydrocarbons. The first tests were conducted with n-octane and benzene to show whether heavier paraffins and aromatics could be reformed and whether the gases produced could be predicted by equilibrium calculations.

Test results for n-octane and benzene reforming are summarized in Table 2. The steam/hydrocarbon ratios were deliberately set high to avoid possible carbon formation with these heavier or aromatic feedstocks.

Table 2.-TEST RESULTS FOR STEAM REFORMING OF n-OCTANE AND BENZENE

Feedstock	n-Octane	Benzene
Pressure, psig	375	353
Temperature at Center of Bed, °F	768	905
Steam/Hydrocarbon Weight Ratio	2.07	4.42
Hydrocarbon Space Velocity, lb/hr-cu ft catalyst	300	324
Product Gas Composition, mole % (water-free)		
N_2 + CO	0.4	0.9
CO_2	21.7	30.7
H_2	11.3	31.3
CH_4	66.4	36.7
C_3H_8	0.2	--
C_6H_6	--	0.4
Total	100.0	100.0
Scrubbed Gas Composition, mole % (water-free)		
+ CO	0.5	1.3
CO_2	2.0	2.0
H_2	14.2	44.3
CH_4	83.1	52.4
C_3H_8	0.2	--
C_6H_6	--	--
Total	100.0	100.0
Scrubbed Gas Heating Value, Btu/SCF	879	675

The remaining commercial feedstocks studied were propane, light naphtha, light kerosene, and JP-4 jet fuel. The results with these feedstocks are given in Table 3. As can be seen, a higher methane content gas can be produced from the lighter hydrocarbons. This result agrees with results of equilibrium calculations shown in Fig. 5. These feedstocks were all highly paraffinic, of course, but as can be seen from Table 1, the kerosene contained 1.1 volume percent olefins and 5.3 volume percent aromatics; the naphtha contained 2.0 volume percent aromatics, and the jet fuel contained 4.6 volume percent olefins and 10.6 volume percent aromatics. This indicates that over short time periods, aromatics and olefins are not likely to be a problem. However, earlier studies on the methanation process have shown that sulfur compounds may react with the nickel in nickel catalysts almost quantitatively, resulting in catalyst poisoning. Therefore, for commercial operation, low-sulfur-content feedstocks would be preferred.

Table 3.-TEST RESULTS FOR STEAM REFORMING OF SEVERAL COMMERCIAL FEEDSTOCKS

Feedstock	Propane	Naphtha	Jet Fuel	Kerosene
Pressure, psig	355	355	350	375
Temperature at Center of Bed, °F	890	935	900	832
Steam/Hydrocarbon Weight Ratio	1.26	2.16	2.36	2.03
Hydrocarbon Space Velocity, lb/hr-cu ft catalyst	834	328	254	226
Product Gas Composition, mole % (water-free)				
N_2 + CO	0.1	0.2	0.2	1.1
CO_2	16.8	21.5	22.5	23.6
H_2	1.9	12.1	14.5	18.1
CH_4	80.1	66.2	62.6	57.2
C_2H_6	0.1	--	--	--
C_3H_8	1.0	--	--	--
C_6H_{14}	--	--	0.2	--
Total	100.0	100.0	100.0	100.0
Scrubbed Gas Composition, mole % (water-free)				
N_2 + CO	0.1	0.3	0.3	1.4
CO_2	2.0	2.0	2.0	2.0
H_2	2.2	15.1	18.3	23.2
CH_4	94.4	82.6	79.1	73.4
C_2H_6	0.1	--	--	--
C_3H_8	1.2	--	--	--
C_6H_{14}	--	--	0.3	--
Total	100.0	100.0	100.0	100.0
Scrubbed Gas Heating Value, Btu/SCF	980	883	860	809

ACKNOWLEDGMENT

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