

FISCHER-TROPSCH SYNTHESIS

Differential Reaction Rate Studies with Cobalt Catalyst

ROBERT B. ANDERSON, ABRAHAM KRIEG¹, AND R. A. FRIEDEL

Central Experiment Station, U. S. Bureau of Mines, Bruceton, Pa.

L. S. MASON

University of Pittsburgh, Pittsburgh, Pa.

THE rate of synthesis of cobalt Fischer-Tropsch catalysts is dependent upon temperature, operating pressure, composition, and flow of synthesis gas, as well as the chemical and physical nature of the catalyst (17). Weller (20) and Anderson (5) showed that the rate of the synthesis was strongly dependent on temperature, overall activation energies being about 25 kg.-cal. per mole. Fischer and Pichler (10) and Weller (20) found that the rate of synthesis at subatmospheric pressures was dependent upon the operating pressure to a power less than 1. At atmospheric pressure and above, the pressure coefficient of the synthesis rate was found to be about 0; however, the catalyst remained active considerably longer at elevated pressures than at atmospheric pressure. Operation at atmospheric pressure necessitated periodic reactivation by hydrogen or by solvent extraction (13).

Tsuneoka and Fujimura (18) studied the synthesis as a function of gas composition; however, their data have little kinetic value because the conversion of the synthesis gas was maintained at such a high value that either the hydrogen or the carbon monoxide was nearly completely consumed in each test. The usage ratios of hydrogen to carbon monoxide remained about 2 for the wide ranges of gas composition; as would be expected, the yields were greatest with 2 hydrogen to 1 carbon monoxide gas.

Studies of variation of flow at constant temperature (12, 15) indicate that the rate increases with throughput of synthesis gas, which may be due to either the increased partial pressure of reactants or the decreased partial pressure of products. The presence of such diluents as nitrogen or carbon dioxide in amounts less than 20% had no marked effect on the rate of synthesis (19). Fischer and Pichler (11, 16) found that carbon dioxide in hydrogen-carbon monoxide mixtures was not hydrogenated until virtually all of the carbon monoxide was consumed, and under these conditions chiefly methane was formed.

Craxford (8) showed that methane was formed by hydrocracking of higher-molecular-weight hydrocarbons and carbon dioxide by the water-gas shift reaction on parts of the catalyst not actively engaged in the synthesis. Craxford postulated that these reactions occur on parts of the catalyst not covered by cobalt carbide—that is, on bare cobalt atoms on which sizable amounts of atomic hydrogen were adsorbed.

Craxford (6), Anderson (4), and others showed that the catalyst in the synthesis was heavily covered by hydrocarbon wax. At atmospheric pressure the rate of synthesis was retarded when

Differential reaction rate data are presented for the Fischer-Tropsch synthesis with cobalt catalysts at atmospheric pressure. The synthesis rate was high in the initial part of the bed, lower and nearly constant throughout a large portion of the catalyst bed, until the reactants were fairly completely consumed. Over the range of relatively constant rate of synthesis, the gas composition varied considerably. Methane and carbon dioxide were formed by primary reactions; methane was also formed by secondary hydrocracking of higher-molecular-weight hydrocarbons and carbon dioxide by the water gas reaction. These reactions occurred throughout the catalyst bed, and their extent depended upon the composition of the gas in contact with the catalyst. The postulates of Craxford involving the synthesis occurring on cobalt carbide and the secondary reactions on cobalt atoms do not appear to be an adequate explanation of author's data.

this wax rather completely filled the pores of the catalyst, but at higher pressures the catalytic activity remained constant even though the pores of the catalyst were filled with hydrocarbon. It has been postulated that the rate of synthesis depends upon some process at the catalyst surface and not upon rates of diffusion or adsorption of reactants (4).

Craxford (7) postulated that cobalt carbide is an intermediate in the synthesis and that its presence is desirable in the normal synthesis. Work at the Bureau

of Mines (4, 21) showed that bulk-phase cobalt carbide was not formed in the synthesis and that its presence in large amounts seriously decreased the catalytic activity. Thus, cobalt carbide does not appear to be the active catalyst in the synthesis.

Data are reported here on the rates of synthesis and the rates of formation of methane and carbon dioxide as a function of bed length, with argon as an inert reference component, for a cobalt-thoria-kieselguhr catalyst operated at atmospheric pressure with three different gases with hydrogen-carbon monoxide ratios of 3.5-1, 2-1, and 0.9-1. Possible mechanisms for the synthesis and reactions forming methane and carbon dioxide are discussed. Similar experiments are in progress with iron catalyst at elevated pressures.

PROCEDURE AND COMPUTATION

Pelleted cobalt-thoria-kieselguhr (100-18-100) catalyst 108B was used. The method of preparation and properties of this catalyst and the method of testing in small, fixed-bed, externally cooled converters have already been described (2-5, 17). In the present experiments a special sampling tube was used in place of the thermocouple well in the usual fixed-bed converters, as the schematic drawing (Figure 1) shows. The outer tube of the sampling assembly had ports at 10-cm. intervals along the 90-cm. catalyst bed. By suitable calibration it was possible to place the holes near the end of the snug-fitting inner tube at any desired port in the outer tube. About 5% of argon was added to the original synthesis gas as an inert reference component. Gas was slowly withdrawn (about 10 cc. per minute) to ensure that all of the gas would come from the desired portion of the bed. The samples were taken from the bottom to the top of the bed so as to minimize errors due to the removal of the previous sample. In every case the rate of withdrawal of gas was less than 2% of the gas flowing in that part of the bed. The gas samples were analyzed in a mass spectrometer (Consolidated Engineering Company).

¹ Present address, General American Transportation Corporation, East Chicago, Ind.

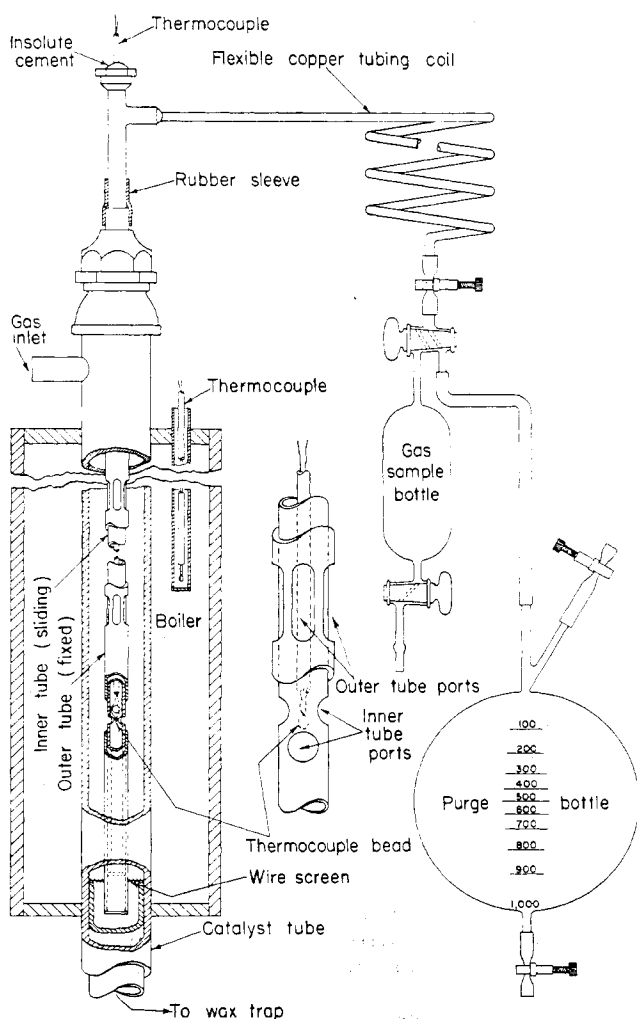


Figure 1. Sampling Device in Converter

The gases (synthesis gas, hydrogen, and argon of high purity) were premixed in cylinders. Argon was chosen as inert reference gas because of the accuracy and simplicity of its analysis by the mass spectrometer. From the increase in concentration of argon, the apparent contraction and the volume of any component at that point in the bed per unit volume of synthesis gas entering the converter could be computed. The following equations were used in the computations. Because the argon does not react,

$$f_{A0}V_0 = f_{Ax}V_x \quad (1)$$

where f_{A0} , f_{Ax} = fractions of argon in gas entering converter and at position x in catalyst bed, respectively
 V_0 , V_x = volumes of gaseous components entering bed and at position x

Since the gases were sampled at room temperature and analyzed on a water-vapor-free basis, water vapor and heavy hydrocarbons are not included in these volumes. The apparent contraction C is defined as

$$C = 1 - \frac{\text{volume out, per unit time}}{\text{volume in, per unit time}} \quad (2)$$

with the volumes measured at room temperature, or using Equations 1 and 2,

$$C_x = 1 - f_{A0}/f_{Ax} \quad (3)$$

where C_x = apparent contraction to point x

The volume of gas at any point, x , is $V_0(1 - C_x)$. Thus, the volume of component B at point x is given by

$$V_{Bx}/V_0 = (1 - C_x)f_{Bx} \quad (4)$$

The partial pressure of component B is equal to $V_{Bx}/V_{\text{total},x}$, where $V_{\text{total},x}$ is the sum of the volumes of all components at position x . The volume of water vapor was not determined directly, but obtained from an oxygen balance,

$$V_{H_2O_x} = V_{CO_0} - V_{CO_x} - 2V_{CO_{2x}} \quad (5)$$

This is permissible since nearly all of the oxygen in the products occurs as water and carbon dioxide. The volume of hydrocarbons other than methane was assumed to equal one tenth of the volume of water vapor present. This assumes an average molecular weight of these hydrocarbons of C_3 to C_9 ; since the volume of hydrocarbon vapor was usually less than 3% of the total volume, these assumptions introduce no significant error. The total conversion from the beginning of the bed to any point is expressed as liters of hydrogen plus carbon monoxide consumed per hour.

The accuracy of the experimental method is difficult to determine. The relative errors of the gas analyses were less than 1% except for percentages less than 2%, where the absolute accuracy was about 0.05%. The apparent contraction over the entire bed as computed from the change in concentration of argon was usually about 3 to 5% lower than the apparent contraction computed from the in- and outflows. The greater part of this difference was due to the fact that most of the gaseous hydrocarbons were removed by the charcoal scrubber placed before the outmeter. The accuracy of the sampling method probably was satisfactory, since the usage ratios of hydrogen to carbon monoxide computed between alternate ports were nearly equal to 2 in the parts of the bed where the normal synthesis might be expected to occur.

There was no indication of local overheating within the catalyst bed. The catalyst tube was surrounded by a bath of boiling

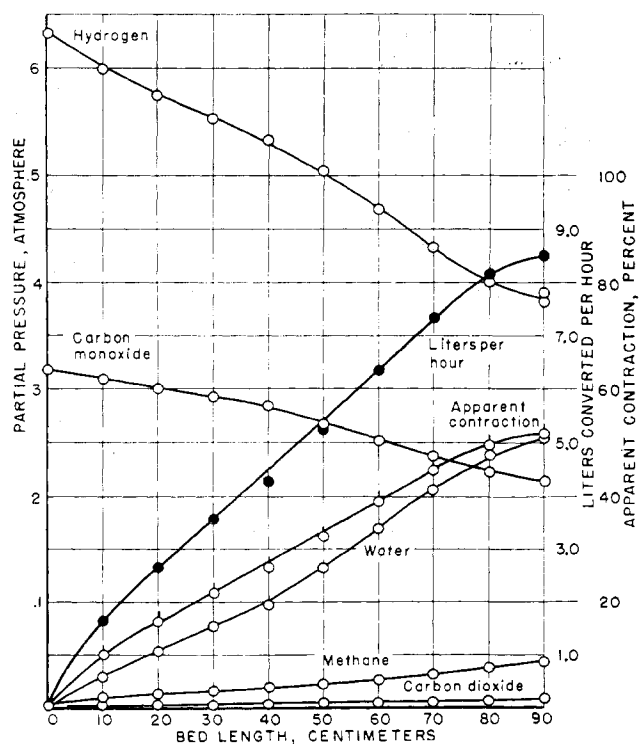


Figure 2. Data for Test 8

2H₂ to 1CO gas at 192° C. and space velocity of 102 per hour; inflow, 0.134 liter (S.T.P.) per gram unreduced catalyst per hour

Tetralin, the temperature being controlled by regulating the pressure at which the Tetralin was boiling (14, 17). Unfortunately the effect of the hydrostatic pressure of the boiling liquid on its boiling point was not anticipated, and this resulted in a 4° C. or less temperature gradient along the catalyst bed, the temperature increasing from the top to the bottom of the reactor. About the same temperature gradient was observed with no catalyst in the reactor. All of the temperatures reported in this paper were measured at the middle of the length of the boiling liquid bath by a thermocouple in the well in the boiler, as Figure 1 shows.

In these experiments 150 cc. of pelleted catalyst, weighing 114.4 grams, were used. The catalyst was reduced with hydrogen in the reactor at a space velocity of 3000 for 2 hours at 360° C. (space velocity taken as volumes of feed gas, at standard temperature and pressure, per bulk volume of catalyst per hour). All of the tests were made at atmospheric pressure.

CATALYST ACTIVITY

Previous studies (13) of the synthesis on cobalt catalysts at atmospheric pressure showed that the activity of a freshly reduced catalyst decreased considerably during the first 12 hours and then remained relatively constant for 10 or more days. After hydrogen reactivation, the activity was restored to its initial value, and the cycle was repeated. The average activity remained the same over many such cycles (5). In the present work the synthesis was studied with gases of hydrogen-carbon monoxide ratios of approximately 1, 2, and 3. The experiments with each gas mixture

TABLE I. GAS ANALYSIS DATA, IN VOLUME PER CENT, FOR TEST 10

	(2H ₂ to 1CO at 192° C.)												
Gas sample	A	H ₂	CO	CH ₄	C ₂	C ₂ -- ^a	C ₃	C ₃ --	C ₄	C ₄ --	C ₅	C ₅ --	CO ₂
Synthesis gas	4.54	62.91	32.16	0.32									0.06
Port a	5.62	59.00	32.85	1.80	0.13	(0.00)	0.03	...	0.07	0.16	0.07	0.07	0.20
Port b	6.31	56.97	32.67	2.89	0.17	(0.01)	0.13	0.13	0.10	0.20	...	0.10	0.33
Port c	7.01	55.62	32.09	3.70	0.23	(-0.04)	0.16	0.10	0.13	0.26	0.06	0.13	0.48
Port d	7.75	53.86	31.68	4.47	0.33	(-0.02)	0.20	0.16	0.07	0.36	0.13	0.20	0.69
Port e	9.30	50.79	31.25	5.87	0.42	(0.02)	0.26	0.32	0.16	0.35	0.10	0.19	0.90
Port f	11.37	46.24	29.98	8.07	0.62	(0.01)	0.46	0.42	0.29	0.62	0.20	0.29	1.34
Port g	14.01	40.46	28.95	10.85	0.86	(0.01)	0.66	0.49	0.43	0.73	0.26	0.36	1.81
Port h	16.36	35.61	26.96	13.48	1.10	(0.01)	0.91	0.75	0.52	0.75	0.29	0.32	2.82
Port i	17.07	34.11	25.85	14.43	1.17	(0.02)	1.01	0.52	0.62	0.78	0.42	0.39	3.43

^a Percentages of ethylene are given as actually calculated and represent upper limits. True contents of ethylene, if present, are probably less than 0.01%.

were planned to be made in the range of relatively constant catalytic activity, as just described. Prior to the special experiments under consideration, the catalyst was operated for 30 days with 2H₂ to 1CO gas at atmospheric pressure with reactivations with hydrogen at 200° C. every sixth day. Before the special experiment was started, the catalyst was reactivated with hydrogen at 200° C. and operated with 2H₂-1CO for 3 days to ensure constant activity. Then the catalyst was operated at the desired temperature and with the special gas mixture for 16 hours before the gas samples at various bed lengths were taken. The experiments with a given gas composition were performed on successive days, and the catalyst was reactivated with hydrogen before a series with another gas composition was started. The series of experiments were performed in the following order: 3H₂ to 1CO gas, 2H₂ to 1CO gas, and 1H₂ to 1CO gas.

The decrease in activity in a given series of experiments was usually small, and it is believed that these data may be compared without uncertainty. However, comparison of activities in different series of experiments with different gas compositions may be uncertain because the nature of the catalyst surface or the hydrocarbons adsorbed upon it may change. The data are inter-

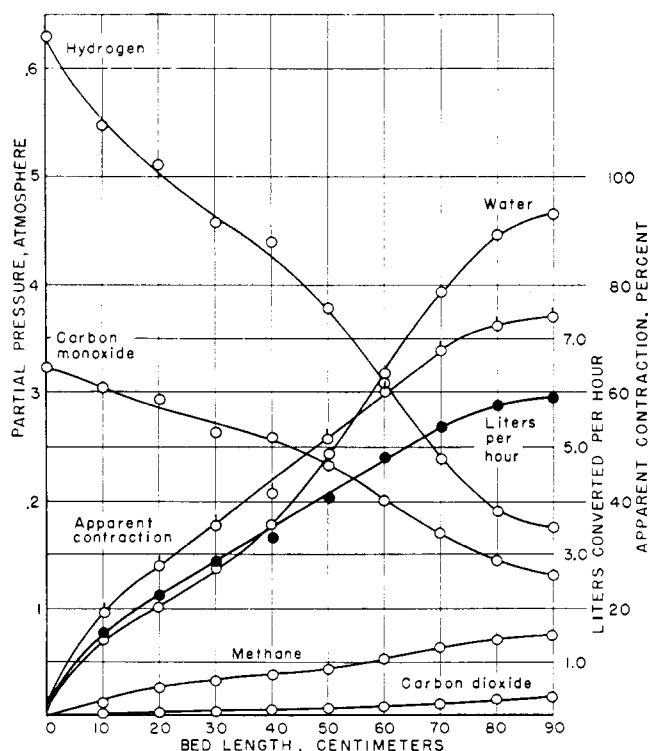


Figure 3. Data for Test 10

2H₂ to 1CO gas at 192° C. and space velocity of 49.5 per hour; inflow, 0.065 liter (S.T.P.) per gram unreduced catalyst per hour

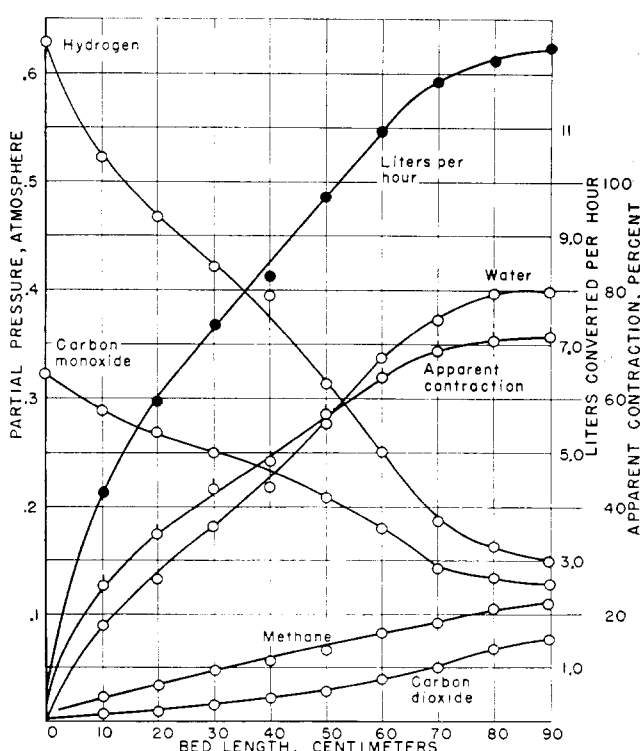


Figure 4. Data for Test 11

2H₂ to 1CO gas at 206° C. and space velocity of 102 per hour; inflow, 0.144 liter (S.T.P.) per gram unreduced catalyst per hour

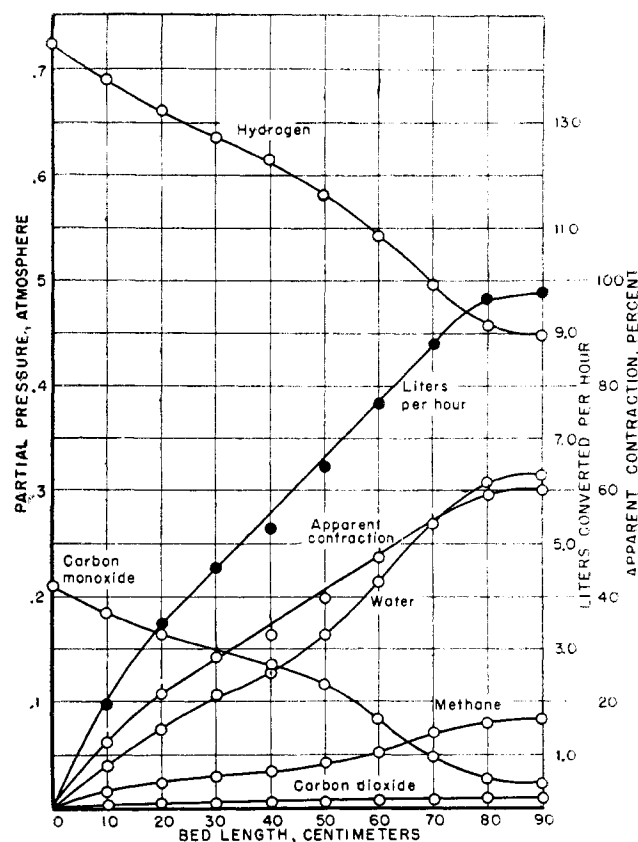


Figure 5. Data for Test 4

3.5H₂ to 1CO gas at 186° C. and space velocity of 99.5 per hour; inflow, 0.130 liter (S.T.P.) per gram unreacted catalyst per hour

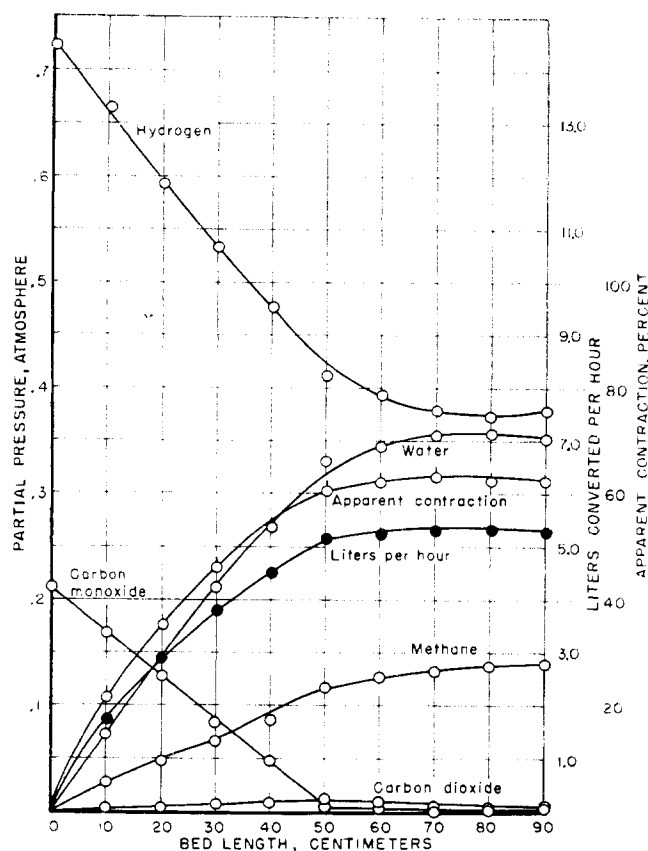


Figure 6. Data for Test 5

3.5H₂ to 1CO gas at 187° C. and space velocity of 49.3 per hour; inflow, 0.0646 liter (S.T.P.) per gram unreacted catalyst per hour

interpreted to indicate that the activity in terms of volumes of hydrogen plus carbon monoxide converted per hour at a given flow were about equal for hydrogen-carbon monoxide ratios of 3 and 2, but that the activity with 1 to 1 gas was considerably lower.

Table I gives gas analysis data for a typical experiment. The percentages of C₂ and higher hydrocarbons are too small to permit a detailed treatment of their rates of formation; however, it was possible to compare the total amount of saturated and unsaturated hydrocarbons present at any point in the bed for C₂ to C₄ hydrocarbons.

EFFECT OF SPACE VELOCITY

Figures 2, 3, and 4 present data for experiments with 2H₂ to 1CO gas; Figures 5, 6, and 7, data for 3.5H₂ to 1CO gas; and Figures 8 and 9, for 1H₂ to 1CO gas. In Figure 2, at 192° C. and 102 space velocity, the partial pressures of hydrogen and carbon monoxide decreased and the partial pressure of water vapor increased continuously throughout the bed. The slope of the curve for synthesis gas converted from the beginning of the catalyst bed to any port was large in the first part of the bed, then became nearly constant, and finally decreased near the outlet end of the bed. The partial pressure of carbon dioxide was small and increased throughout the bed, and the curve of the partial pressure of methane was concave upward. Decreasing the space velocity to 49.5 (Figure 3) increased the degree of conversion (apparent contraction) but decreased the space-time-yield as shown by the liters-per-hour curve. These curves and those of the partial pressures had the same general shape as in Figure 2. The partial pressures of methane and carbon dioxide were greater than in the previous figure. In Figure 4, at 206° C. and a space velocity of 102, the space-time-yield (liters per hour) curve was consider-

ably above those of Figures 2 and 3, and the partial pressures of methane and carbon dioxide were greater.

In a test with 3.5H₂ to 1CO gas at a space velocity of 99.5 and 186° C. (Figure 5), the curves had the same general shape as in Figures 2, 3, and 4, except that the partial pressure of carbon monoxide decreased more rapidly than that of hydrogen and the partial pressure of methane was greater. In tests 5 and 7 (Figures 6 and 7) the carbon monoxide was completely consumed by the middle of the catalyst bed. The partial pressures of methane were high and continued to increase even after the carbon monoxide was consumed. The partial pressure of carbon dioxide decreased after the carbon monoxide was completely consumed. Increases in flow and temperature increased the space-time-yield.

The activity of the catalyst had decreased considerably before tests 15 and 16 (Figures 8 and 9) were made. This was due to several days of operation in 1H₂ to 1CO gas in which tests 12 and 13 were made. The curves had the same general shape as in the experiments with 2H₂ to 1CO and 3H₂ to 1CO gas, except that the activities and space-time-yields were lower and the partial pressure of carbon monoxide remained constant over most of the catalyst bed. For 1H₂ to 1CO gas the partial pressure of carbon monoxide should remain constant as long as the hydrogen and carbon monoxide are consumed in the ratio of 2 to 1.

CONSUMPTION OF HYDROGEN AND CARBON MONOXIDE

Table II gives the ratios of usage of hydrogen to carbon monoxide along the catalyst bed for the data of tests 8, 5, and 14. The ratios were computed for the gas consumed in the catalyst bed between alternate ports—i.e., the first to third, second to fourth, etc. This tends to smooth the data and eliminates unimportant fluctuations. The usage ratio was somewhat greater than

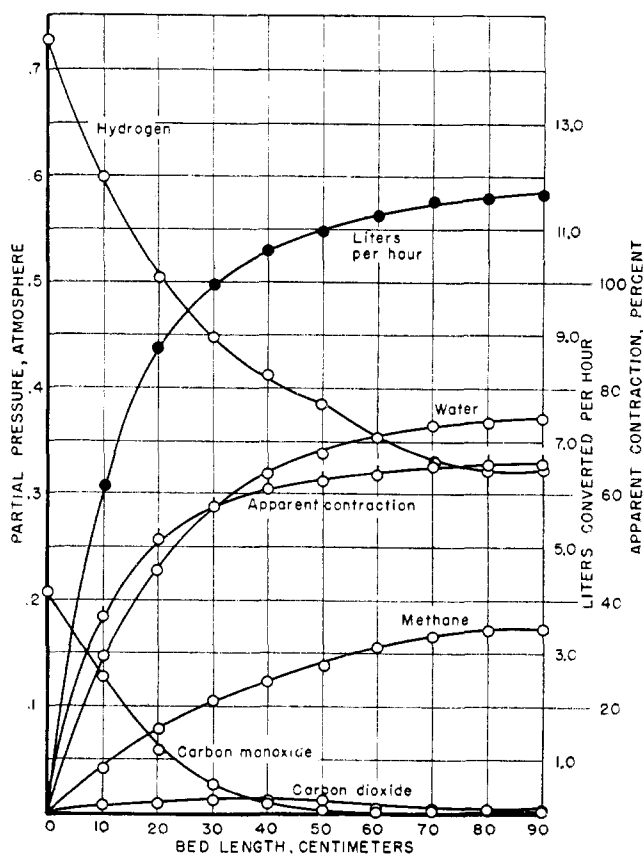


Figure 7. Data for Test 7

3.5H₂ to 1CO gas at 200° C. and space velocity of 102 per hour; inflow, 0.134 liter (S.T.P.) per gram unreduced catalyst per hour

2 at the beginning of the bed in all tests. With 2H₂ to 1CO gas the ratio remained somewhat above 2 throughout the catalyst bed except for the last part. With 3H₂ to 1CO gas the usage ratio remained somewhat above 2 in the first half of the bed and increased to very high values when nearly all of the carbon monoxide had been consumed. With 1H₂ to 1CO gas the ratio remained about 2, decreasing considerably near the bottom of the bed.

TABLE II. USAGE RATIOS OF HYDROGEN TO CARBON MONOXIDE AS A FUNCTION OF BED LENGTH

Port	Usage Ratio, H ₂ :CO		
	Test 8 2H ₂ :1CO	Test 5 3.5H ₂ :1CO	Test 14 1H ₂ :1CO
a	2.39	2.40	2.18
b	2.17	2.20	1.89
c	2.20	2.20	1.77
d	1.98	2.27	2.00
e	1.90	2.63	2.05
f	2.12	7.62	2.17
g	2.13	8.50	1.74
h	1.85	∞	1.25

In Figures 10, 11, and 12 the yield of methane formed in each portion of the catalyst bed per cubic meter of hydrogen plus carbon monoxide consumed is plotted against bed length for tests with 2H₂ to 1CO, 3.5H₂ to 1CO, and 1H₂ to 1CO, respectively. The data were smoothed by calculating the methane formed per cubic meter of gas consumed in an interval of two holes. With 2H₂ to 1CO gas the methane-bed length curves passed through a minimum in the middle of the catalyst bed. With 3.5H₂ to 1CO gas the methane curves increased from the beginning of the bed, becoming very high in tests 5 and 7 above the point in the bed where most of the carbon monoxide had been consumed. These

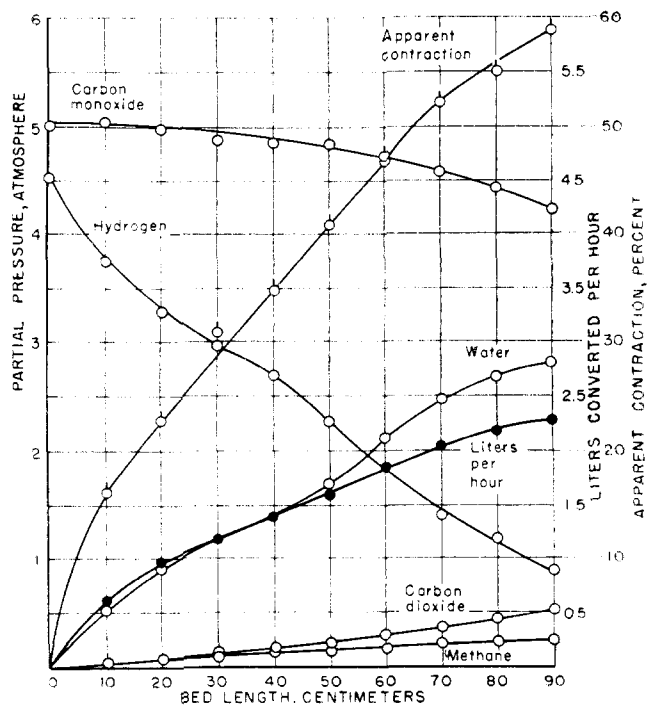


Figure 8. Data for Test 15

1H₂ to 1CO gas at 197° C. and space velocity of 24.1 per hour; inflow, 0.0316 liter (S.T.P.) per gram unreduced catalyst per hour

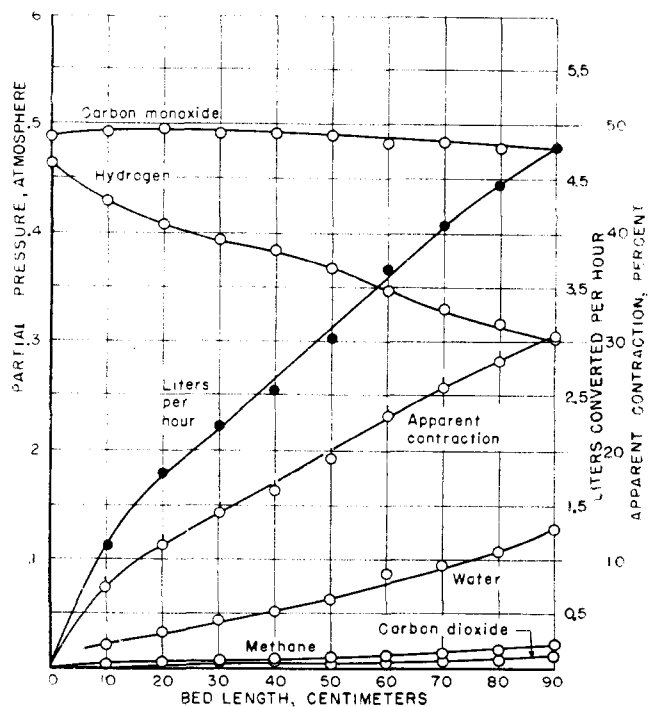


Figure 9. Data for Test 16

1H₂ to 1CO gas at 207° C. and space velocity of 95.5 per hour; inflow, 0.125 liter (S.T.P.) per gram unreduced catalyst per hour

large yields of methane per cubic meter of gas converted can be explained only by the assumption of hydrocracking of higher-molecular-weight hydrocarbons. With 1H₂ to 1CO gas (Figure 12), the yield of methane either remained constant or decreased throughout the catalyst bed. In all cases the yields of methane were greater at higher temperatures.

The percentages of light hydrocarbons other than methane in

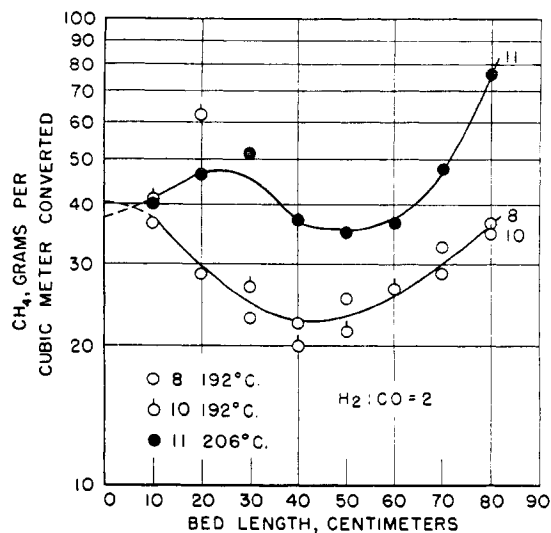


Figure 10. Differential Formation of Methane-Bed Length Curves for Tests 8, 10, and 11 with 2H_2 to 1CO Gas

Methane yields (in grams per cubic meter of H_2 plus CO consumed) were computed between alternate ports

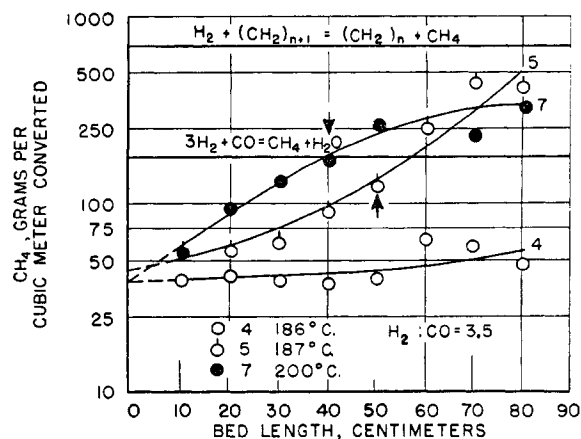


Figure 11. Differential Formation of Methane-Bed Length Curves for Tests 4, 5, and 7 with 3.5H_2 to 1CO Gas

Methane yields (in grams per cubic meter of H_2 plus CO consumed) were computed between alternate ports; arrows indicate position within bed where pressure of CO had decreased below 0.01 atm

the gas samples were too small to permit a detailed calculation of the amounts formed per cubic meter of gas reacted, but it was possible to prepare informative plots of ratios of saturated to unsaturated hydrocarbons in the gas against bed length, as shown for C_4 hydrocarbons in Figure 13. With 2H_2 to 1CO gas this ratio remained about constant in the first half of the bed and increased in the last half. The fraction of saturated hydrocarbons increased although the ratio of hydrogen to carbon monoxide decreased. With 3.5H_2 to 1CO the fraction of saturates increased throughout the bed, and with 1H_2 to 1CO gas it decreased.

FORMATION OF CARBON DIOXIDE

Figures 14 to 16 illustrate the formation of carbon dioxide as a function of bed length. Again the data are smoothed by computing the carbon dioxide formed over intervals of two ports. Since the total number of moles of hydrogen and carbon monoxide is unchanged if carbon dioxide is formed by the water gas shift reaction, the formation of carbon dioxide was computed as grams

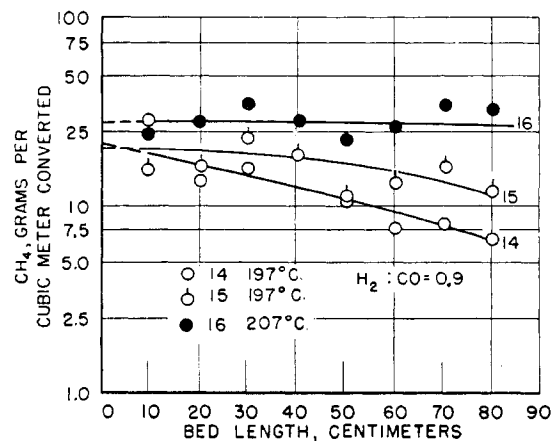


Figure 12. Differential Formation of Methane-Bed Length Curves for Tests 14, 15, and 16 with 1H_2 to 1CO Gas

Methane yields (in grams per cubic meter of H_2 plus CO consumed) were computed between alternate ports

of carbon dioxide formed per cubic meter of carbon monoxide consumed.

For 2H_2 to 1CO gas (Figure 14) the differential amount of carbon dioxide formed increased with bed length, the amount of carbon dioxide being greater for the experiments in which the fractional conversion was the greatest. With 3.5H_2 to 1CO the amount of carbon dioxide also increased with increasing percentage of conversion until the carbon monoxide was practically consumed (experiments 5 and 7). Beyond this point the carbon dioxide formed in previous portions of the bed was consumed either by hydrogenation to methane or by the reversal of the water gas reaction. With 2H_2 to 1CO gas the amount of carbon dioxide formed was greater than with 3H_2 to 1CO gas for similar conversions. With 1H_2 to 1CO gas (Figure 16) the yields of carbon dioxide increased with increasing extents of conversion, and for similar extents of conversion the carbon dioxide was greater than for either 2H_2 to 1CO or 3.5H_2 to 1CO gas.

The amount of carbon dioxide formed was shown to increase with the extent of conversion and thus with the partial pressure of water vapor in the gas stream, and also increased with the partial pressure of carbon monoxide. Thus, the data strongly suggest the water gas shift reaction as the source of carbon dioxide, water being the predominant oxygen-containing product of the primary reaction. The amount of carbon dioxide usually increased with temperature, but its formation was more strongly a function of partial pressure of water vapor than of temperature.

The data of Figures 2 to 9 are summarized in Figure 17, where percentage of incoming hydrogen plus carbon monoxide consumed is plotted against the reciprocal of the space velocity for tests with hydrogen to carbon monoxide ratios of 3.5 to 1, 2 to 1, and 1 to 1. These plots show the same characteristic mentioned previously, and the points obtained at the same temperature but with different initial flows fall about the same curve. The middle portion of the conversion curves is almost linear, the slope of this part decreasing only slightly with decreasing space velocity. In the initial portions of the bed the slope of the conversion curve is greater than that of the "linear" portion, and when the reactants are about 70% consumed the slope is lower. The rate curve for 1H_2 to 1CO gas flattens at a lower fractional conversion than those for the other gas mixtures.

With 2H_2 to 1CO gas the over-all activation energies computed from the rates of reaction at equal extents of conversion were about 29.0 kg.-cal. per mole at high extents of conversion and were somewhat larger at low conversions. With 3H_2 to 1CO gas larger activation energies than 29.0 kg.-cal. per mole were observed, and with 1H_2 to 1CO gas, lower activation energies.

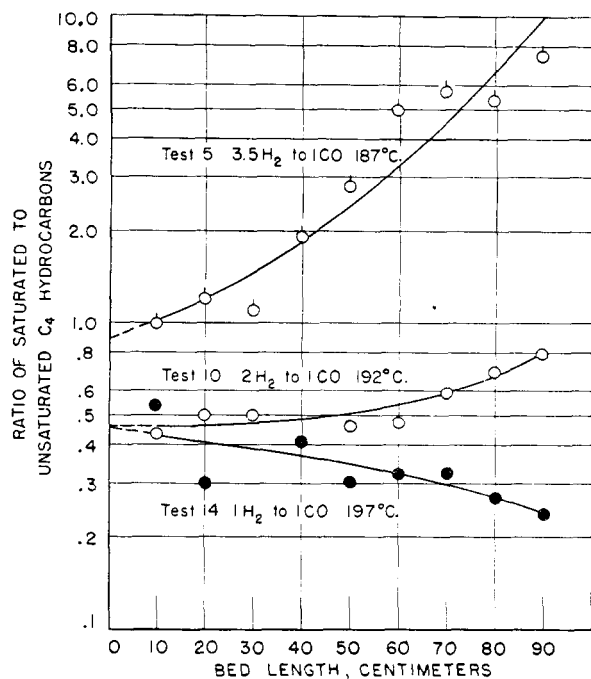
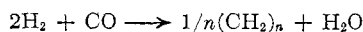


Figure 13. Ratio of Saturated to Unsaturated C_4 Hydrocarbons vs. Bed Length for Tests 5, 10, and 14

Ratios of C_4 hydrocarbons were computed from total amounts of these components present at any given position in bed and are not differential values

DISCUSSION OF RESULTS

The principal primary reaction of the synthesis on cobalt catalysts may be represented by the equation,



the usage ratio of H_2 to CO being about 2 over a wide range of gas composition. The rate of the synthesis was large at the beginning of the bed, then decreased to a nearly constant value in the middle section, and finally decreased near the end of the bed or at a point where the reactants were strongly depleted. In the middle portion the rate was nearly constant although the partial pressures of reactants and products changed considerably. It is difficult to estimate to what extent the integral rate curve was influenced by the temperature gradient along the bed; however, the extent of divergence of the data in Figure 17 indicates that the temperature differences did not influence the data greatly. The fact that the extent of conversion at a given temperature can be correlated with the space velocity (Figure 17) suggests that the rate is a function of gas composition. The rate was found to be practically independent of total pressure above atmospheric (4). This and the data of Figure 17 indicate that the dependence on partial pressure of the various components was slight. The data suggest that the rate-controlling step is some process at the catalyst surface and not the rate of adsorption of reactants which would be strongly dependent upon the partial pressures of the reactants. A mechanism in which desorption of products is the rate-determining step predicts qualitatively many of the characteristics of the synthesis. The application of simplified rate equations, such as derived by Hougen and Watson (14) will be discussed in a later paper. The rather high values of the apparent activation energies probably exclude diffusional processes as rate-controlling steps. The reaction is very complicated, because the catalyst is heavily covered with the hydrocarbon products, and differences in the nature of the catalyst surface may be a function of the composition of the gas in contact with catalyst. Prob-

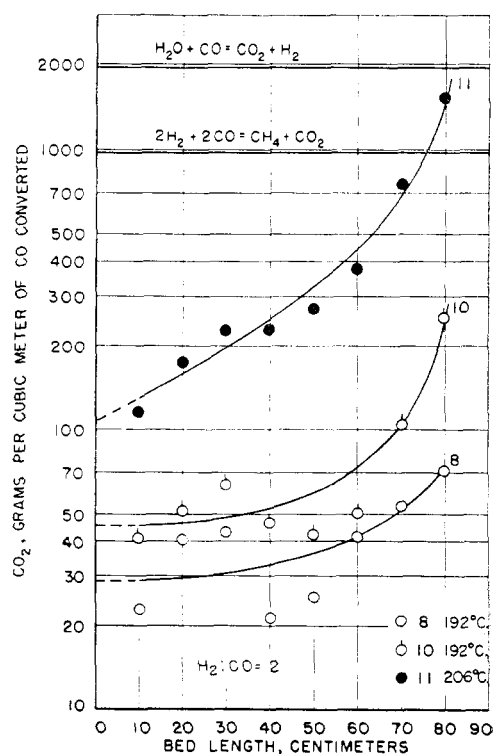


Figure 14. Differential Formation of Carbon Dioxide-Bed Length Curves for Tests 8, 10, and 11 with $2H_2$ to $1CO$ Gas

CO_2 yields were computed between alternate ports

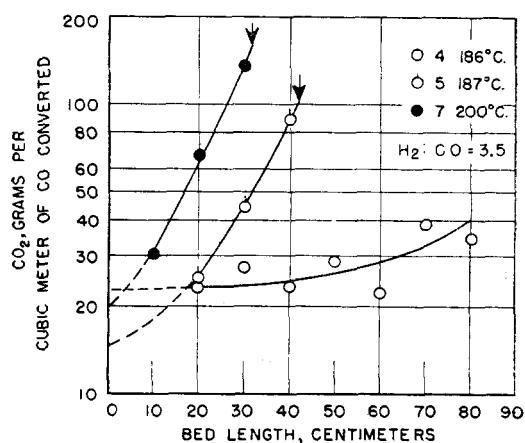


Figure 15. Differential Formation of Carbon Dioxide-Bed Length Curves for Tests 4, 5, and 7 with $3.5H_2$ to $1CO$ Gas

CO_2 yields were computed between alternate ports. Arrows indicate position within bed where pressure of CO had decreased below 0.01 atm.; beyond these points in the bed CO_2 was consumed

ably no simple rate equation should be expected to express the observed rate.

The rate of synthesis was about equal for $2H_2$ to $1CO$ and $3.5H_2$ to $1CO$ gases, but was smaller for $1H_2$ to $1CO$ gas. With 1 to 1 gas the activity decreased more rapidly with time, which is in agreement with data reported previously (6). This may result from a reversible poisoning by the high carbon monoxide concentration similar to, but much less rapid than, the poisoning of iron catalysts in the ammonia synthesis by water vapor (1, 9). This poisoning effect may be related to formation of greater

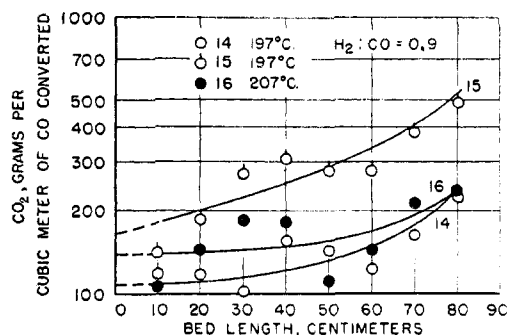


Figure 16. Differential Formation of Carbon Dioxide-Bed Length Curves for Tests 14, 15, and 16 with 1H_2 to 1CO Gas

CO_2 yields were computed between alternate ports

quantities of surface carbide by the gas with high carbon monoxide content. The rate appears to be only slightly "inhibited" by high partial pressures of carbon monoxide.

Some conclusions may be drawn as to the nature of the reactions forming methane, saturated and unsaturated hydrocarbons, and carbon dioxide. With 2H_2 to 1CO gas, methane formation was large in the first part of the bed, passed through a minimum, and then increased in the latter part of the bed. The high yield of methane in the first part of the bed may have been due to either primary or secondary reactions, while the increasing amounts of methane formed in the latter parts of the bed may have been produced by hydrocracking of higher hydrocarbons. With 3.5H_2 to 1CO gas the yields of methane increased throughout the catalyst bed, and in these experiments the ratio of hydrogen to carbon monoxide increased continually down the catalyst bed. In experiments 5 and 7 (Figure 11) there is definite evidence for the hydrocracking reaction since the yields of methane exceeded 179 grams per cubic meter of hydrogen plus carbon monoxide converted, corresponding to the reaction $3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ (179 grams per cubic meter is also the maximum yield for the reaction $4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$). With 1H_2 to 1CO gas (Figure 12) the yields of methane either remained constant or decreased down the catalyst bed. In these experiments the ratio of hydrogen to carbon monoxide decreased down the catalyst bed. The yields of methane were higher at higher temperature. Thus, for each of the three compositions of synthesis gas, the reactions producing methane were favored by high ratios of hydrogen to carbon monoxide, high partial pressures of hydrocarbon products in the gas stream, and high temperatures.

The ratio of saturated to unsaturated hydrocarbons present at any point in the catalyst bed varied with the ratio of hydrogen to carbon monoxide in the gas at that part of the bed as shown for the C_4 hydrocarbons in Figure 13. This indicates that olefins may be a primary product of the reaction, and that these olefins may then be hydrogenated or undergo further reaction to form a hydrocarbon of higher molecular weight at the point of formation or in later parts of the catalyst bed.

Carbon dioxide formation was chiefly a function of the partial pressure of water vapor in the gas and to some extent of the ratios of hydrogen to carbon monoxide. Most of the carbon dioxide appears to be formed by a secondary water-gas reaction. Even with the hydrogen-rich gas, carbon dioxide was formed in sizable quantities until almost all of the carbon monoxide had been consumed. When the partial pressure of carbon monoxide decreased to less than 0.01 atmosphere, the carbon dioxide formed in the reaction was consumed with the formation of methane. At the point in the bed where carbon dioxide began to be consumed, the quotient of the product of the partial pressures of carbon monoxide and water vapor divided by the product of the partial pressures of carbon dioxide and hydrogen was fifty to a hundred times

greater than the equilibrium constant. This indicates that carbon dioxide was consumed by direct reduction to methane and not by reversal of the water gas reaction. However, this interpretation assumes that the gases reacting at the catalyst surface have the same composition as those in the main gas stream.

The results on the consumption of carbon dioxide agree with the work of Fischer and Pichler (11, 16) in which carbon dioxide was not consumed in the synthesis until almost all of the carbon monoxide had reacted. Methane was the only hydrocarbon formed by the hydrogenation of carbon dioxide.

Thus, the processes that form methane appear to be functions of the partial pressures of hydrogen and hydrocarbons, and processes forming carbon dioxide appear to be functions of the partial pressures of water vapor and carbon monoxide. The formation of both methane and carbon dioxide increased with increasing tem-

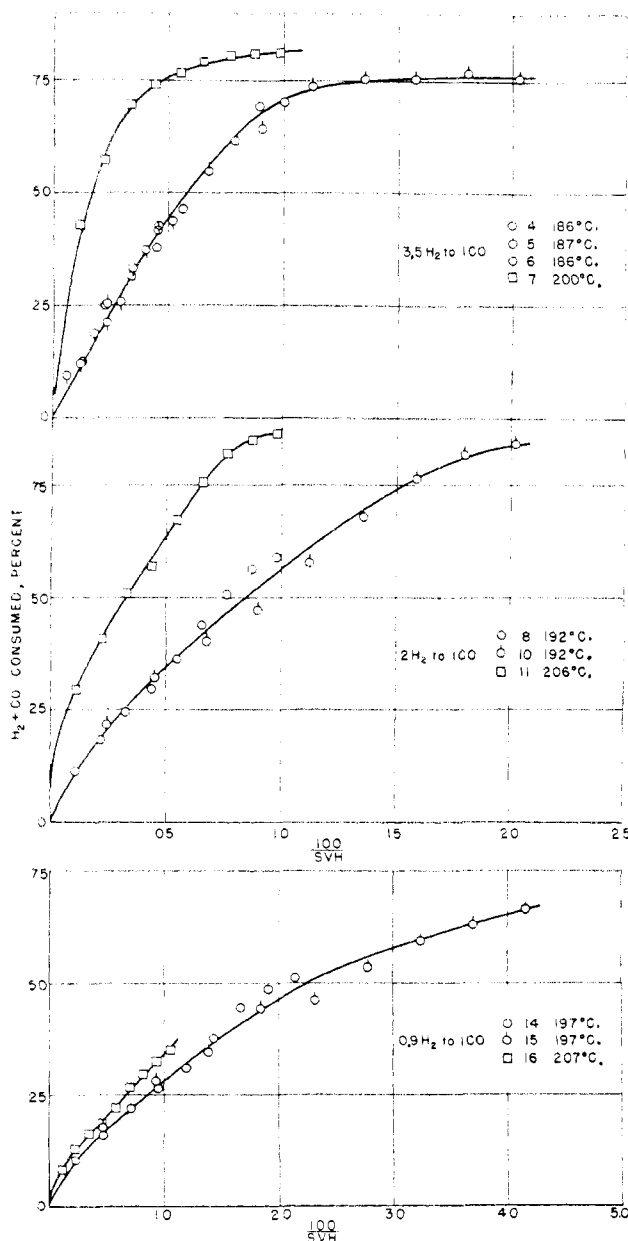


Figure 17. Variation of Extent of Conversion of H_2 plus CO Gas with Reciprocal of Space Velocity at Atmospheric Pressure with Synthesis Gas Having Ratios of H_2 to CO of 3.5, 2, and 1

perature. These reactions occur to at least some extent over the entire catalyst bed.

The data in Figures 10 to 16 were extrapolated to zero bed length, as shown by the broken extensions of the curves. Although the validity of this extrapolation is rather uncertain, the extended curves indicate that at least part of the methane, saturated and unsaturated hydrocarbons, and carbon dioxide are formed by primary processes.

Craxford (8) reported data on the formation of methane and carbon dioxide which are similar to those reported in this paper, and attributed the formation of these components to secondary hydrocracking of hydrocarbons and the water-gas reaction, respectively. However, Craxford (8) postulated that the normal synthesis occurs on parts of the surface converted to cobalt carbide whereas the secondary reactions occur on parts of the surface covered by cobalt atoms that are not actively engaged in the synthesis of hydrocarbons. The authors' data indicate that these reactions occurred throughout most of the catalyst bed, where the synthesis of hydrocarbons was proceeding in a normal manner. In their experiments carbon dioxide was formed in greater amounts with 1H_2 to 1CO gas than with 2H_2 to 1CO gas. The gas with the higher carbon monoxide concentration should favor formation of carbide on the surface and, according to Craxford's postulates, should produce less rather than more carbon dioxide. It has never been established that a surface carbide is the active catalyst in the synthesis, and it has been shown that cobalt catalysts rather completely converted to carbide were inactive in the synthesis (4, 21). Thus, the postulates of Craxford are not a simple explanation of methane and carbon dioxide formation. The authors' data indicate that these products are formed concurrently with the normal synthesis by secondary and to some extent by primary reactions, and that their formation is a function of the gas composition and temperature.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the assistance of several persons in this work: H. H. Storch for helpful criticisms of the final manuscript; J. Lecky, A. Dudash, and the crew of operators for assistance in obtaining and computing the data; and A. Sharkey, R. Borgman, and the mass spectrometer group for the gas analysis data.

LITERATURE CITED

- (1) Almquist and Black, *J. Am. Chem. Soc.*, **48**, 2814 (1926).
- (2) Anderson, Hall, Hewlett, and Seligman, *Ibid.*, **69**, 3114 (1947).
- (3) Anderson, Hall, and Hofer, *Ibid.*, **70**, 2465 (1948).
- (4) Anderson, Hall, Krieg, and Seligman, *Ibid.*, **71**, 183 (1949).
- (5) Anderson, Krieg, Seligman, and O'Neill, *IND. ENG. CHEM.*, **39**, 1548 (1947).
- (6) Craxford, *Fuel*, **26**, 119 (1947); *J. Soc. Chem. Ind.*, **66**, 440 (1947).
- (7) Craxford, *Trans. Faraday Soc.*, **35**, 946 (1939).
- (8) *Ibid.*, **42**, 576 (1946).
- (9) Emmett and Brunauer, *J. Am. Chem. Soc.*, **52**, 2682 (1930).
- (10) Fischer and Pichler, *Brennstoff-Chem.*, **12**, 365 (1931).
- (11) *Ibid.*, **14**, 306 (1933).
- (12) *Ibid.*, **20**, 41 (1939).
- (13) Hall and Smith, *J. Soc. Chem. Ind.*, **65**, 128 (1946).
- (14) Houghton and Watson, *IND. ENG. CHEM.*, **35**, 529 (1943).
- (15) Jerosejev, Runtso, and Volkova, *Acta Physicochim. U.R.S.S.*, **13**, 111 (1940).
- (16) Pichler, *Brennstoff-Chem.*, **24**, 39 (1943).
- (17) Storch *et al.*, *Bur. Mines, Tech. Paper 709* (1948).
- (18) Tsuneoka and Fujimura, *J. Soc. Chem. Ind. Japan*, **37**, suppl. binding, p. 363 (1934).
- (19) *Ibid.*, p. 704.
- (20) Weller, *J. Am. Chem. Soc.*, **69**, 2432 (1947).
- (21) Weller, Hofer, and Anderson, *Ibid.*, **70**, 799 (1948).

RECEIVED July 30, 1948. From a thesis presented by Abraham Krieg to the University of Pittsburgh in partial fulfillment of the requirements for the degree of master of science, 1948. Previous articles of this series have appeared in *IND. ENG. CHEM.*, **40**, 2347 (1948); **39**, 1548 (1947); and *J. Am. Chem. Soc.*, **71**, 183 (1949); **70**, 2465 (1948); **69**, 3114 (1947).

Viscose Processing of Cellulose

CHANGES IN BASIC PROPERTIES

R. L. MITCHELL

Rayonier Incorporated, Shelton, Wash.

Changes in degree of polymerization, α -cellulose, carboxyl, and pentosan content which occur during the steeping, aging, xanthation, and spinning stages of viscose processing are shown for several pulps of different initial degrees of purity. Special consideration is given to depolymerization reactions since the permanent drop in degree of polymerization has perhaps the greatest effect on the other basic analytical properties of the cellulose.

IN THE manufacture of rayon or cellophane by the viscose process, certain operations command positions of primary importance—namely: (1) steeping, which under suitable conditions serves the double function of purifying and mercerizing the cellulose starting material; (2) aging, which serves in large measure to effect the desired degree of depolymerization; (3) xanthation, which converts the cellulose to the soluble form; and (4) spinning, which regenerates the cellulose in a desired physical form more usable than the original.

In these steps, not only is the native cellulose changed to hydrate cellulose of a different physical structure, but many of the basic analytical properties of the cellulose are modified as well.

Some effects of time, temperature, and oxygen concentration on the extent and type of alkaline degradation are shown. The presence or absence of oxygen may be the factor determining which of two types of alkaline degradation will occur. A special recovery technique is described for retaining low degree of polymerization gamma constituents as the water-insoluble nitrate derivatives.

These alterations in analytical properties result mainly from cleavage of the cellulose chain due to alkaline oxidation which occurs at certain stages of processing, notably in alkali cellulose aging and in xanthation. A typical wood pulp—for example, having an initial degree of polymerization of 1150—is converted by present commercial practice into a rayon having a degree of polymerization of 350. Analytical properties of the cellulose are affected also by the removal in the steeping operation of varying amounts of hemicellulose and of noncellulosic impurities. Certain of the properties are further affected by the physical form and molecular order of the structure laid down in the spinning operation.