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DEPARTMENT OF INTERIOR
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SYNTHESIS OF HYDROCARBONS AND OXYGENATED COMPOUNDS FROM
WATER AND CARBON MONOXIDE

By Herbert Koelbel and Friedrich Engelhardt

Brennstoff-Chemie, volume 33 (1952), pages 13-21

Translated by

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February, 1952

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Rheinpreussen A.G. für Bergbau und Chemie, Homberg (Niederrhein)
Received December 5, 1951

Franz Fischer stated on November 25, 1925 in his first communication on hydrocarbon synthesis:^{1/} "The reduction of carbon monoxide seems to be of similar importance to industry, to the carbon dioxide assimilation in processes of nature."

The prediction might have seemed to be too prophetic at that time. A glance at the rapid development during the last 25 years illustrates the fundamental importance of carbon monoxide chemistry, and in particular of the reduction of carbon monoxide.

Figure 1 shows some of the available methods which lead today to the production of homologous series of paraffin hydrocarbons and the principal groups of oxygenated compounds. There exist in addition a large number of other methods of industrial or scientific interest which furnish us with a multitude of carbon, hydrogen and oxygen compounds.

This path, highlighted by the names of Sabatier, B.A.S.F., Fischer, Reppe, Roelen, and others, does indeed disclose the methods for the production of a large number of substances starting with carbon monoxide and water, which living nature furnishes us so plentifully and in such inimitable manner.

Franz Fischer and Hans Tropsch state further in the above work, that "The reason for not starting industrial catalytic reactions with carbon dioxide is the ease of direct production of an oxide of carbon containing less oxygen.

Fischer, Koch, Kuester, and others,^{2/} have succeeded in producing gaseous hydrocarbons from mixtures of the higher-oxygen carbon dioxide and hydrogen. A few years ago, one of us (K) showed with Ackermann,^{3/} that 132 grams gaseous, liquid and solid hydrocarbons and some oxygenated compounds can be produced per cubic meter of a gas containing 20 percent CO₂ and 58 percent H₂.

It thus is possible to obtain carbon-hydrogen-oxygen compounds starting with a higher oxidation product of carbon, i.e. one with the lowest energy content.

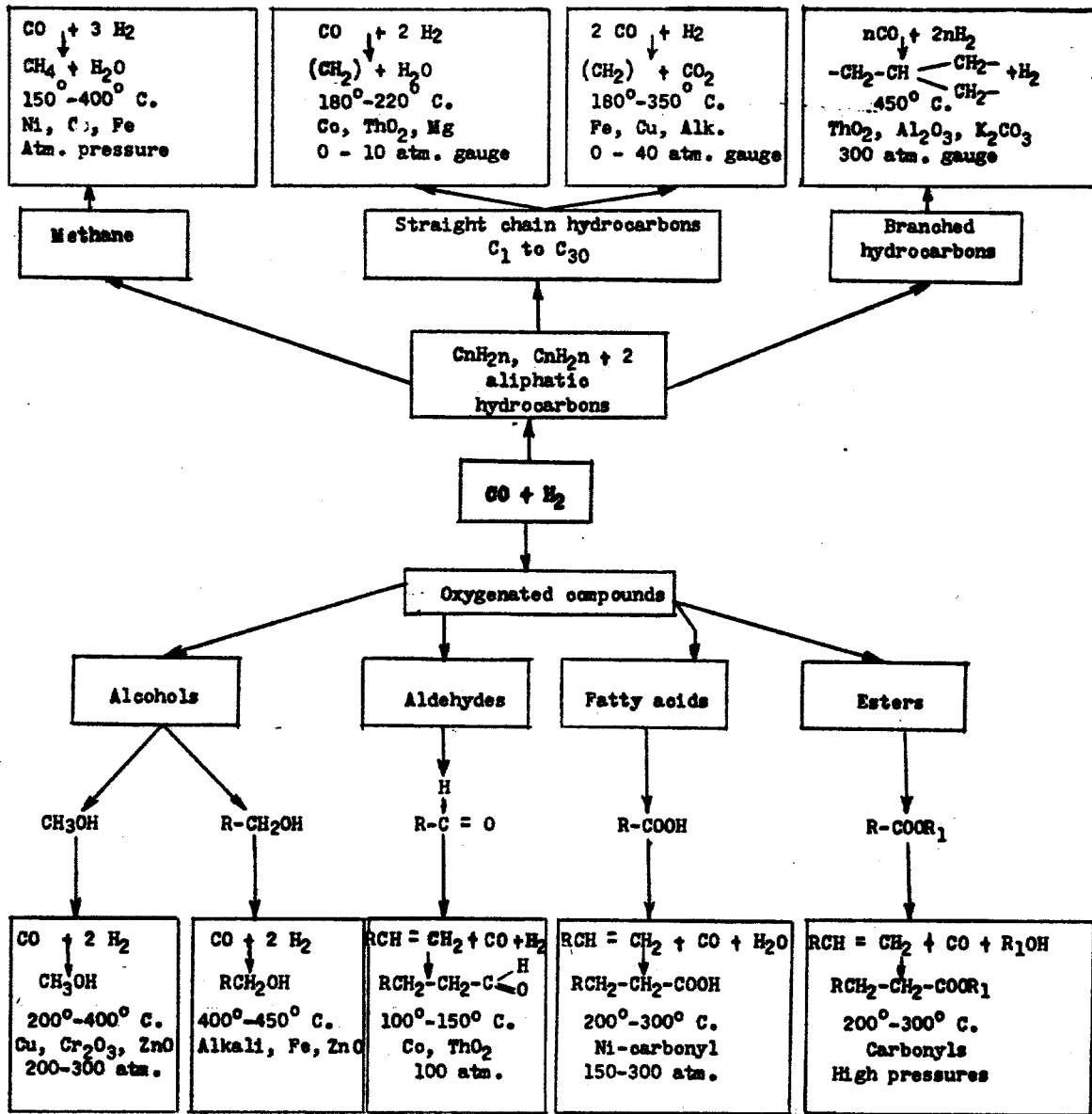


Figure 1. - Carbon monoxide hydrogenation processes.

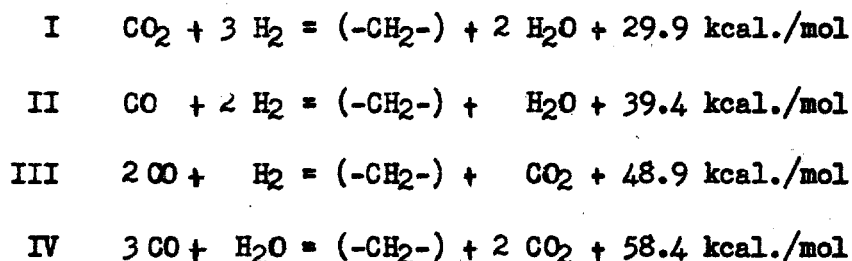
TABLE 1. - Heat of reactions (in kcal.) for the reduction of CO and CO₂ to hydrocarbons at 227° C.

	1		2		3		4	
	CO ₂ + 3 H ₂ = (CH ₂) + 2 H ₂ O		CO + 2 H ₂ = (CH ₂) + H ₂ O		2 CO + H ₂ = (CH ₂) + CO ₂		3 CO + H ₂ O = (CH ₂) + 2 CO ₂	
	Total	Per C-atom	Total	Per C-atom	Total	Per C-atom	Total	Per C-atom
Methane	41.9	41.9	51.3	51.3	60.8	60.8	79.8	79.8
Hexane	179.8	30.0	236.3	39.4	293.4	48.9	358.8	59.8
Hexene	149.0	24.7	205.4	34.2	262.5	43.7	318.9	53.2
Eicosane	572.5	28.6	760.5	38.0	944.2	47.2	1148.4	57.4
Eicosene	541.6	27.2	729.6	36.5	913.7	45.7	1108.0	55.4

We will show in the present article that we have succeeded in converting in a single stage and with good yields carbon monoxide to hydrocarbons and oxygen-containing compounds with a hydrogen compound of low energy content, namely water.

Thermodynamic Considerations

This reaction completes the possibilities of conversion of oxides of carbon into carbon-hydrogen-oxygen compounds. These possibilities of production of higher hydrocarbons will be briefly summarized:



When the reduction of oxides of carbon is arranged in order of the amount of energy liberated, our new synthesis, with a heat of reaction of 58.4 kcal./mol of CH_2 at 225°C . reacts with the liberation of the largest amount of heat. Next comes the Fischer-Tropsch reaction by way of formation of carbon dioxide with 48.9 kcal./mol, of water with 39.4 kcal./mol, and the CO_2 reduction with H_2 with 29.9 kcal.

The heats of reaction are important industrially because of the problem of dissipating the heat, and they are shown in table 1 for the formation of methane, hexane, hexene, eicosane, and eicosene, all at an assumed synthesis temperature of 227°C . The table shows the total heat of reactions of formation of the hydrocarbon molecules and also the heat of reaction per C-atom or CH_2 radical. The heat of formation of olefins is known to be smaller than of the saturated hydrocarbons.

Differences in the heats of reaction per C-atom in the four above reactions are 9.5 kcal. or a multiple thereof, as is shown schematically in figure 2. Should the four reactions be arranged on the abscissa in order of the CO consumption at equal arbitrary distances, and the heat of the individual reactions at 227°C . plotted on the ordinate, the intersections fall upon a straight line. Starting with reaction I, reduction of CO_2 , the heat of reaction increases by way of reactions II, III, and IV additively by a constant amount. This constant is the heat of the water gas reaction which is equal to about 9.5 kcal., and which enters into the total heat of reaction as an additive member according to the law of Hess. We see further that the heat of reaction increases with increasing consumption of CO , and drops with increasing H_2 consumption. It increases further with increasing formation of CO_2 and drops with increasing formation of H_2O .

It was shown in earlier work,⁴ that the formation of hydrocarbons from CO and H_2 takes place primarily by way of formation of

water. Should we start with reaction II, the other reactions, I, III, and IV can be derived by the addition of the water gas reaction, as may be seen from the formulas in the bottom part of the figure. Thus, reaction III which proceeds preferentially with iron catalysts, can be separated into the fundamental reaction II and the secondary water gas reactions of 1 mol CO. The reaction IV breaks down into the water gas reaction of 2 mols of CO and the reaction II.

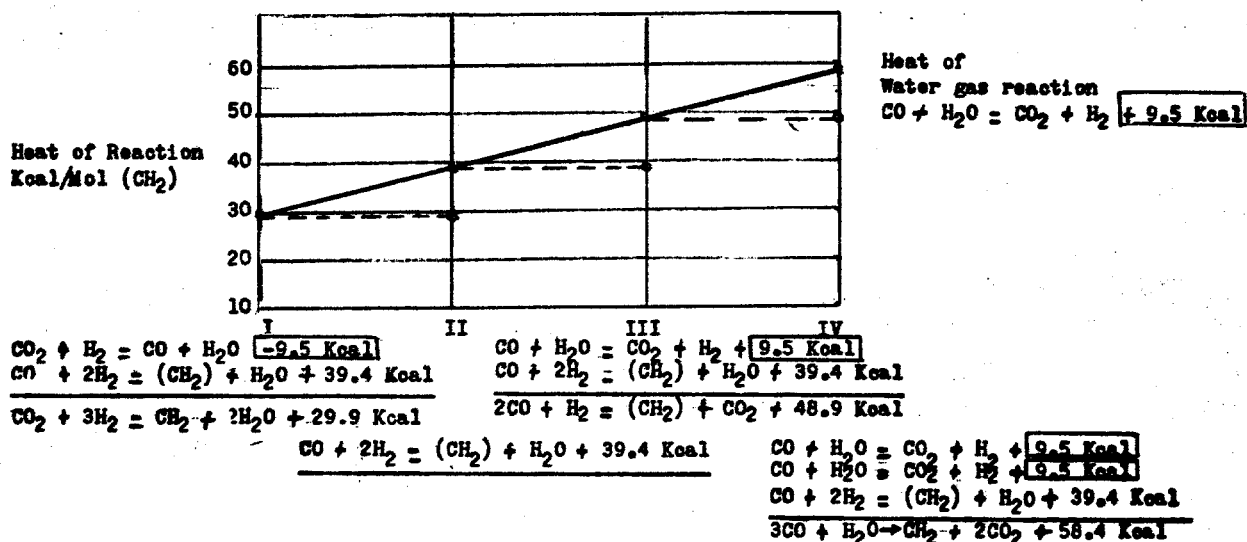


Figure 2. - Water gas reactions as partial reactions of reduction of CO and CO₂.

Reaction I, the reduction of CO₂, breaks down into reaction II and the water gas reaction of 1 mol CO. In this case, the water gas reaction proceeds, however, in the reverse direction as an endothermal reaction, so that the heat reaction II is not increased by the heat of the water gas reaction as in the reactions III and IV, but is reduced by it. This treatment tells, of course, nothing about the reaction mechanism or the true reaction, but illustrates very clearly the connection between the four reactions.

Figure 3 shows changes in free energy against temperature to permit comparison of the affinity of our synthesis with the affinities of the other reactions discussed. These curves present a sort of thermodynamical probability of the course of the different reactions. One hydrocarbon, hexane, was used as an example, and changes in the free energies, ΔF , are expressed in kcal./C-atom of the hexane chain. The curve shows that the affinity of the system steam-CO is considerably greater than the affinity of the classical Fischer-Tropsch synthesis. For instance, at a synthesis temperature of 200° C., ΔF is greater in our synthesis by the factor 2. Temperatures, for which $\Delta F = 0$, i.e. at which the systems possess no longer any affinity on our example of hexane, are arranged in the order of reactions I, II, III, IV at 340°, 405°, 453°, and 505° C. It may be seen that our system is located in

the region of negative ΔF values, where the equilibrium tends to be displaced towards the side of the reaction products at temperatures at least 100° C. higher, with still the same affinity as the classical Fischer-Tropsch synthesis by way of water formation.

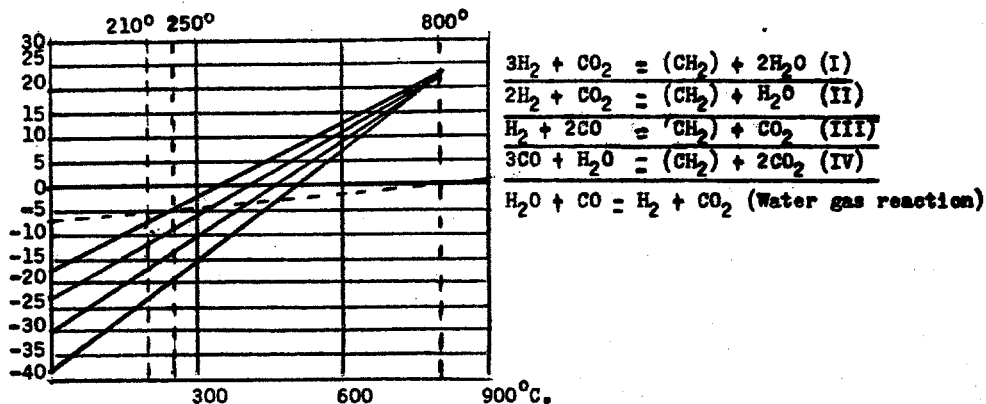


Figure 3. - Changes of free energies of hexane formation for different syntheses.

The four reactions can be theoretically derived from reaction II by the addition of the water gas reaction, as mentioned previously. The same applies also to changes in free energy. The vertical distances of the different curves in figure 3 at all temperatures are the reductions in free energy of the water gas reaction, or its multiple, at the corresponding temperatures. At 800° C., ΔF is the same for all four reactions, because the ΔF for the water gas reaction is equal to zero at that temperature.

It remained to be proven for the new synthesis, how far the conversion of H_2O with CO may theoretically proceed, and at what temperatures the formation of higher hydrocarbons appears possible. Equilibrium constants are basis for judging this theoretically possible conversion and their logarithms are plotted in figure 4.

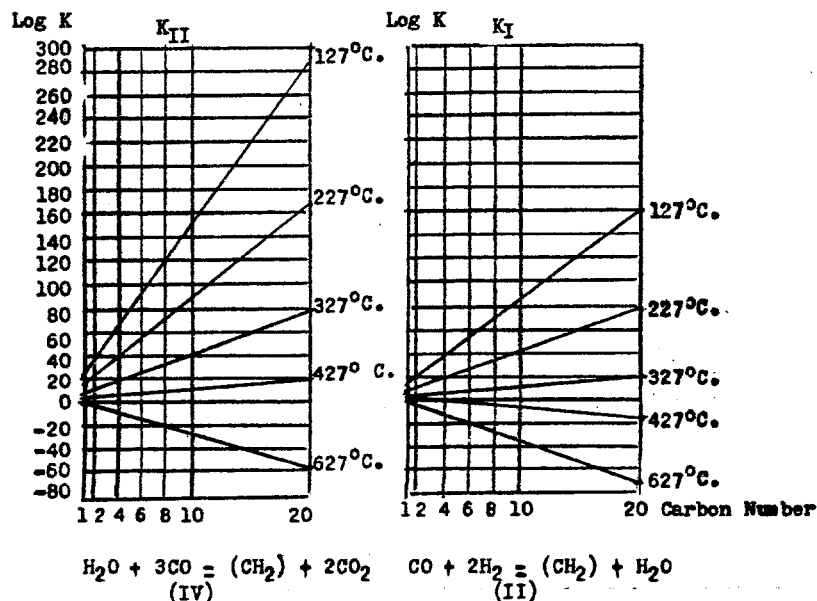


Figure 4. - K for H_2/CO synthesis and Fischer-Tropsch synthesis at different temperatures.

The C-number of the chain of the n.paraffin hydrocarbons is plotted on the abscissa, and the logarithm of the equilibrium constant plotted on the ordinate for the production of hydrocarbons according to the equation

$$k_{\text{equil. IV}} = \frac{p(\text{CH}_2) \cdot p^2\text{CO}_2}{p^3 \text{CO} \cdot p \text{H}_2\text{O}} \quad (\text{on the left in the figure})$$

The equilibrium constants are entered for temperatures 127°, 227°, 327°, and 627° C. We see immediately the relationship between the constants and the length of the chain, and the formation of gaseous hydrocarbons appears to be thermodynamically favored over the formation of the higher molecular weight hydrocarbons in the temperature range 210°-250° C. of our synthesis. The lower the temperatures, the more is the equilibrium displaced towards the hydrocarbon side. At higher temperatures, equilibria are displaced in favor of the hydrocarbon formation, and the tendency is increased to form gaseous hydrocarbons in preference to the higher molecular weight hydrocarbons. The equilibrium constant is equal to about 1 at around 450° C., for all hydrocarbons; this indicates a molar conversion of 50 percent. Above 500° C. only gaseous hydrocarbons can form, with the preponderance of methane.

The ideal requirements for synthesis of liquid hydrocarbon from CO are: (1) The displacement of equilibrium towards the side of hydrocarbons at such high temperatures as to result in a sufficient reaction velocity; and (2) that the formation of high molecular weight hydrocarbons is favored over the formation of methane and ethane at these temperatures. A comparison of equilibrium constants of our synthesis with those of the classical Fischer-Tropsch synthesis

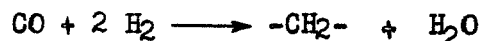
$$k_{\text{equil. II}} = \frac{p(\text{CH}_2) \cdot p \text{H}_2\text{O}}{p^2\text{H}_2 \cdot p \text{CO}} \quad (\text{on the right in the figure})$$

shows that at the same temperature the equilibrium constants of our synthesis are considerably above those for the Fischer-Tropsch synthesis. At a given equilibrium, temperatures of our synthesis are but 100° C. higher than for the Fischer-Tropsch synthesis. The second requirement of an equilibrium constant favorable to the formation of liquid hydrocarbons instead of the methane formation appears to be better satisfied thermodynamically in our system than in the Fischer-Tropsch synthesis. To permit a comparison of the theoretical maximum conversions in all four reactions discussed, temperatures are plotted against the chain length of hydrocarbons in figure 5, at which the equilibrium constant equals 1, or the change of the free energy equal 0. This value for $k = 1$ provides a rough measure of the temperature at which comparable and satisfactory conversions can be obtained. In our synthesis, e.g. the formation of hexane, this conversion can still be expected at 505° C., in the Fischer-Tropsch synthesis by way of CO₂ only below 453° C., with H₂O only below 405° C. The reduction of CO₂ is finally possible with a comparable conversion only up to 340° C.

The four reactions discussed naturally can be arranged in the same order, and namely so that the temperatures for $k = 1$ rise with increasing CO-consumption and decreasing H_2 -consumption, and are reduced with increasing water formation or reduced CO_2 formation.

In summarizing the theoretical considerations in the hydrocarbon synthesis from CO and H_2O , the following may be stated:

- (1) The heat of reaction is 59.8 kcal./mol CH_2 , referred to the formation of hexane at synthesis temperatures. It is about 20 kcal./mol greater than with the classical Fischer-Tropsch reaction with water as the reaction product.
- (2) The reactions of reduction of oxides of carbon differ by the heat of the water gas reaction or its multiple. All four reactions can be derived theoretically from the reaction



by the addition of the heat of the water gas reaction.

- (3) The affinity of the reaction of CO and H_2O , measured by changes in free energy, is greater than in the Fischer-Tropsch reactions by a factor of about 2 at $200^\circ C$. The free energies of the discussed reactions differ by a simple or multiple of the free energy of the water gas reaction, which is equal to 0 at $800^\circ C$.
- (4) The formation of hydrocarbons from steam and CO is possible at temperatures of up to $500^\circ C$. according to the equilibrium constants. This temperature is but around $100^\circ C$. higher than the corresponding temperatures of the Fischer-Tropsch reaction with water as the oxidation product. These reaction temperatures at which the equilibrium constant $k_{equil.} = 1$ differ either by $50^\circ C$. or its multiple. At these temperatures, the log k of our synthesis is about twice as high as for the reduction of CO by H_2 with H_2O as the product of oxidation.

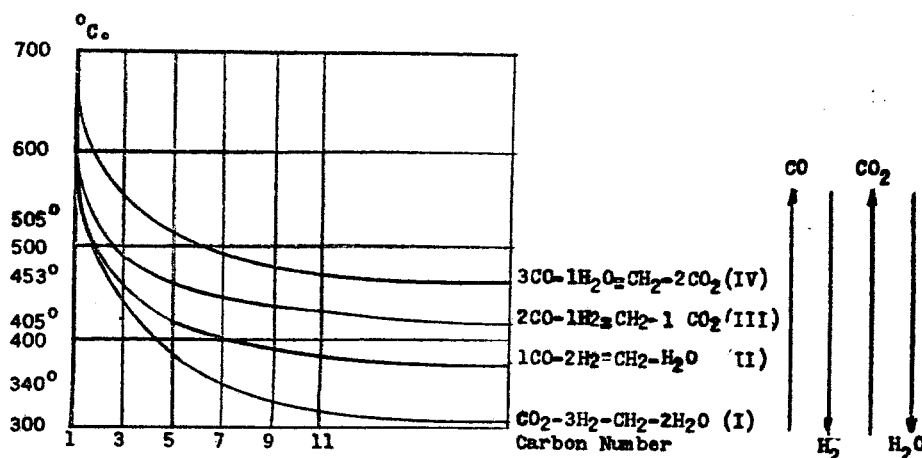


Figure 5. - Equilibrium temperatures for $k = 1$.

These thermodynamic considerations give, naturally, information on the energy relationship, but not on the actual course of the synthesis which is determined by the reaction velocities, selective activation by catalysts and other factors.

Experimental Results

The conversion of steam with CO with the formation of hydrocarbons and oxygen-containing compounds proceeds extraordinarily smoothly and leads in a single stage to a complete conversion. Table 2 summarizes briefly the results and the range of operating conditions, and will be discussed subsequently to show the effect of these conditions.

TABLE 2. - Operating conditions and results

Temperature	150°-400° C., preferably 110°-260° C.
Pressure	Normal pressure and higher
Space velocity	Up to 1,000 and higher
Ratio - steam:CO	Less than 0.5
Catalyst	Fe, Co, Ni, and others
H ₂ O conversion	Over 90%
CO conversion	Over 90%
Consumption proportion, H ₂ O/CO. .	1:3 - 1:2
Yield	So far up to 216 gm. hydrocarbons + oxygen-containing compounds per cubic meter of CO used
Composition of products	Paraffin hydrocarbons, methane to hard waxes, up to 60% olefins in total products, up to 40% oxygen-containing compounds

Apparatus

The apparatus used by us is sketched in figure 6. CO is made to pass through the gas meter, compressor, pressure equalizer, 3-stage pressure regulator, flow meter, and water vaporizer. Measured amounts of steam can be supplied to the vaporizer by the pressure pump. The amount of steam vaporized is regulated depending on the desired steam partial pressure by varying the temperature of the vaporizer, taking into consideration the CO pressure used. After mixing the CO in the vaporizer with a definite amount of steam, the mixture is permitted to enter through a thermostatically controlled electrically heated reaction tube with the granulated catalyst. The liquid products are condensed

in front. The end gas is pressure released through a valve, passes through a flow meter for the determination of the residual water in a CaCl_2 tube, then through two activated carbon tubes (for absorption of the light ends hydrocarbons) and through a gas meter into the end gasometer. A CO_2 scrubber is located between the activated carbon tubes.

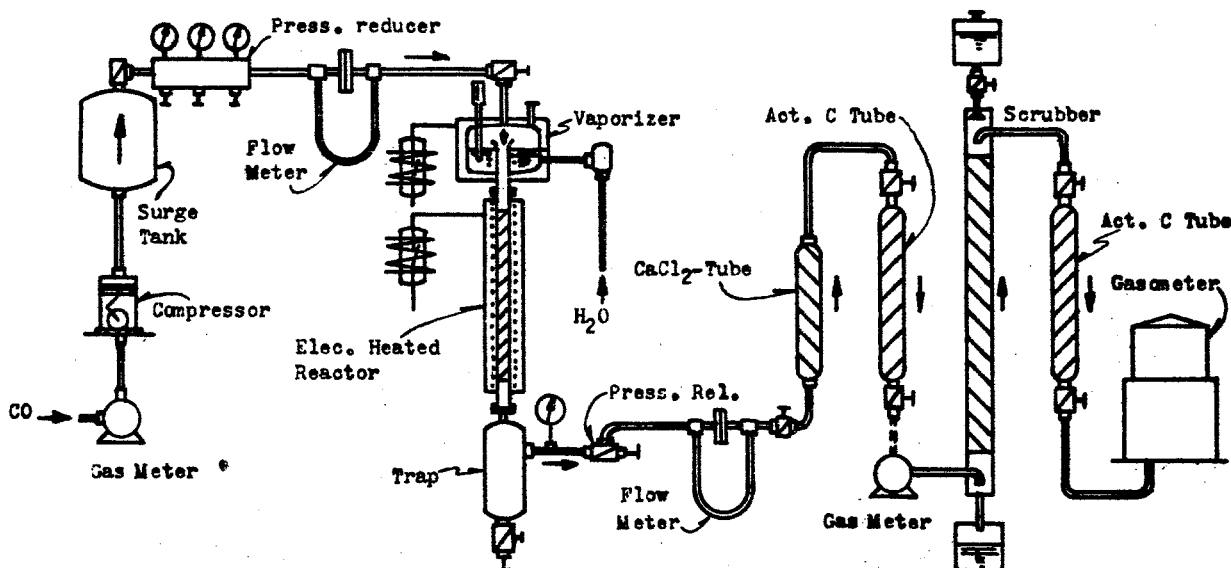


Figure 6. - The experimental apparatus.

The synthesis over fixed-bed catalysts can also be carried out in liquid phase with the catalyst suspended in oil, as described in an earlier work,^{5/} or possibly in a fluidized bed with suspended finely subdivided catalysts.

Proportion of Water to Carbon Monoxide

The production of a definite proportion of steam to CO was exceptionally important in carrying out our synthesis. The general rule could be established that H_2O and CO must be present in the same proportion in the intake gas as is used in the synthesis reaction. The equation



of formation of hydrocarbons shows that 1 part of H_2O must be present for 3 parts of CO. The equation of formation of alcohols, for instance of ethyl alcohol by the formula



shows that the $\text{H}_2\text{O}:\text{CO}$ proportion required is 1:2, and approaches the 1:3 proportion necessary for the maximum hydrocarbon formation for increasing chain length. Experience has also shown that synthesis proceeds satisfactorily only when the proportion required by the theory is approximately maintained without any appreciable excess of any of the reaction

participants. If the reacting gases are not consumed in the same proportion as introduced, the excess of the reaction participants produces an undesired effect upon the catalysts. An excess of CO introduces the danger of carbon deposition and blocking of the catalyst; an excess of water introduces the danger of damaging the catalyst by oxidation.

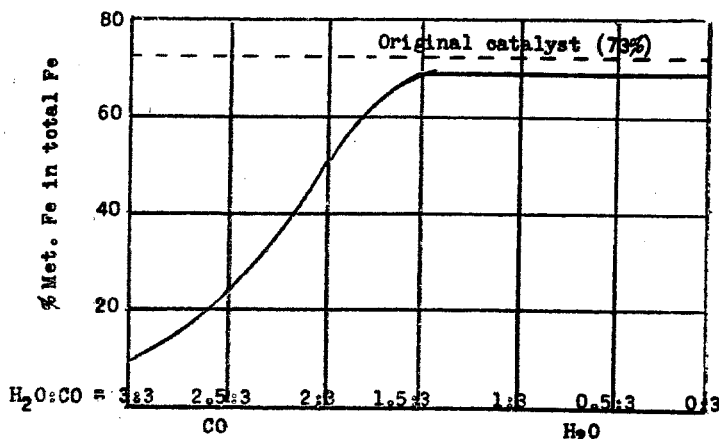


Figure 7. - Reduction of Fe catalyst in relation to H₂O/CO proportion.

We will consider the effect of H₂O/CO proportion on the oxidation of the catalysts. Figure 7 shows the reduction of iron catalyst upon a carrier, i.e. its metallic iron content referred to total iron, in relation to the H₂O/CO proportion of the synthesis gas after an operating time of 70 hours. The reduction gives us a rough measure of activity, because the CO activates preferentially compounds of a metallic nature. With a proportion of 3:3, the reduction dropped from the original 73 to 8 percent. A noticeable oxidation can be observed even with a proportion of 1.75:3, and the reduction is reduced to 64 percent. Only with a H₂O proportion of 1.5 to 3 parts CO is the reduction not appreciably reduced, and no oxidation takes place. From the standpoint of the catalyst, the optimum H₂O/CO proportion with metallic catalyst varies between 1.5 to less than 1 part of water to 3 parts of CO.

Figure 8 shows the relationship between theoretical hydrocarbon yield and oxygen-containing compounds and the H₂O/CO proportion. The highest yield of hydrocarbon C_nH_{2n} is 208 gm./nm.³ CO and must be expected according to the equation when the H₂O/CO proportion is 1:3.

With increasing deviation from the proportion 1:3, either in higher proportion of H₂O or of CO, the hydrocarbon yield must theoretically become lower with complete CO conversion. The same is fundamentally true for the synthesis of alcohols as is shown on the example of ethyl alcohol. In this case, according to equation II, $3 \text{ H}_2\text{O} + 6 \text{ CO} = \text{C}_2\text{H}_5\text{OH} + 4 \text{ CO}_2$. The ethyl alcohol yield reaches a maximum with a proportion of 1.5 parts containing compounds (III) the optimum proportion approaches asymptotically the most favored ratio of 1:3 of the hydrocarbon formation. When the H₂O/CO proportion is derived from the maximum yield, it must also fall from 1.5 to less than 1 part of H₂O to 3 parts CO.

Optimum yields can therefore only be reached with the gas corresponding to the reaction ratio, and only under such condition can catalysts be expected to produce maximum yields and have a long life. The one is causatively connected with the other.

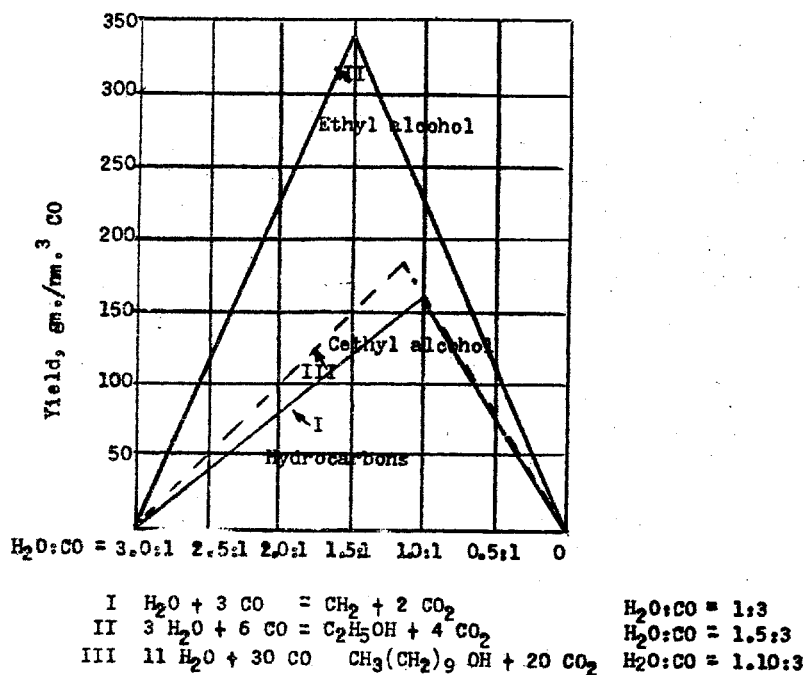


Figure 8. - Relation between theoretical yield and the H₂O/CO proportion.

Reacting Gases

Fundamentally all gases containing CO and free from catalyst poisons, like sulfur, gums or gum formers, can be considered as reacting gases for our synthesis. Naturally the presence of water does not interfere. The new process could, however, be most economically realized starting with low-hydrogen gases. Most of our tests were carried out with pure CO. In this connection we were interested in finding out how the cheapest CO-containing gases, such as generator gas or blast furnace gas containing only 28 to 30 percent CO and 55 to 60 percent N₂ would behave during synthesis. The question specifically to be tested in this connection was whether the high content of inerts would interfere, and whether a relatively low partial pressure of the reactants would permit complete conversion.

The conversion of a gas containing only 29 percent CO was 97 percent and differed hardly at all from the conversion obtained using practically pure CO. The analyses of the reacting and product gases in table 3, with an average operating time of 240 hours, showed that the utilization of CO could progress to such an extent, that the end gases contained only 1 percent of it; the yield corresponding to this CO conversion amounts to about 195 grams total hydrocarbons per nm.³ CO.

TABLE 3. - Conversion of CO-poor gas (29% CO with steam)

	CO ₂	Oxygenated H.C.	O ₂	CO	H ₂	H.C.	C- No.	N ₂
Reacting gases	0.0	0.0	0.0	29.0	1.0	0.0	-	70.0
End gas	17.45	0.7	0.0	1.07	2.4	1.5	1.35	76.88

CO conversion: 97% → 195 gm. H.C./nm.³ CO.

Fe carrier catalyst, precipitated and reduced, 235° C., 10 atm., space velocity 100-200.

H₂O/CO = 1:3 average over 240 hours.

Space Velocity and Operating Pressure

The amount of gas converted by catalyst per unit time, the gas throughput or the space velocity, are important yield criteria for any catalytic process. This space velocity is limited by the reaction velocity or by the time of residence of a gas over catalyst necessary for the course of the reaction.

The time of residence of a gas in a stream increases with increasing volume proportionally to the pressure, and the question was raised whether the normal pressure referred to gas throughput could be increased with a space velocity corresponding to the increased pressure.

Figure 9 represents tests with different pressures plotted on the abscissa and the maximum space velocities on the ordinate, with which the CO conversion of over 90 percent was still possible.

These tests show an almost regular pressure relationship, about such that the maximum space velocity with a CO conversion of 90 percent is equal to 9 to 12 times the pressure (expressed in atmospheres). Within this range which is shown by a band limited by two straight lines are the optimum values of space velocities for the catalyst used in this particular example. This relationship was not directly to be expected from the earlier experience of the Fischer-Tropsch synthesis.

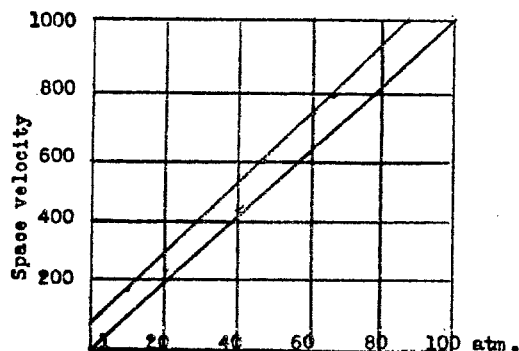


Figure 9. - Relationship between space velocity and pressure.

Table 4 shows the influences of the operating pressure upon the nature of the products and the yield.

TABLE 4. - Effect of pressure upon the yield and composition of the products

Pressure, atm. gauge	CO conversion %	Yield gm./nm. ³ CO	d ₂₀ ⁴	Ultimate analysis			Wt. % alcohols	Acid number, mg. KOH/gm.
				% C	% H	% O		
0	94.0	163.2	0.747	85.5	14.40	0.10	0.1	0.7
10	93.5	168.5	0.744	85.44	13.84	0.72	0.4	3.0
30	92.5	175.5	0.747	85.15	13.81	1.04	3.0	5.3
50	92.6	174.0	0.762	84.84	14.16	1.00	5.2	7.2
70	96.0	195.0	0.775	83.61	13.36	3.03	12.1	10.8
100	91.5	216.0	0.768	79.90	13.00	7.10	29.5	30.5

The CO conversion is apparently unaffected by pressure when temperature and space velocity remain constant. The oxygen content of the products rises, however, appreciably, particularly between 30 and 100 atmospheres from 1 to 7.1 percent, corresponding to an alcohol content increase from 3 to nearly 30 percent. Alcohol formation was already observed from the other side. The acid number rises in this range from 5.3 to 30.5. In agreement with the incorporation of oxygen into the molecule, the total product yield with the same CO conversion rises from 163 to 216 gm./nm.³ CO. The olefin content of the products varied between 39 and 56 volume percent in these tests.

Effect of Temperature

The optimum temperature range of the synthesis, between 180° and 280° C. with metallic catalysts, is immediately limited by two conditions. The temperature must be sufficiently high for sufficient conversion, but not high enough to favor the undesired side reactions such as methane formation and carbon deposition. The effect of temperature is very well illustrated in results shown in figure 10, where the CO conversion, the yield of total hydrocarbons and the methane formation are presented in relation to the temperature. A freshly reduced iron catalyst upon a carrier was always heated for 150 hours with a temperature rise of 10° C. between 200°-300° C. with a H₂O/CO mixture at normal pressures, and the average values for the CO conversion, the

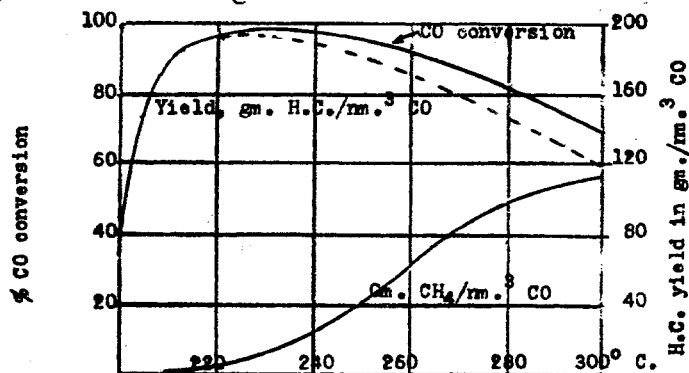


Figure 10. - Effects of temperature on the conversion and CH₄ formation.

hydrocarbon yield and the methane formation were found. With the catalyst used, only the water gas reaction is prominent at 200° C. without noticeable hydrocarbon formation. However, even as low as at 210° C. the yield equals to 186 grams, and this amount represents about 90 percent of the theoretical. The methane formation is only 4 grams, or about 2 percent of the hydrocarbons formed. At 230° C. the hydrocarbon formation amounts to 200 grams, or 96 percent of the theoretical, the methane formation is 12 grams or 6 percent of the total hydrocarbons. Up to about 250° C. the average CO conversion during 150 hours varies between 93 and 97 percent and then drops slowly with further increases in temperature. At these high temperatures the CO conversion was complete in the beginning of the 150-hour operating period, but the catalyst became gradually weakened. The methane formation begins to rise stronger at 240° C. and at this temperature it amounts to 25 gm./m.³ CO, or to 12.6 percent of the total hydrocarbons. Nor does the hydrocarbon yield increase at this temperature parallel to the CO conversion, because the formation of higher-hydrogen CH₄ consumes more hydrogen. It is available in the water of the inlet gases, in which the proportion of H₂O:CO is set for the formation of the CH₂ polymers. The methane formation keeps increasing with higher temperatures, and above 300° C. practically methane alone is formed.

In the example discussed, the optimum synthesis temperature is between 220° and 230° C. In this range the CO conversion is practically complete, being 95 to 98 percent, the catalyst life is satisfactory, and the methane formed fluctuates between 2.5 and 6 percent of the total hydrocarbons. With other catalysts and other operating conditions the optimum temperatures are naturally somewhat different, although the effect of the temperature is basically the same as in the example cited.

Material Balances

Material balances were calculated in our first basic series of tests in order to control the accuracy of the tests with respect to yields. The short form of such a balance (Fig. 11) seems to us convenient to express the course of the synthesis and the relationship of the two raw materials to the reaction products. An iron-carrier catalyst was used, and the gas was at 30 atmospheres and consisted of H₂O/CO = 1.24:3, which permitted a theoretical yield of hydrocarbons of 181 gm./nm.³ CO. With a 93.3 percent conversion a maximum of 169.0 percent hydrocarbons could be obtained per normal cubic meter of CO. The amount of products found in the test was 175 gm./nm.³ CO. The increased amount was caused by formation of alcohols. The balance test was run for 79 hours. The CO introduced was measured in gas meters, the steam consumed from the difference of the amount of water weighed into the vaporizer and the amount of water recovered in front of the absorption system and in the calcium chloride. CO₂ was measured by absorption in potassium hydroxide, CO and H₂ were found from analysis and measurements of the end gas; the hydrocarbons were determined in the usual way by deposition in condensers and by adsorption on activated charcoal. The amount of CO found in the reaction products is higher by a negligible amount than the amount introduced. Less water was found in the products than was used. The errors of 0.7 to 2 percent are within the limits of errors to be expected in such balances.

The figure shows that about two-thirds of the CO reappears as CO₂, 27 percent as hydrocarbon, 0.5 percent as alcohols, and 6.7 percent as unconverted CO. 64.3 percent of the water used was converted to hydrocarbons, 22.9 percent converted to hydrogen, 1.8 percent to alcohols;

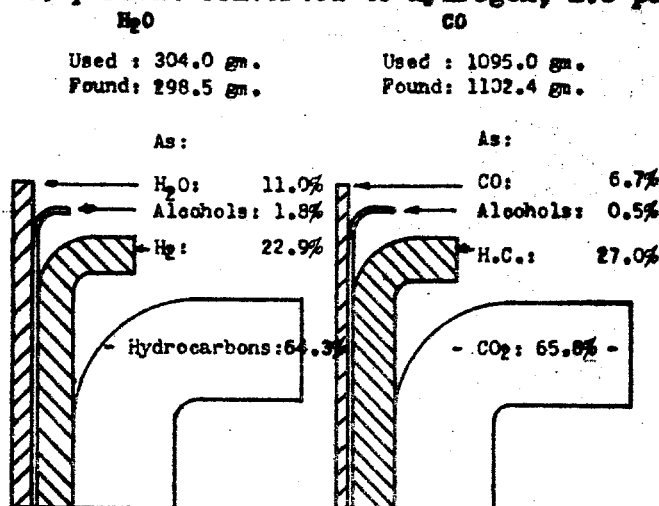


Figure 11. - Material balance.

11.0 percent leave the apparatus unchanged. When considering the alcohol formation and the relatively strong water gas reaction, this case indicates the synthesis of hydrocarbon formation according to the equation: $3 \text{ CO} + 1.001 \text{ H}_2\text{O} = 1.002 (-\text{CH}_2-) + 2.003 \text{ CO}_2$, which confirms the formula given in the beginning.

Catalysts

Two fundamental requirements are made upon the catalysts:

1. A maximum activity which would permit operations at minimum temperatures, and
2. Maximum selectivity in the sense of favoring the desired principal reactions and suppressing the undesired side reactions.

In general, all such materials may be used as catalysts, which can sufficiently strongly activate CO and H₂O. Such are in particular metals of the eighth group of the periodic system, which possess particularly high affinity for the strongly reactive CO because of the unfilled electron shell. Iron was found to be particularly well suited amongst these metals because of its strongest affinity for CO. Synthesis can also be successfully carried out with cobalt and nickel, but these metals cause a higher methane formation than iron.

It should be noted that for practical reasons only such results are included in this present paper which were obtained with a definite catalyst type, namely with iron catalysts upon carriers. Some of the other catalyst types investigated by us behaved in part very differently. A report on them will be published at an opportune time.

The undesired side reactions are in our case: The decomposition of CO, the water gas reaction, methane formation and the oxidation of the catalyst. These side reactions are to be taken into consideration in the same way as in the Fischer-Tropsch synthesis. The methane formation is thermodynamically favored over the formation of hydrocarbons at the synthesis temperature as may be seen in figure 12, where changes in free energies of these side reactions are expressed in relation to temperature in comparison to the hexane formation reaction. The change in the free energy of water gas reaction is smaller than for all the other reactions; it does not appear therefore to be favored. The carbon deposition and methane formation must be considered in our synthesis as in the Fischer-Tropsch synthesis, and the catalyst must be selectively poisoned by suitable additions against favoring these reactions.

The addition of alkali salts was found satisfactory for suppressing methane formation. Deposition of carbon is retarded by the introduction of nitrogen into the metal lattice of the catalyst, or by the addition of a difficult-to-reduce oxide. Copper and silver additions are desirable to facilitate reduction. They permit an extensive reduction at relatively low temperatures which reduces the sintering of catalysts. When fixed-bed catalyst is used, dolomite or Kieselgur are convenient as carriers. When operating in the liquid phase with a catalyst sludge in oil, carriers can be omitted.

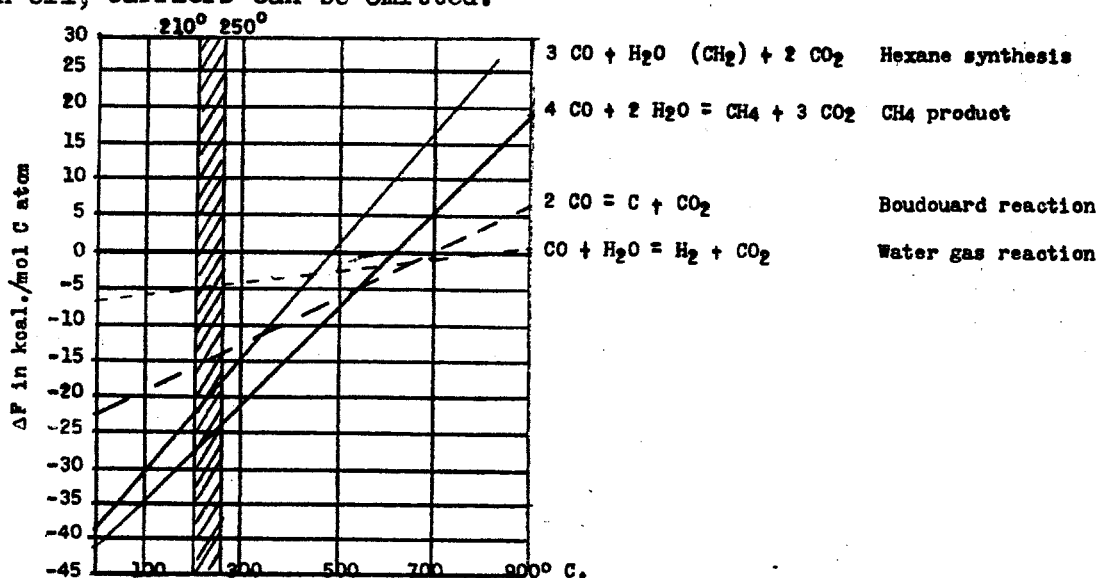


Figure 12. - Changes in the free energy of synthesis and side reactions.

Synthesis proceeds especially smoothly on precipitated and reduced iron catalysts. The reduction can be carried out with H₂, CO, or gases which contain both gases.

At the correct H_2O/CO proportion, the catalyst life extends to over 1,000 hours with over 90 percent CO conversion. The catalyst load amounts at present to 7 liters of gas per 1 gram of iron per hour.

Properties of Synthesis Products

The synthesis products consist primarily of saturated and unsaturated paraffin hydrocarbons. The whole homologous series from methane to solid paraffins is formed. The olefin content of the total products varied in our experiments between 35 and 60 percent. We can as yet say nothing about the location of the double bond and the extent of branching, and these problems are still being investigated. Alcohols can form with the paraffin hydrocarbons; aldehydes, esters, and fatty acids are produced only to a negligible extent.

Most of the alcohols belong to the low molecular weight members, with ethanol forming up to 80 percent. In the examples here cited, higher molecular weight alcohols were produced only in minor quantities.

TABLE 5. - Composition of the products. Examples at 0 and 1,000 atm. gauge.

Fractions	1 atm. gauge, 235° C. ($d_{20}^4 = 0.7455$)		100 atm. gauge, 238° C. ($d_{20}^4 = 0.7682$)	
	Wt. % of the total product	Gm./m. ³ CO	Wt. % of the total product	Gm./m. ³ CO
C ₁ + C ₂ H.C.	16.2	26.6	10.7	23.1
C ₃ + C ₄ H.C.	15.2	25.0	17.6	38.0
B.p. 30°-200° C.	40.7	66.8	27.0	60.0
B.p. over 200° C.	19.4	31.9	5.7	12.4
Wax (butanone method)	8.5	12.9	8.7	18.8
Alcohols	0.0	0.0	29.5	63.7
Total	100.0	163.2	100.0	216.0

Table 5 gives the composition of two synthesis products obtained at atmospheric pressure and at 100 atmospheres. The table must only be considered as representing two cases, and does not give the optimum conditions. It is furthermore definitely possible to change the character of the synthesis products by varying operating conditions.

The higher density of the 100 atmospheres products shows already that a considerable proportion of it consists of oxygenated compounds.

These are primarily alcohols which form 30 percent of the total product. At atmospheric pressure the formation of no appreciable amounts could be proven. With approximately the same CO conversion the yield of 216 grams in the 100 atmosphere tests is higher than at the atmosphere pressure tests where it amounted to 163.2 gm./m.³ of CO; between 23 and 26 grams C₁ + C₂ hydrocarbons were formed in both tests, but at 100 atmospheres the percentage of these products amounts to 10.7 as against 16.2 at atmospheric pressure. The formation of C₁-C₂ hydrocarbons is relatively high in these tests. It was found possible in the meantime to reduce the proportion of this fraction to about 5 percent of the total product. The percentage of C₃ and C₄ hydrocarbons is just as high in both runs. The yield of gasoline boiling between 30° and 200° C. is of the same order of magnitude in the two tests, but its percentage is lower in the 100 atmospheres fraction than in the atmospheric pressure products. The hydrocarbon oil boiling above 200° C. amounts to 20 weight percent in the atmospheric pressure product while in the 100 atmosphere product it forms only 5.7 percent. Solid wax was formed to the same extent in both cases.

Distillation curve of some of the products is shown in figure 13. The curve at the left was obtained with a normal pressure product,

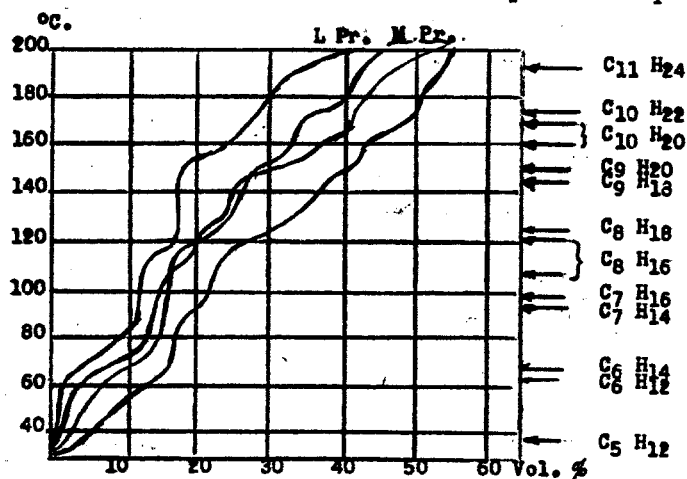


Figure 13. - Distillation curve of a few products.

those to the right obtained with products of pressure synthesis. The Jantzen column was used in fractionation up to 100° C. and the Widmer column above 100° C. The distillation curves make no claims on accuracy, but show rather plainly the points of arrest in the boiling point ranges of the saturated and unsaturated aliphatic hydrocarbons. The distillation curves of the pressure synthesis products appear more differentiated than those of the atmospheric pressure products.

The work on kinetics and reaction mechanism of the synthesis is not yet concluded and will not be considered here in the present communication. It will merely be stated that the opinion expressed in one of our earlier communications 6/ on the mechanism of the Fischer-Tropsch synthesis in which a chemisorption of the reactants on the catalyst

surface and a breakdown of the adduct complexes is assumed with reorientation of the compounds, can also be readily applied also to our new synthesis.

We will also intentionally avoid at this stage the discussion of the pros and cons of industrial application and the economic aspects of our synthesis. We will limit ourselves here to discussion of the fundamental reactions, the continuation of the study of which appears desirable to us.*

The present results were obtained in our investigations of the mechanism of CO hydrogenation which we have frequently reported.^{7/} They are based upon the experience and lessons learned in the many years of activity in the field of the Fischer-Tropsch synthesis by one of us (K). Heartly thanks and acknowledgements are extended to Dr. Ackermann, Dr. Ruschenburg, and Dr. R. Langheim.

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* We wish to emphatically deny our connection with any exaggerated and in part erroneous presentation which has appeared in the daily press without any active part played by us.