

PREFACE

In the summer of 1945, when it was evident that invasion of the Japanese home islands was imminent, the U. S. Naval Technical Mission to Japan was established to evaluate the accomplishments of the Japanese in naval technology and related fields. Of primary importance to the object of the mission was the acquisition of the maximum amount of information in the shortest possible time after the country was entered. Each day's delay allowed additional Japanese equipment and documents to be destroyed and made it easier for key Japanese personnel to disappear. With this in mind, the first entry into Japan by mission personnel was made early in September, and the activities of the mission were highly concentrated over the next few months, terminating finally in December.

One of the many phases of the Japanese technical war effort in which mission investigators were interested was the program directed toward obtaining liquid fuels from coal and other sources. The Japanese navy attached tremendous importance to research in this direction, and in 1945 approximately 3,200 persons, including about 400 technically trained personnel, were employed at the First Naval Fuel Depot at Ofuna, where every known phase of fuel and lubricant technology was being investigated. Research and development work involving both direct and indirect coal-hydrogenation processes was also being carried out in such places as the Institute of Fuel Technology at the Imperial University of Kyoto, the Imperial Fuel Research Institute of the Department of Commerce and Industry, the Hokkaido Synthetic Petroleum Co., Inc., and the Tokyo Institute of Physical Chemical Research. The relation of the Imperial Fuel Research Institute to the Japanese economy corresponds rather closely to that of the Bureau of Mines in the United States. In coal hydrogenation investigations conducted there, emphasis was placed on assays and fundamental studies rather than production. It was said that over a hundred Japanese coals had been so studied.

As Japan is extremely deficient in petroleum, it is not surprising to discover that organized effort had been expended to obtain liquid fuels from sources that would otherwise appear fantastic. In attempts to supplement their supplies of motor fuel, so necessary to the prosecution of mechanized warfare, the Japanese investigated the potentialities of such source materials as orange peels, rubber, and pine needles and studied the hydrogenation of coal more extensively than any other nation except Germany. Their rewards for these efforts, however, were meager. Although plants for producing synthetic liquid fuels were constructed and operated, their output fell disastrously short of the magnitude necessary to support the Japanese military machine. Maximum production was attained in 1944, for which the total synthetic fuel output was reported as 1,055,000 barrels, divided among the various processes as follows: hydrogenation (of tars and other oils) = 5,780 barrels; Fischer-Tropsch process = 149,250 barrels; and low-temperature carbonization = 899,970 barrels.

To provide an insight into Japanese research methods and to determine the direction taken by synthetic fuel research in Japan both before and during World War II, mission investigators obtained a number of papers and reports from the organizations listed above. These papers, of which the following is exemplary, have been translated and carefully examined. For many reasons, the English translations must be regarded with reservations. The conversion of Japanese text to its English equivalent is complicated by extreme language difficulties; in many cases, words do not exist in the one language for ideas expressed in the other. The task was complicated further by a lack of familiarity with the field of synthetic liquid fuels on the part of some of the translators. In addition, it must be emphasized that many of the discussions to be found in these papers were based on theories which, at that time were accepted as valid by most of the scientific world, but which have since been discarded in the light of subsequent experimental evidence. Despite the accompanying qualifications, it is felt that these papers are instrumental in establishing an appreciation of Japanese research efforts in the field of synthetic liquid fuels.

INTRODUCTION

The rapid development of transportation facilities in Japan focused the attention of this country on the possibility of converting the existing coal resources (of which there was an abundance) into liquid fuels, for which there was a constantly increasing demand. Previous work had indicated that this could be accomplished by utilizing one of two processes - the Bergius process, in which high temperatures and high pressures were employed to effect direct liquefaction of the coal, and the Fischer-Tropsch process, in which an indirect liquefaction of coal was accomplished by the production of liquid hydrocarbons from hydrogen-carbon monoxide mixtures. This report describes some investigations into the latter process, which was first developed by Fischer and his colleagues in the Coal Laboratory in Muhlheim, Germany, in 1923. By 1932, these investigators had achieved a 60-percent theoretical yield (152 ml. of liquid hydrocarbons per cubic meter of $2H_2:1CO$ synthesis gas) by using a precipitated $Co-ThO_2$ catalyst.^{3/} At the same time (1932), Dr. Kita of Kyoto Imperial University and Messrs. Fujimura and Tsunooka obtained 145 ml. of gasoline (C_5+) per cubic meter of synthetic gas by using a $Co-Cu-Th-U$ catalyst.^{4/} This report is a description of the experimental results subsequently obtained at the Fuel Research Institute, Kawaguchi City, Saitama, up to 1935.

EXPERIMENTAL

Apparatus

The apparatus used in laboratory-scale studies of the Fischer-Tropsch synthesis is shown schematically in figure 1. Synthesis gas was stored in

^{3/} Fischer, F., and Koch, H., [Recent Developments of Cobalt Catalysts for the Synthesis of Hydrocarbons]: Brennstoff Chem., vol. 13, No. 4, February 15, 1932, pp. 61-68.

^{4/} Fujimura, Kenji, and Tsunooka, Shunzo, [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure XII]: Jour. Soc. Chem. Ind. Japan, vol. 35, 1932, p. 1022; supplemental binding pp. 415-416; Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 22, 1933, pp. 198-201.

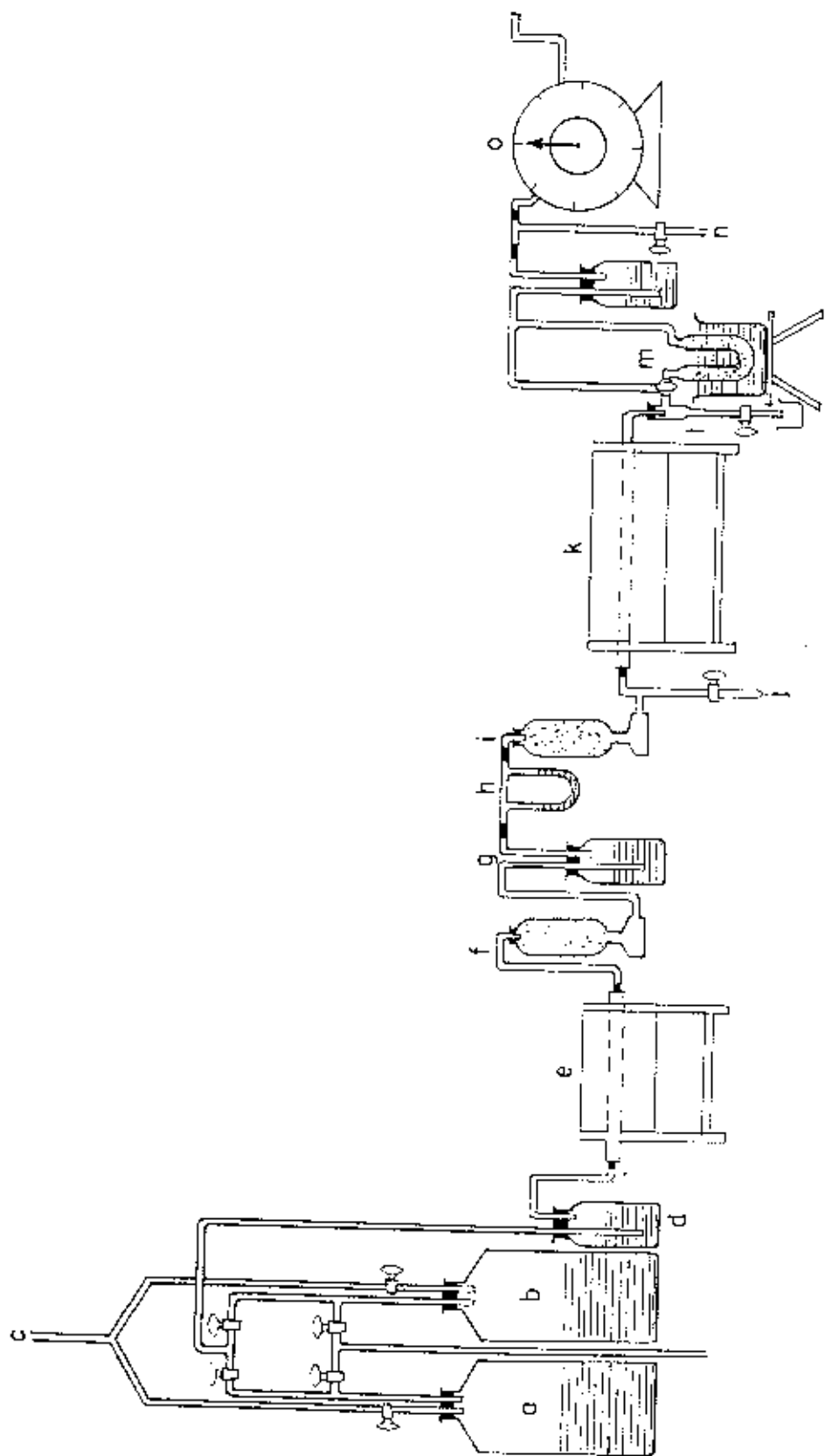


Figure 1.—Laboratory-scale apparatus (6 m.³/hr. throughput) used in studies of the hydrocarbon synthesis.

the 10-liter bottles, A and B; by proper manipulation of the stopcocks, one bottle could be filled with gas while gas from the other bottle was being used. Synthesis gas leaving the storage bottles was maintained at a constant velocity and was passed through a purification train, where oxygen was eliminated by passage through a solution of pyrogallol (D) followed by a bed of red-hot copper (E); water vapor and carbon dioxide were removed by passage through calcium chloride (F) and potassium hydroxide solution (G). After passing through a manometer (H), the gas was redried over calcium chloride (I) and entered the reaction tube (K), a crystalline quartz tube 2 cm. I.D. and 60 cm. long, heated externally by an electric furnace. The temperature of the furnace midway between the ends was obtained either with platinum-platinum-rhodium thermocouples or with thermometers corrected at the tin and naphthalene points. The oil and water produced were condensed in the burette L, and the uncondensed products were adsorbed in two U-tubes (M; only one shown) containing activated charcoal. The volume of the gas produced was measured by a gasmeter, and the contraction was computed from this value and the volume of gas at the same conditions passed to the reactor from storage bottles A and B. Correction of these calculations for the oxygen and other impurities removed by the purification train was unnecessary, because the synthesis gas was produced from carefully purified materials and generally contained less than 0.2 percent of these contaminants.

Samples of synthesis gas and the product gases were withdrawn at outlets J and N, respectively, for analysis. In addition, to obtain an insight into the quantitative relationships of the synthesis, the product gases were analyzed by means of a Mariott gas-extracting bottle placed after the gas gage. In analyzing the product gas samples, a Hempel gas-analysis apparatus was used; carbon dioxide was absorbed by potassium hydroxide solution, unsaturated hydrocarbons by fuming sulfuric acid, and carbon monoxide by an ammonia solution of cuprous chloride. The hydrogen content was computed by measuring the decrease in volume following combustion over palladized asbestos; the quantity of saturated gaseous hydrocarbons was measured by determining the amounts of hydrogen and carbon dioxide produced by combustion.

As will be shown later, the synthesis of hydrocarbons from carbon monoxide and hydrogen is very sensitive to temperature; hence, particularly close attention was directed to the temperature distribution within the converter. The heating element used in this equipment consisted of a Nichrome coil 50 cm. long. In order to study the temperature distribution in the converter, heating was continued until the center of the converter was maintained at a constant temperature of 200° C. Temperature readings were then taken at intervals of 2 cm. from the center. The constant temperature section was found to lie within 4 cm. on each side of the center; at a point 12 cm. from the center the temperature was lower by 3° C. A large amount of catalyst could not be placed in this 8-cm. zone of constant converter temperature, however, because a thick layer of catalyst makes a uniform catalyst temperature very difficult to obtain; because the hydrocarbon synthesis is violently exothermic, a thick layer of catalyst favors the formation of local hot spots in the catalyst bed. Hence, in the experiments to be described, the catalyst was spread over a distance of 12 cm. on each side of the center of the converter. The temperature at the center of the converter was assumed to be the average reaction temperature with a possible deviation of $\pm 3^{\circ}$ C.

Method of Yield Determination

The oil and water phases condensed in burette I were mutually saturated and contained dissolved oxygen-containing compounds such as alcohols, acetone, and fatty acids produced by secondary reactions. The volumes of the oil and water phases were measured directly in the burette, which was graduated in units of 0.1 ml. Approximately 100 liters of synthesis gas were used in each experiment; thus, an error of 0.02 ml. in reading the burette amounted to only about 0.2 ml. when calculated on the basis of a cubic meter of synthesis gas.

Volatile products, which were adsorbed in the two glass U-tubes containing activated charcoal, were recovered by reevaporizing with superheated steam at 200° to 250° C. The recovery apparatus is shown in figure 2. In this procedure, stopcock C was first closed, and the U-tubes were heated to 200° to 250° C. in cottonseed oil. Stopcock C was then opened, and superheated steam was injected. (Air-free steam is necessary in order to prevent loss of product.) The distillate vapors were passed through the water-cooled condenser, E, and collected in receiver F. The receiver was a 10 to 20 ml. burette, graduated to read in 0.1 ml., with a stopcock bottom. The oil floated in the upper part of the burette, and the excess water was siphoned out of a side tube attached to the lower part of the burette.

Synthesis Gas

The carbon monoxide in the synthesis gas was produced by dripping formic acid into sulfuric acid that had been heated to 150° to 180° C. The product was washed with potassium hydroxide solution to remove carbon dioxide. Commercial pressurized hydrogen was used after purification by potassium permanganate and potassium hydroxide solution.

Catalysts

Nickel and cobalt catalysts were first prepared from imported Merck or Kahlbaum reagents, but subsequent catalysts prepared from indigenous reagents produced by Kato, Konishi, and Takeda showed almost no difference in activity. The pure native products, such as those listed below, were chiefly used in these experiments.

Nickel nitrate	Kahlbaum product, Kato product (guaranteed)
Cobalt nitrate	Kahlbaum product, Kato product (guaranteed)
Thorium nitrate	Konishi (pure) product
Uranium nitrate	Kato product (guaranteed)
Manganese nitrate	Kahlbaum product
Silver nitrate	Konishi (pure) product
Copper nitrate	Kato product (guaranteed)

Salts such as manganese nitrate and copper nitrate, which are extremely hygroscopic, were dissolved and used as standard solutions. To improve its thermal conductivity, the catalyst was smeared on small fragments of copper or iron gauze before charging into the reaction tube. As carriers, two or three types of diatomaceous earth found in different localities were employed after dissolving out their iron impurities with strong nitric acid, washing with hot water until neutral, and drying at about 120° C.

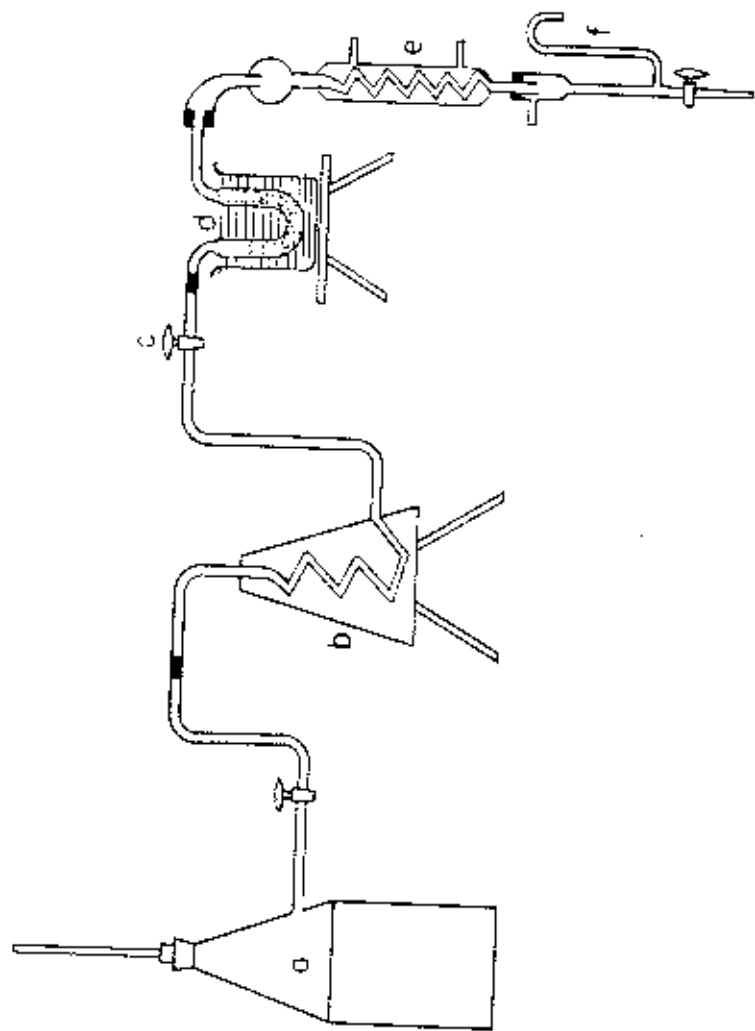


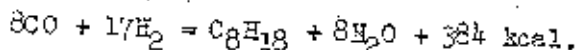
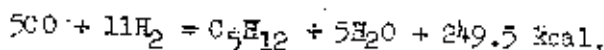
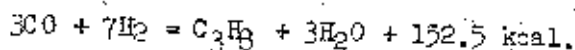
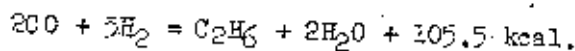
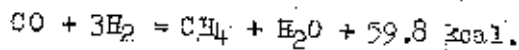
Figure 2.- Steam stripping of light-oil fraction from activated charcoal adsorption tube.

HYDROCARBON YIELD AS A FUNCTION OF OPERATING VARIABLES

The yield of gasoline (C₅+ hydrocarbons) is affected by the following operating variables: (1) reaction temperature, (2) gas velocity, and (3) composition of the synthesis gas. Results of experiments to determine the effects of these variables are described below.

Effects of the Reaction Temperature

The formation of a paraffin series of hydrocarbons from CO and H₂ may be represented by the following equations:



The energies liberated in these reactions were calculated, on the basis of Francis' ^{2/} thermodynamic values, to be as follows:

	ΔF	$t, ^\circ\text{C. } (\Delta F=0)$
CH ₄	-52,830 + 60.3 T	603
C ₂ H ₆	-94,660 + 121.5 T	506
C ₃ H ₈	-135,340 + 181.15 T	474
C ₄ H ₁₀	-176,020 + 240.8 T	458
C ₅ H ₁₂	-216,700 + 300.45 T	448
C ₈ H ₁₈	-338,740 + 479.4 T	434

In general, chemical reactions act in the direction in which the liberated energy, ΔF , decreases; that is, the more negative the value ΔF , the greater the degree to which the reaction will be completed. By considering the values listed above, it is evident that the lower the value of T (reaction temperature in absolute units), the more the reactions are favored from left to right. The temperature at $\Delta F=0$, that is, the temperature at which the direction of the reaction shifts from right to left, decreases as the higher members of the series are formed. Thus, the lighter, gaseous hydrocarbons are stable at fairly high temperatures, but the heavier, liquid hydrocarbons are stable only at low temperatures. Accordingly, the formation of liquid hydrocarbons (C₅+

^{2/} Francis, A. W., The Free Energies of Some Hydrocarbons: Ind. Eng. Chem., vol. 20, No. 3, March 1928, pp. 277-282.

is limited to temperatures below 448° C. However, the rate of reaction increases with increasing temperature, and although the effect of temperature on the production of liquid hydrocarbons is disadvantageous, especially in the case of a reaction that proceeds to only a small degree, it is sometimes necessary to increase the temperature to obtain a practical reaction rate. Designating the rate of reaction of carbon monoxide as R and the percentage transformed into liquid hydrocarbons as L, it is evident that the yield of gasoline will be governed by the product of R x L with a given synthesis gas. In view of the fact that increasing the reaction temperature tends to both increase and decrease the yield of liquid hydrocarbons by two different effects, a value of T should be expected at which the value R x L is a maximum. Fischer,^{6/} in his report, succeeded in lowering the reaction temperature to 220° C. with a cobalt catalyst but considered 270° C. as the most suitable. Erdley and Nash^{7/} established the most practicable temperature for Co-Cu-Al₂O₃ catalyst as 280° to 290° C. and did not acknowledge reactions below 230° C. Smith^{8/} placed 275° C. as the most appropriate for Co-Cu-Mn catalysts, and Kodama^{9/} designated 250° C. as that best suiting Co-Cu-Th catalysts. Whereas Smith^{10/} and Berl and Jungling^{11/} claimed that the higher hydrocarbons were produced at higher reaction temperatures, Fischer and Koch^{12/} established in their study of nickel and cobalt catalysts that the most suitable temperature for the production of liquid hydrocarbons was about 200° C. and that, as the temperature increased, the formation of gaseous hydrocarbons and carbon dioxide was increased and that of liquid hydrocarbons decreased. Watanabe, Morikawa, and Igawa^{13/} used weight calculations to theorize on the effects of reaction temperature upon the liquid hydrocarbon yield.

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- 6/ Fischer, F. and Tropsch, H., [The Synthesis of Hydrocarbons at Ordinary Pressures from the Gasification Products of Coal]: Brennstoff Chem., vol. 7, No. 7, April 1, 1926, pp. 97-104.
- 7/ Erdley, A., and Nash, A. W., A Contribution to Our Knowledge of the Catalysts Used in the Synthesis of Higher Hydrocarbons from Water Gas: Jour. Soc. Chem. Ind. (Transactions), vol. 47, Aug. 10, 1928, pp. 219-223.
- 8/ Smith, D. F., Davis, J. D., and Reynolds, D. A., Synthesis of Higher Hydrocarbons from Water Gas, I: Ind. Eng. Chem., vol. 20, No. 5, May 1928, pp. 462-464.
- 9/ Kodama, Shinjiro, [Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen at Atmospheric Pressure, III. Preparation of Liquid Hydrocarbons with a Cobalt-Copper-Thoria Catalyst]: Jour. Soc. Chem. Ind. Japan, vol. 32, 1929, p. 959; supplemental binding (in German), pp. 285-286.
- 10/ Smith, D. F., Hawk, C. O., and Reynolds, D. A., Synthesis of Higher Hydrocarbons from Water Gas II: Ind. Eng. Chem., vol. 20, No. 12, December 1928, pp. 1341-1348.
- 11/ Berl, E., and Jungling, K., [Synthesis of Higher Hydrocarbons from Water Gas at Atmospheric Pressure]: Ztschr. angew. Chem., vol. 43, 1930, pp. 435-440.
- 12/ Fischer, F., and Meyer, K., [The Applicability of Nickel Catalysts to the Hydrocarbon Synthesis]: Brennstoff Chem., vol. 12, No. 12, June 15, 1931, pp. 225-232.
- 13/ Watanabe, S., Morikawa, K., and Igawa, S., [The Synthesis of Hydrocarbons by Catalytic Reduction of Carbon Monoxide at Atmospheric Pressure II. The Effect of Temperature on the Synthesis]: Jour. Soc. Chem. Ind. Japan, vol. 37, 1934, p. 891; supplemental binding, pp. 385-389.

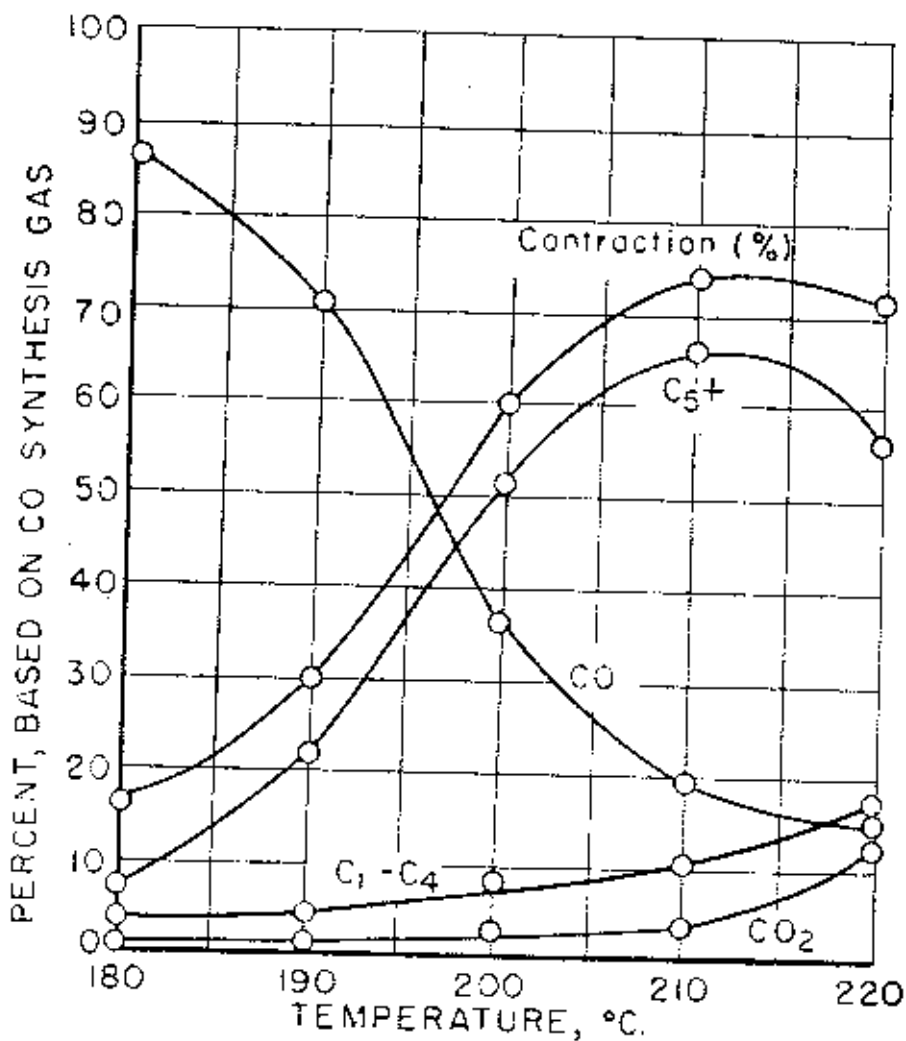


Figure 3. - Effect of reaction temperature on hydrocarbon synthesis.

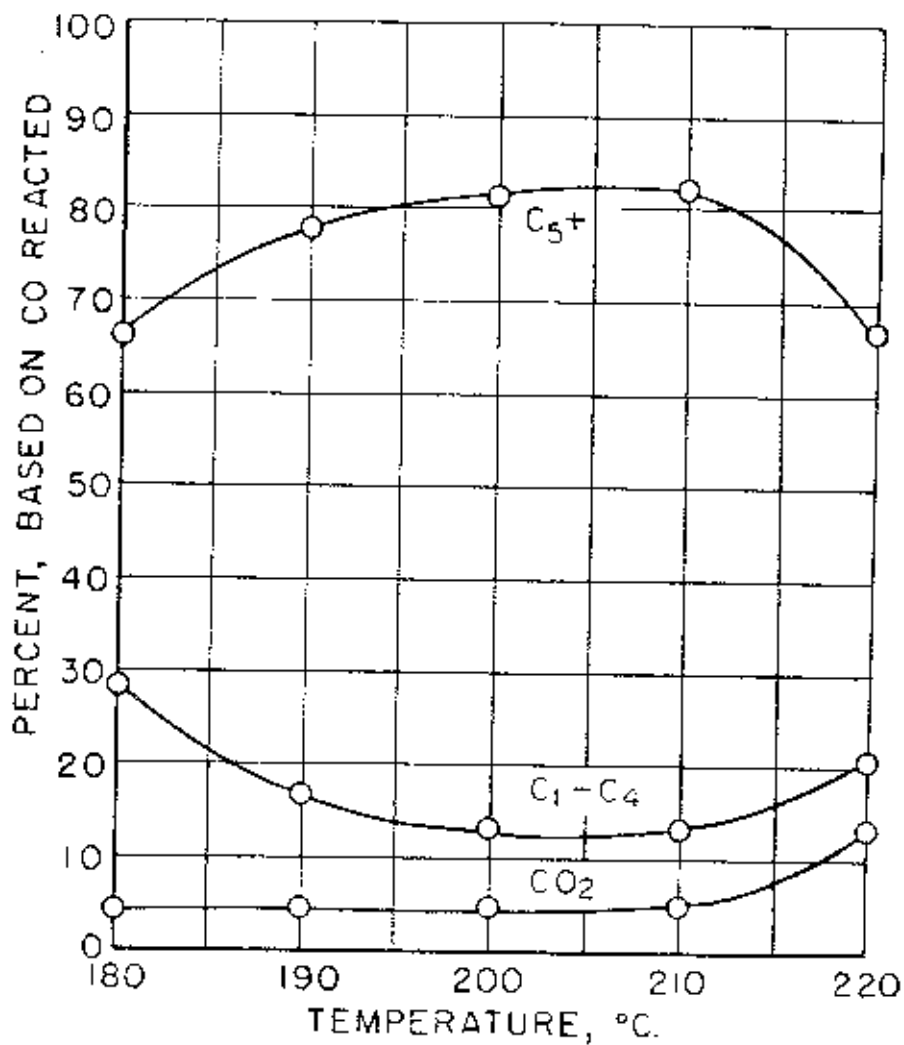


Figure 4.- Effect of reaction temperature on hydrocarbon synthesis

Experimental Methods and Results

The catalyst used was 100 Co:10 Cu:12 U_3O_8 :100 diatomaceous earth, corresponding to 3 gm. Co; 72.0 liters of synthesis gas was used at a gas velocity of 6.0 l./hr. at each of the five reaction temperatures employed, namely, 180°, 190°, 200°, 210°, and 220° C. Table 1 shows the yield of liquid products and the results of the analyses of the product gases for a 36-liter product-gas sample.

From the analyses of the synthesis gas and product gas and from the gas contraction, the percentage distribution of carbon among the carbon dioxide, carbon monoxide, and gaseous saturated hydrocarbons in the product gas was calculated based on the carbon monoxide in the synthesis gas. The difference between the sum of these three values and 100 was taken as the percentage of carbon monoxide that had been converted to gasoline. The formation of unsaturated hydrocarbons (C_nH_{2n-2}) was so small as to fall within the experimental error of the determination and, therefore, was not considered in the calculations. The results of these calculations are listed in table 2 and plotted graphically in figures 3 and 4.

A summary of the above experimental results shows that:

- (A) The ratio of carbon monoxide conversion to hydrogen conversion increased with increase in temperature.
- (B) On the basis of carbon monoxide in the synthesis gas, the percentage of carbon monoxide converted to carbon dioxide and the percentage converted to gaseous saturated hydrocarbons increased with increasing temperature; the percentage of carbon monoxide converted to gasoline began to increase at 180° C. and passed through a maximum between 210° and 220° C.
- (C) On the basis of carbon monoxide reacted, the percentage of carbon monoxide converted to carbon dioxide increased gradually with temperature to 210° C., where it increased rapidly; the percentage converted to gaseous saturated hydrocarbons decreased with increase in temperature and showed a minimum value at about 210° C.; conversely, the percentage converted to gasoline increased progressively from 180° C. and reached a maximum at 210° C., decreasing rapidly to 220° C.

TABLE 1. - Effect of reaction temperature

(72.0 l. of synthesis gas at a velocity of 6 l./hr. used at each temperature)

Experiment number	Reaction temperature, ° C.	Synthesis gas composition, percent			Contraction, percent	Liquid products, ml./m.3 of synthesis gas		Product gas composition, percent						
		Gasoline (C5+)		Water		CO ₂	C ₂ H ₆	CO	H ₂	CH ₄	C ₂ H ₄	n	M ₂	
		CO	H ₂											N ₂
1	180	30.4	64.5	5.1	16.2	20.9	53.6	0.2	0.2	31.4	61.4	0.4	3.53	6.4
2	190	30.6	64.4	5.0	30.0	52.5	22.2	-	0.2	31.0	50.4	0.7	3.00	6.9
3	200	32.6	64.0	3.4	60.4	110.6	150.5	2.6	-	30.0	56.1	2.4	2.97	8.9
4	210	32.5	65.2	2.3	74.0	139.0	180.5	4.6	0.2	24.4	54.2	7.7	1.72	8.9
5	220	32.6	65.0	2.4	71.8	125.5	195.6	12.8	0.2	17.6	45.0	16.2	1.24	8.2

TABLE 2. - Effect of reaction temperature

(72.0 l. of synthesis gas at a velocity of 6 l./hr. used at each experiment)

Experiment number	CO conversion, percent	H ₂ conversion, percent	Carbon distribution						
			Percent of CO in synthesis gas			Percent of CO reacted			
			CO ₂	CO	C ₂ H ₆ +C ₂ H ₄ (C ₁ -C ₄)	CO ₂	C ₂ H ₆ +C ₂ H ₄ (C ₁ -C ₄)	Gasoline (C ₅ +)	
1	13.5	20.2	0.6	86.5	3.9	7.4	4.5	23.9	66.6
2	29.1	34.3	1.4	70.9	4.8	22.0	4.9	15.5	78.7
3	63.6	65.3	3.2	36.4	8.7	51.7	5.0	13.7	81.3
4	80.5	78.4	3.7	19.5	10.6	66.2	4.6	13.2	82.2
5	54.8	80.5	11.1	15.2	17.4	56.3	13.1	20.5	66.4

Discussion

Although the rate of reaction between carbon monoxide and hydrogen was a maximum at 220° C., the maximum yield of gasoline was obtained at 210° C., the result of an acceleration in the production of carbon dioxide and gaseous saturated hydrocarbons beyond 210° C. This is evident from inspection of figure 4, which shows that the production of gaseous hydrocarbons decreased from 180° to 205° C., at which point it increased. However, the value "n" has been defined as the number of carbon atoms in the average gaseous hydrocarbon product, and table 1 shows that this value decreased continuously with increasing temperature, suggesting that the production of gaseous hydrocarbons should increase continuously with increasing temperature instead of first decreasing in the manner shown in figure 4. The cause of this initial decrease may lie in the following theory.

The carbidic carbon produced by reaction of carbon monoxide with the catalyst is hydrogenated to such free radicals as CH -, CH_2 , and CH_3 , which, at about 180° C., polymerize very slowly. The formation of liquid hydrocarbons, therefore, is small and is accompanied by a relatively large formation of low-molecular-weight gaseous hydrocarbons. As the temperature is increased from 180° to 210° C., the rate of polymerization of the free radicals increases so that more liquid hydrocarbons are produced at the expense of the low-molecular-weight products. However, the distribution of free radicals produced by the hydrogenation of carbide also depends on the reaction temperature. Thus, at about 180° C., large amounts of CH - and CH_2 are produced with small amounts of CH_3 . Because the polymerization rate is slow, these free radicals are combined mainly in the form of gaseous hydrocarbons of C_2+ . Very little methane is formed. At higher temperatures, CH_3 is produced along with CH - and CH_2 ; the structure of the CH_3 radical makes the chances of polymerization very much smaller than in the case of CH_2 and CH - radicals, and thus, at the higher temperatures, considerable methane is produced. As the polymerization rate is greater at the higher temperatures, more liquid hydrocarbons are formed from CH - and CH_2 radicals. Accordingly, the average molecular weight of the gaseous products is less at higher temperatures than at lower temperatures. Thus, from 180° to 210° C., one has the apparently incompatible cases of the value of "n" decreasing as the production of liquid hydrocarbons increases and the production of gaseous hydrocarbons decreases.

It has been shown previously that from thermodynamic considerations the production of liquid hydrocarbons is favored by decreasing temperatures. The apparent anomaly regarding the increase in gasoline production observed with increasing temperature in figure 4 may be resolved by recalling that thermodynamic considerations are based upon the assumption that each reaction attains its theoretical equilibrium, whereas, under actual experimental conditions, reaction equilibrium was not reached at low temperatures. At temperatures below 210° C., the speed at which the reaction approaches its theoretical equilibrium is quite slow.

It is recognized, of course, that on the basis of this experimental evidence alone it is not possible to determine the maximum possible molecular weight of the liquid hydrocarbon product nor the exact optimum temperature at which it may be obtained. It may be said, however, that the optimum temperature is certainly not of the order of 180° C. where the speed of reaction is low.

From these considerations it may be possible to reconcile the apparent differences between the opinions of Smith^{14/} and Berl and Jungling,^{15/} who said that high-molecular-weight hydrocarbons were favored by high temperatures, and that of Fischer,^{16/} who said that high-molecular-weight hydrocarbons were favored by low temperatures, if these investigators were referring to different temperature ranges. Thus, if Fischer's "low" temperature was 210° to 220° C. and corresponded to the "high" temperature of Smith and Berl and Jungling, the results of these investigators are compatible. Fischer considered a reaction temperature of about 200° C. as being the optimum, as compared to the optimum temperature of 250° C. selected by Smith and Berl and Jungling. In view of the previous discussion, this difference may originate in two different basic considerations. Thus, when the reaction takes place at "high" temperatures of about 250° C., the rate of reaction is high and the quantity of gaseous hydrocarbons produced is great, but, with time, because of the deposition of free carbon on the catalyst, the activity of the catalyst is gradually diminished, with a corresponding decrease in hydrogenation of carbide to form free radicals. As, however, the rate of the polymerization of the free radicals that are present is great at this high temperature, solid paraffins or liquid hydrocarbons of high boiling points are produced in accordance with the view point of Smith and Berl and Jungling.

As indicated by table 1, the optimum temperature for production of gasoline (C₅+) is 210° ± 5° C. The extreme temperature-sensitivity of the reaction is a result of the poor thermal conductivity of the catalyst. The utilization in the catalyst of a carrier of diatomaceous earth, a poor conductor of heat, makes transmission of the heat of reaction (an extremely great value) outside the catalytic system very difficult. In addition, because of local superheating at the point of activation, the slightest amount of heat from external sources causes a phenomenal increase in the temperature of the catalyst. (This shows that the activity of the catalyst is extremely high, requiring only a small activation energy.)

Effects of the Gas Velocity

At a given temperature, and using a given quantity of catalyst, the extent of reaction of carbon monoxide and hydrogen tends to increase with decrease in velocity of the gas (increase in contact time). The rate of polymerization of the CH₂, CH₂, and C₂H₃ radicals produced from the carbon monoxide and hydrogen is increased, however, to a smaller degree than that at which hydrogen is added to form methane; therefore, as the velocity of the gas is decreased, the methane-producing reaction is accelerated, and, when this value is large compared to the increase in the extent of reaction between carbon monoxide and hydrogen, the yield of liquid hydrocarbons is reduced. Hence, an optimum gas velocity is to be expected in the production of liquid hydrocarbons. Fischer and Tropech,^{17/} by suitably increasing the gas velocity, found that it was possible to prevent the methane-producing reaction almost entirely and stated that an optimum gas velocity in the production of liquid

^{14/} Work cited in footnote 11, p. 3.
^{15/} Work cited in footnote 12, p. 6.
^{16/} Work cited in footnote 13, p. 6.
^{17/} Work cited in footnote 6.

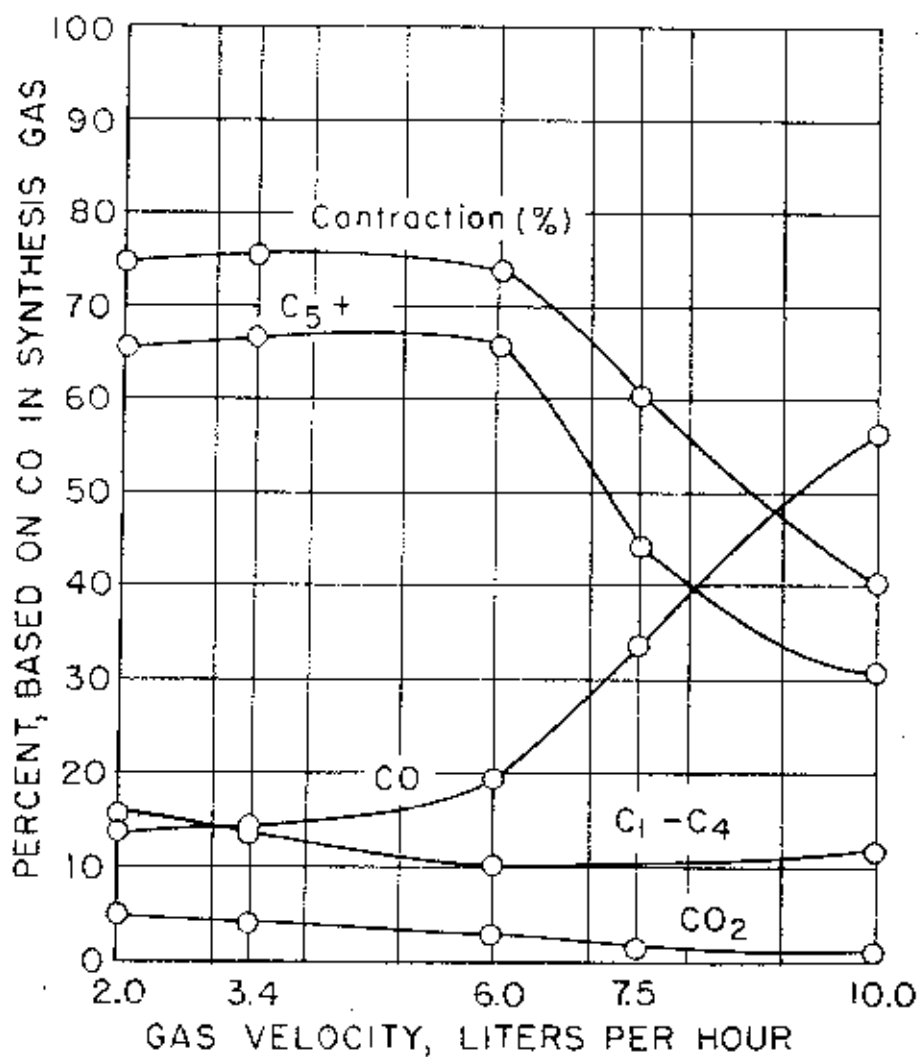


Figure 5.- Effect of synthesis gas velocity on hydrocarbon synthesis.

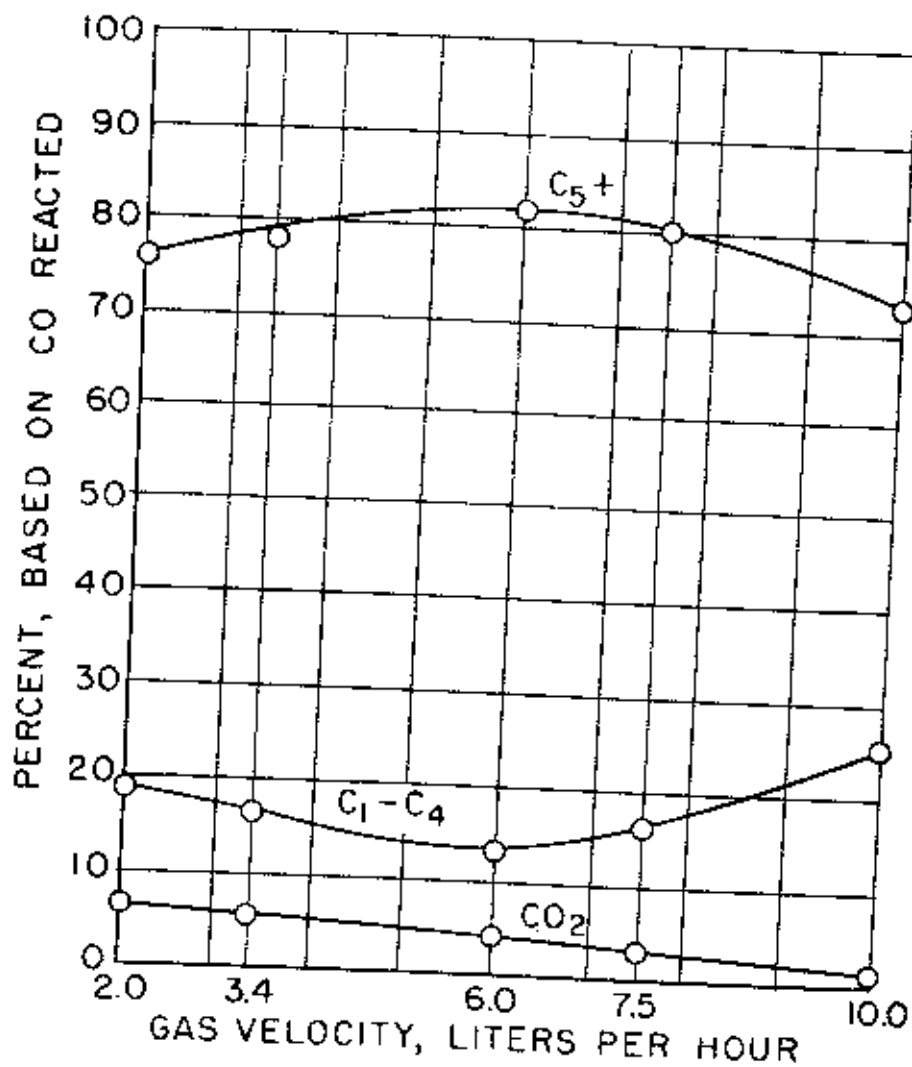


Figure 6.-Effect of synthesis gas velocity on hydrocarbon synthesis.

hydrocarbons should exist. Kodama^{18/} obtained similar results, whereas Smith^{19/} declared that, with decrease in the velocity of the gas, the yield of liquid hydrocarbons increased.

Experimental Methods and Results

Five velocities of feed gas, namely, 2.0, 3.4, 6.0, 7.5, and 10.0 l./hr., were used in experiments with 100 Co:10 Cu:12 U_3O_8 :100 diatomaceous earth catalyst, corresponding to 3 gm. of cobalt and a reaction temperature of 210° C. In each case, 72.0 liters of synthesis gas was used, except in the experiment involving a velocity of 2.0 l./hr., in which 36.0 l. of gas was used. The yields of gasoline (C_5+) and water and the gas contraction were measured, and the product gases from half the initial quantity of feed gas were analyzed; the results are shown in table 3.

From analyses of the synthesis and product gases and from the gas contraction, the percentage distribution of carbon among the carbon dioxide, carbon monoxide, and gaseous saturated hydrocarbons contained in the product gas (based upon the carbon monoxide in the synthesis gas) was obtained. Subtracting the sum of these three values from 100 yielded the percentage of carbon monoxide converted to gasoline. These results are shown in table 4.

The data given in table 4 are plotted in figures 5 and 6. These results show that:

(A) The rate of reaction between carbon monoxide and hydrogen increased with decrease in gas velocity, the largest value being at the smallest flow rate used, 2.0 l./hr.; the degree of conversion of carbon monoxide in the synthesis gas to carbon dioxide and gaseous saturated hydrocarbons increased with decrease in velocity.

(B) The degree of conversion of carbon monoxide to carbon dioxide based on carbon monoxide reacted increased with decrease in velocity. The degree of conversion to gaseous saturated hydrocarbons decreased as the gas velocity increased above 2.0 l./hr., showed a minimum value at 6.0 l./hr., and increased again as the velocity was raised to 7.5 and 10.0 l./hr.

(C) The yield of gasoline per cubic meter of synthesis gas was approximately the same at velocities from 3.4 to 6.0 l./hr. and decreased gradually with either increase or decrease in velocity.

^{18/} Kodama, Shinjiro: Jour. Soc. Chem. Ind. Japan, vol. 32, 1929, p. 362.

(Reference could not be located.)

^{19/} Work cited in footnote 3.

TABLE 3. - Effect of gas velocity

(Reaction temperature = 210° C.; 72.0 l. of synthesis gas used in each case, except as noted)

Experiment number	Gas velocity, l./hr.	Synthesis gas composition, percent		Contraction, percent	Liquid products, ml./m.³ of synthesis gas		Product gas composition, percent							
		CO	H₂		Gasoline (C₅+)	Water	CO₂	C ₁₁ H ₄	H₂	CO	C _n H _{2n+2}		N ₂	
											C ₁₂ H ₂₂	C ₁₃ H ₂₈		
6a/	2.0	32.5	64.0	3.5	74.8	135.6	190.6	6.5	0.2	18.2	48.2	13.6	1.48	13.3
7	3.4	32.2	65.0	2.8	75.5	139.2	195.2	5.6	.1	19.6	52.0	11.7	1.58	11.0
8	6.0	32.5	65.2	2.3	74.0	132.0	180.5	4.6	.2	24.4	54.2	7.7	1.85	8.9
9	7.5	32.6	65.2	2.2	60.5	102.2	148.6	1.6	.2	27.4	60.0	4.7	1.91	6.1
10	10.0	32.5	64.8	2.7	40.6	64.4	118.2	0.4	.2	30.8	61.7	2.8	2.34	4.1

a/ 36.0 liters of synthesis gas used.

TABLE 4. - Effect of gas velocity

(Reaction temperature = 210° C.; 72.0 l. of synthesis gas used in each case, except as noted)

Experiment number	Gas velocity, l./hr.	CO conversion, percent	H₂ conversion, percent	Carbon distribution						
				Percent of CO in synthesis gas		Percent of CO reacted		Gasoline (C ₅ +) distribution		
				CO	C ₁₂ H ₂₂ (C ₁ -C ₁₁)	CO	C ₁₂ H ₂₂ (C ₁ -C ₁₁)	Gasoline (C ₅ +) distribution	Gasoline (C ₅ +) distribution	
6a/	2.0	85.9	81.4	5.0	14.1	15.6	65.3	5.8	18.2	76.0
7	3.4	85.1	80.4	4.3	14.9	14.1	66.7	5.1	16.6	70.3
8	6.0	80.5	78.4	3.7	19.5	10.6	66.2	4.6	13.2	82.2
9	7.5	66.8	63.6	1.9	33.2	10.9	44.0	2.8	16.3	80.9
10	10.0	43.7	43.4	.7	56.3	12.0	31.0	1.6	25.2	73.2

a/ 36.0 liters of synthesis gas used.

Discussion

In (C) above, the yield of gasoline based on the carbon monoxide in the synthesis gas was observed to increase as the gas velocity was decreased from 10 l./hr.; from 6.0 to 3.4 l./hr., however, the yield was approximately constant, and, as the gas velocity was decreased still further, the gasoline yield decreased. This effect is a result of an increase in production of carbon dioxide and gaseous hydrocarbons, which at 3.4 l./hr. reaches about the same value as the increase in the total conversion; whereas, at a gas velocity of 2.0 l./hr. the production of carbon dioxide and gaseous hydrocarbons is increased to an even greater degree. Conversely, as the gas velocity is increased beyond 6 l./hr., although the production of carbon dioxide and gaseous hydrocarbons is reduced, the extent of reaction between carbon monoxide and hydrogen is reduced to an even greater extent, and the yield of gasoline decreases with increase in gas velocity.

As the gas velocity is increased beyond 2 l./hr., the degree of conversion of carbon monoxide to gaseous saturated hydrocarbons decreases and passes through a minimum value at 6.0 l./hr. Simultaneously, the value (n) of the average number of carbon atoms in the gaseous saturated hydrocarbon molecules increases with increase in gas velocity. Comparison of these results with those obtained in studies of the reaction temperature show that when the gas velocity is high, effects are produced similar to those at temperatures below 210° ; conversely, when the velocity is low, changes occur in the production of carbon dioxide and gaseous saturated hydrocarbons with changes in the value (n) of the latter similar to those observed at temperatures above 210° .

These results suggest that the time required for the hydrogenation of CH -, CH_2 , and CH_3 radicals to such gaseous hydrocarbons as methane and ethane is much larger than the time required for their polymerization. Thus, the variation of (n) with gas velocity may be explained on the following basis: When the gas velocity is low (2.0-3.4 l./hr.), not only is the production of methane by secondary reactions enhanced, but, in addition to the production of CH - and CH_2 radicals, a large quantity of CH_3 is produced. The value (n) is small, therefore, because CH_3 is hydrogenated to such gaseous hydrocarbons as methane and ethane. At high gas velocities, CH - and CH_2 are produced almost exclusively, and, because the contact time is short, most of the CH - and CH_2 radicals are transformed into gaseous hydrocarbons instead of polymerizing further to form liquid hydrocarbons. Hence, (n) becomes greater in value.

To eliminate long contact times and the attendant large production of carbon dioxide and gaseous saturated hydrocarbons, the relative area presented by the catalyst layers must be decreased. This may be accomplished by enlarging the cross section of the reaction tube, thereby increasing the volume of synthesis gas contacting the catalyst and decreasing the contact time. This also serves to maintain the original $\text{CO}:\text{H}_2$ ratio, deviation from which, by reaction in the first part of the reactor, is deleterious to the desired reaction in the later portion of the reactor.