VII - REACTION PRODUCTS

The main products which are obtained from the Fischer-Tropsch process are gasoline, Diesel fuel, paraffin wax, lubricants, alcohols, and fatty acids. The low-boiling portion of the product which was given the name "Kogasin" by Fischer, has been shown to contain largely straight-chain paraffinic and olefinic hydrocarbons (412) with minor amounts of aromatic hydrocarbons, naphthenes, and oxygenated organic compounds. The yield of oxygenated compounds may range from almost zero to several percent (403). This value depends upon the operating variables. A typical distribution of the primary product from a powdered iron catalyst is given in Table I. The gasoline fraction boiling from 30 to 200°C. is sometimes called Kogasin I, and the rest of the liquid fraction, boiling between 200 - 300°C. is called Kogasin II.

The hydrocarbons produced in the commercial, cobalt-catalyzed synthesis range from methane to hard waxes with average molecular weights of about 2000 (415, 430, 431). With a ruthenium catalyst, products having molecular weights as high as 23,000 have been obtained (422). The "synthetic crude" obtained from the Fischer-Tropsch process contains no fractions which possess lubricant properties since there is a lack of cyclic hydrocarbons (428). This

Table I

Typical Distribution of Primary Product (401)

Fraction	% by Weight
C_2-C_4 (excluding ethene)	30%
Ethylene	8%
Propylene	9%
Propane	3%
Butylene	8% } ¾ of iso-structure
Butane	3% }
Gasoline (to 200°C.)	48% (7% alcohol content)
Gas oil	14% (4% alcohol content)
Paraffin	1%
Alcohol (in water)	7% (mainly C_2)

makes further treatment of the product necessary in order to produce synthetic fuels.

As already mentioned, the product distribution varies greatly with the catalyst and the operating conditions. Tables II, III and IV illustrate the product distributions for single and multi-stage processes which are operated at atmospheric or elevated pressures. The increase in the amount of wax in Table III is due to the fact that the second stage is operated at pressures above atmospheric (up to 150 psi).

Table II

Product Distribution - Single Pass, Atmospheric Synthesis

Product	% by Wt. of Total	% Olefins by Volume
C_3-C_4 fraction	8	55
C_5-300°F. fraction	46	45
300°F.-390°F. fraction	14	25
390°F.-600°F. fraction	22	10
Wax from oil	7	m.p. 120°F. (approx.)
Ceresin from catalyst	3	m.p. 190°F. (approx.)

Table III

Primary Products from Prewar Two-stage Synthesis

Product	Boiling Range	Specific Gravity	% by Wt. of Total		% Olefins by Volume	
			1st Stage	2nd Stage	1st Stage	2nd Stage
C_3-C_4 fraction	----	--	5	2	50	25-30
C_5-300°F. fraction	85°-300°F.*	0.66	26.5	8	35-40	20
300°F.-575°F. fraction	200°+-575°F.*	0.74	26.5	11	12	12
Paraffin Wax	----	0.85	--	21	--	--

* The overlapping boiling ranges of the liquid fractions resulted from the method of recovery; the lighter fraction was adsorbed on activated charcoal after condensation of the heavier fraction.

Table IV

Product Distribution Three-stage, Medium Pressure Synthesis

Product	% by Wt. of Total	% Olefins by Volume
C_3-C_4 fraction	10	40 (13% of C_4's are iso)
C_5-340°F. fraction	25	24
340°F.-535°F. fraction	30	9
535°F.-640°F. fraction	20	Soft Wax
Hard Wax	15	m.p. about 195°F.

As illustrated in Table IV, operation at medium pressures results in much higher wax yields and in smaller quantities of hydrocarbons in the gasoline boiling range.

Much work has been done in trying to augment the olefin content of the reaction products. This has a dual purpose: a) to increase the octane rating of the gasoline, and b) to produce a product which can in subsequent treatment undergo polymerization, alkylation, etc. In general, it has been found that gas-recycle operations over either a cobalt (397) or a sintered iron catalyst result in increased yields of unsaturated hydrocarbons. Friedel and Anderson (404) made a study of the distribution of saturated products for the synthesis over a cobalt catalyst. They found that a curve of the yield (in grams/m^3 of synthesis gas) vs. the number of carbon atoms had a pronounced maximum for methane followed by a minimum at $C = 2$. An approximate analysis of the olefins showed the predominance of the internal double bond olefins over the α-form. This predominance increased with molecular weight. Montgomery and Weinberger (419) obtained a distribution curve for the normal paraffin hydrocarbons from the calculation of the thermodynamic equilibrium, using a modification of the Brinkley method. The curve obtained agrees very well with one obtained from experimental data. Weller and Friedel (429) determined the isomer distribution for the saturated hydrocarbons produced over a cobalt Fischer-Tropsch catalyst from probability considerations. This method has been found to describe the distribution satisfactorily.

The reaction products are recovered in three stages, viz., direct condensation, oil washing, treatment with activated charcoal (412). However, the oil washing process was not considered satisfactory in Germany since only partial recovery of the C_3-C_4 fraction was attained (410). The heavier products (all but the light gasoline and the C_3-C_4 fraction) are condensed by direct contact with water. The lighter fractions are then adsorbed by activated charcoal (427). Upon the recovery of the C_3 and higher products, the residual gas consists mainly of methane, unconverted synthesis gas, carbon dioxide, and nitrogen. It also may contain small amounts of ethane and ethylene. The methane which is produced (14 - 15% of product) is used to "upgrade" manufactured gas (411).

The C_3-C_4 fraction generally constitutes about 13% of the crude liquid product from the normal pressure synthesis and about 7% of the product from the medium-pressure operation (420). This fraction of the product is of particular interest because of the possibilities which it offers for the preparation of high-octane polymers or alkylate gasolines. Synthetic alcohols may also be prepared from this fraction.

The synthetic gasoline prepared by the Fischer-Tropsch process over a cobalt catalyst has a very low octane number (about 45) (409). This was used to blend with benzol to produce motor fuel with an octane number of 72 - 78. The Hydracol process, using a fluid iron catalyst is said to produce gasoline with an octane number of 85 - 90 (414). The raw gasoline fraction requires no desulfurization since the synthesis gas is made as sulfur-free as possible nor does it require treatment to improve its gum stability. According to Dannefelser (396) practically no gum formation takes place during prolonged storage of the synthetic gasoline and the mono-olefin content remains unchanged. Thus, the only treatment required (aside from octane number betterment) is a light alkaline wash to remove organic acids (426).

The diesel oil which is produced by the Fischer-Tropsch process is of an exceptionally high cetane number. Cetane numbers of 100 and more have been obtained in the conventional cobalt-catalyzed synthesis (412). A typical diesel oil fraction might boil from 390 - 680°F. and have a heat of combustion of 18,900 to 20,300 Btu per pound (424). Those procedures which are designed to increase the olefin content of the products will, of course, yield diesel fractions with a lower cetane number. However, even these have higher cetane values than diesel fuels from other sources. It has been reported that the straight synthetic fraction does not make the most satisfactory diesel fuel and that by blending the synthetic fraction with oils from other sources, a fuel of superior combustion characteristics is produced (394). The results of combustion studies on a series of fuels of narrow distillation range and having a cetane number in the range 40 - 90 (418) showed that these fuels produced more black smoke and exhibited a lower rate of pressure rise. It is believed that highly paraffin fuels may be more subject to pyrolysis in the combustion chamber. The low rate of presssure rise may be increased by blending with aromatic fuels (425). Thus, the blending of the high-cetane, synthetic oil with low-cetane fuels from other sources improves the combustion properties of the former and the cetane value of the latter. Kolbel (416) studied the blending of the synthetic fuel. He found that mixtures made up of 40 - 55% of the synthetic product had a cetane-number of 65 - 85 and compared favorably in other respects with the petroleum product. It is reported (414) that the diesel fuel which is to be produced in the Hydracol plant will have a cetane number of 45 - 50 and a pour-point below 0°F.

The residue, left after the removal of the diesel oil and the light fractions, is made up of waxes which vary in their melting points and molecular weights depending upon the catalyst and the operating conditions. A hard wax is also recovered from the catalyst by extraction (410). These waxes are a mixture of normal and iso-paraffins. Koch and Ibing (415) published a detailed study of the waxes which were produced over a cobalt catalyst. Pichler and Buffleb (422) studied the properties of waxes which were produced over a ruthenium catalyst. In the German plants, the waxes were separated into three groups by fractional distillation, pressing and sweat-in (410). These fractions were soft paraffin (m.p. 85 - 95°F.) slab wax (m.p. 124 - 128°F.) and hard wax (m.p. 195°F.). The soft waxes were used for conversion to fatty acids which were then used to produce soaps and edible fats (397, 408, 409). Some were used for the preparation of lubricating oils (416). The hard wax was used in ceresin, polishes, explosives, etc. (407). It is said to have excellent electrical properties (426).

No lubricants are prepared directly by the Fischer-Tropsch synthesis since the predominant product, straight-chain paraffins, have poor lubricating properties. However, lubricants have been produced from the Fischer-Tropsch products by some of the following types of reactions: a) polymerization of the olefins, b) alkylation of aromatics with long-chain olefins, c) chlorination of the synthetic waxes or heavy oil followed by condensation with aromatics, and d) the treatment of heavy fractions with a silent electrical discharge (398, 399, 406).

Although not primary products of the Fischer-Tropsch reaction, the small amounts of oxygenated compounds are of wide-spread interest. As already stated, the amount of oxygenated compounds which are formed depend upon the operating conditions and the catalyst. In the normal pressure process with a cobalt catalyst, they comprise only 1°/o of the total yield. This increases with increased pressure. The use of a fluid iron catalyst at increased pressure yields approximately 15°/o of the oxygenated compounds (407). An analysis of the aqueous by-product indicated the presence of the lower fatty acids, predominantly acetic acid. Fersanova (402) analyzed the water condensed from the Fischer-Tropsch synthesis over a fused Ni-Co-Al catalyst. His analyses showed the presence of small amounts of acids, aliphatic alcohols and aldehydes. Of the alcohols, methanol, ethanol, propanol, butanol and amyl alcohol were identified. Some oil-soluble fatty acids (C_5-C_{10}) have also been found in the normal pressure process (407). Eidus and his co-workers (400) investigated the liquid products for the hydrocondensation of carbon monoxide and ethylene. They found that 2 - 3°/o by volume, of oxygenated compounds are present in the oil condensate and up to 10°/o by volume, in the water condensate. Propyl alcohol and propionic aldehyde were identified as the main constituents. There were no ketones present.

Besides their direct use as primary products, the reaction products serve as sources for the production of many useful products. In fact, the statement has been made that the practical application of the Fischer-Tropsch process will depend largely upon the economic utilization of the various by-products. The German plants used the reaction products for the production of fatty acids which were in turn used in a number of ways. The C_1-C_4 fraction was used for the treatment of fodder silos, in the esterification of cellulose and the propionic acid (as the calcium salt) was used as a preservative in bread (393, 395). The C_5-C_8 fraction was hydrogenated to higher alcohols which were in turn used to prepare alkyl resins. The C_8-C_{11} fraction was used in flotation processes. The C_{10}-C_{18} fraction was used in the production of soaps and edible fats (413, 417) and the C_{18}-C_{24} acids were used in greases as lubricants for plastic molding and for artificial vaseline (392). Ohme (421) describes a method for the conversion of the fatty acids into ketones. Both liquid and wax-like substances are formed which may find use as plasticizers and in the perfume industry.

VIII - REACTION MECHANISM

The question of the mechanism of the catalytic conversion of CO and H_2 has been a topic of much controversy since Fischer and Tropsch (446) published their first paper on the subject. In 1926, the authors proposed that the reaction took place through the intermediate formation of carbides. They also postulated that the carbide was not the normal low-carbon compound which is stable at high temperatures, but that it was, instead, a compound which was rich in carbon and stable only at relatively low temperatures. They considered that these carbides, in turn, were hydrogenated to CH_2 groups which polymerized to form hydrocarbons. Because of the absence of oxygen-containing compounds, they rejected the presence of HCHO or CH_3OH as an intermediate in the reaction.

In order to test the validity of this proposal, Audibert and Raineau (432) treated an iron catalyst with CO to form the carbide. This carbide, in turn, was treated with H_2 to determine whether hydrocarbons were formed. No hydrocarbons were formed. Therefore, they proposed that the carbide was not an intermediate stage. Fischer and Koch (445) performing a similar experiment with a cobalt catalyst found that only CH_4 was produced.

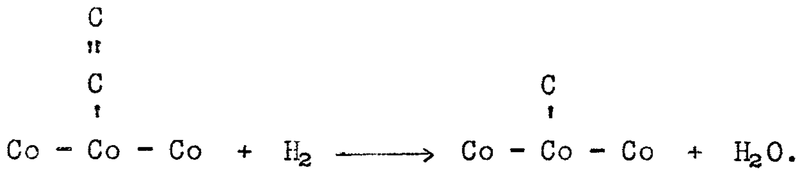
S. R. Craxford (437) made a study of the rate of formation and reduction of carbides using a standard Fischer catalyst (Co-ThO_2-kieselguhr 100:18:100). The reaction for the carbide formation is:

$$2Co + 2CO \longrightarrow Co_2C + CO_2$$

and that for the reduction is:

$$Co_2C + H_2 \longrightarrow CH_2 + 2Co.$$

He found that the rate of reduction was much greater than the rate of carbide formation. Therefore, he postulated the formation of the carbide by means of the following reaction:



$$\mathrm{Co - \overset{\substack{C\\ \| \\ C\\ |}}{Co} - Co + H_2 \longrightarrow Co - \overset{\substack{C\\ |}}{Co} - Co + H_2O.}$$

The fact that water is formed in the reaction indicates that this reaction is possible.

Craxford and Rideal (438) pointed out that the presence of carbide in the used catalyst is an indication that the carbide formation must be more rapid than the reduction. They also found that the carbide formation took place stepwise. The first step, which was the more rapid, is the formation of surface carbide. This reaction has an apparent activation energy of 10,000 cal per mol. The second step, which proceeds more slowly and which has an apparent activation energy of 18,000 cal. per mol., is the formation of bulk carbide.

S. Weller (464), in a study of the rate of carbide formation, came to the conclusion that the initial rate of carbiding is comparable to the synthesis rate, but that the steady rate of bulk carbiding is approximately one-tenth of the synthesis rate. This value is in agreement with the value found by Eidus and Zelinskii (444) as the over-all rate of carbiding. These authors came to the conclusion that the carbide could not be an intermediate product in the hydrocarbon synthesis. Weller points out that Eidus and Zelinskii obtained their first data for five hours of carbiding, failing thereby, to obtain the initial rate of carbide formation.

A study of equilibrium data by Kummer, Browning and Emmett (454) showed that the direct reaction of hydrogen with Fe_2C cannot account for the synthesis of mono-olefins or of paraffin hydrocarbons with more than six carbon atoms. The authors calculated the equilibrium constants for the reactions:

$$nFe_2C + nH_2 \longrightarrow C_nH_{2n} + 2nFe$$

and

$$nFe_2C + (n + 1)\,H_2 \longrightarrow C_nH_{2n+2} + 2nFe$$

from data on the free energy of formation.

Schuman (460), however, carried out the same calculations using the general equations:

$$Fe_2C + (2n - 1)H_2 + (n - 1)CO = C_nH_{2n} + 2Fe + (n - 1)H_2O$$

and

$$Fe_2C + 2nH_2 + (n - 1)CO = C_nH_{2n+2} + 2Fe + (n - 1)H_2O$$

for $n = 2$ and $n = 8$. The results indicate that the formation of hydrocarbons is thermodynamically possible under the conditions of the Fischer-Tropsch Synthesis.

Kummer, Dewitt and Emmett (455) studied the mechanism of the Fischer-Tropsch synthesis, using C^{14} as a tracer. By this method, they found that surfaces or bulk carbide plays a very insignificant role in the formation of hydrocarbons. By carbide, they referred specifically to such carbide as was formed by pre-treatment of the metal catalyst and not any momentary formation of carbide at the catalyst surface. Matsumura, Tamara and Kodama (456) proposed the following mechanism:

$$CO + 3Me \longrightarrow Me_2C + MeO$$

$$Me_2C + 2H \longrightarrow CH_2 + 2Me$$

in which the CO molecule is ruptured at the catalyst surface forming metallic carbide and the oxide of the catalyst metal. Bahr and Bahr also postulated that CO cleavage was the basic reaction in the catalytic formation of methane. Hamai (447) refutes this theory, pointing out that from an energy standpoint, this mechanism would be most unlikely, since the heat of dissociation of C-O is 235.5 Kcal/mole whereas for Co_2C, the heat of formation is 9.33 Kcal/mole and for Co-O, it is 57.5 Kcal/mole.

Much work has been done on the various metal carbides. Hofer (451), in studying the preparation and properties of metal carbides, found that in all cases, the carbiding takes place in two steps as described above (438). The second, slow reaction, is identified with carbide formation in the lattice. He also found that the carbides of the Fischer-Tropsch catalysts are more unstable than the true refractory carbides and that for all known Fischer-Tropsch catalysts, the ratio of the radius of the carbon atom to the radius of the metal atom is equal to or greater than 0.58.

Tibboth (462) working with nickel catalysts found that unpromoted and unsupported nickel catalysts showed little activity in the decomposition of CO. However, in a supported and promoted catalyst, the nickel was converted almost quantitatively to Ni_3C. Above 250°C., decomposition of the carbide took place according to the reaction:

$$Ni_3C \longrightarrow C + 3Ni.$$

It is possible that the decomposition took place in two stages with the intermediate formation of Ni_6C.

Braude and Bruns (436) found that upon the action of CO and H_2 on an iron catalyst, the following reaction takes place:

$$nFe + CO + H_2 \longrightarrow Fe_nC + H_2O.$$

They found that this reaction occurred at a higher rate than the formation of the carbide by the reaction:

$$nFe + 2CO \longrightarrow Fe_nC + CO_2.$$

They give the energy of activation of the first reaction as 15,500 cal/mol. and for the second reaction, 6900 cal/mol.

To explain the fact that with a cobalt or nickel catalyst, water is formed whereas with an iron catalyst, carbon dioxide is the reaction product, Bashkirov, Krinkov and Kogan (434) proposed that in both cases, the reaction is:

$$CO + 2H_2 \longrightarrow CH_2 + H_2O.$$

However, on an iron catalyst, the following reaction also takes place:

$$CO + H_2O \longrightarrow CO_2 + H_2.$$

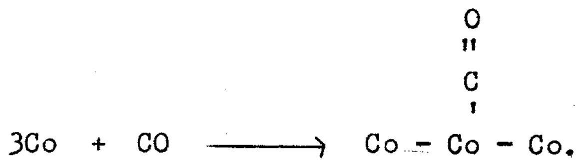
Therefore, on an iron catalyst, the over-all reaction may be summarized as follows:

$$2CO + H_2 = CH_2 + CO_2.$$

The second reaction is many times faster than the first, at times by a factor of 13. Thus, there is no water found in the product.

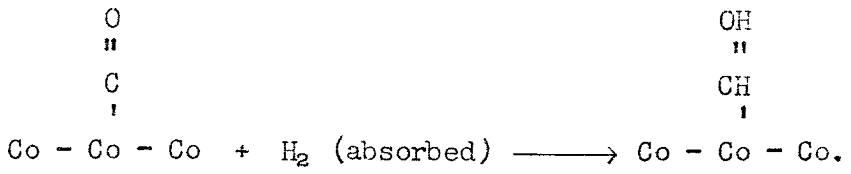
In 1927, Elvins (439) suggested the possibility that metallic carbonyls acted as an intermediate in the Fischer-Tropsch reaction. No direct experimental evidence was presented to support this theory. However, the author pointed out that in using a Co-Cu-MnO catalyst, a mirror of copper was formed on the glass contact tube.

Hamai (447) proposed the following theory for the mechanism of the Fischer-Tropsch reaction on a cobalt catalyst. He suggested that the first step was the adsorption of the CO according to the following scheme:



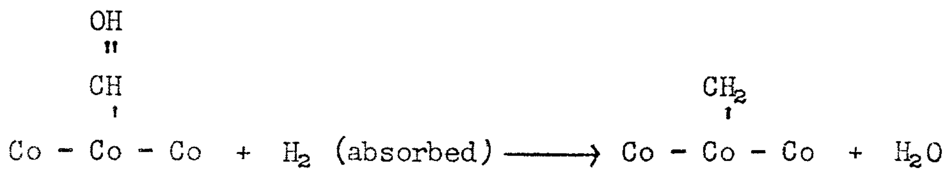
$$3Co + CO \longrightarrow Co - \underset{}{\overset{\overset{\displaystyle O}{\|}\atop\displaystyle C}{\overset{|}{Co}}} - Co.$$

These then, serve as active centers for the following reaction:

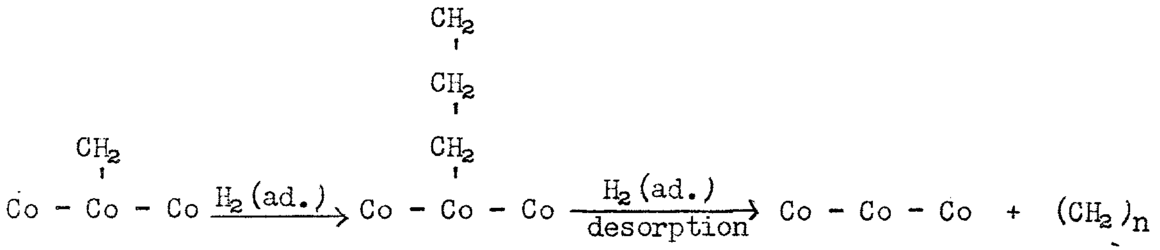


$$\begin{matrix}\text{O}\\ \| \\ \text{C}\\ | \\ \text{Co}-\text{Co}-\text{Co}\end{matrix} \;+\; H_2\text{ (absorbed)} \longrightarrow \begin{matrix}\text{OH}\\ \| \\ \text{CH}\\ | \\ \text{Co}-\text{Co}-\text{Co.}\end{matrix}$$

The apparent activation energy for this step is 1000 cal/mol. The following steps then take place in consecutive order:



$$\begin{matrix}\text{OH}\\ \| \\ \text{CH}\\ | \\ \text{Co}-\text{Co}-\text{Co}\end{matrix} \;+\; H_2\text{ (absorbed)} \longrightarrow \begin{matrix}CH_2\\ | \\ \text{Co}-\text{Co}-\text{Co}\end{matrix} \;+\; H_2O$$



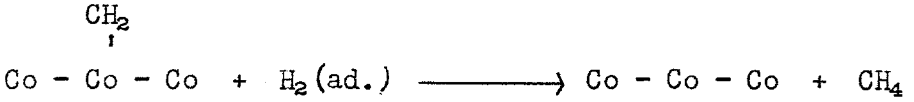
$$\begin{matrix}CH_2\\ | \\ \text{Co}-\text{Co}-\text{Co}\end{matrix} \xrightarrow{H_2\text{(ad.)}} \begin{matrix}CH_2\\ | \\ CH_2\\ | \\ CH_2\\ | \\ \text{Co}-\text{Co}-\text{Co}\end{matrix} \xrightarrow[\text{desorption}]{H_2\text{(ad.)}} \text{Co}-\text{Co}-\text{Co} \;+\; (CH_2)_n$$

$$(CH_2)_n \xrightarrow{H_2} \text{higher hydrocarbons.}$$

He explains the formation of methane in the first stages as probably due to the reaction

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

and not by



$$\begin{matrix}CH_2\\ | \\ \text{Co}-\text{Co}-\text{Co}\end{matrix} \;+\; H_2\text{(ad.)} \longrightarrow \text{Co}-\text{Co}-\text{Co} \;+\; CH_4$$

since there is only a small concentration of the active centers at the beginning of the synthesis. There is an apparent contradiction to the evidence cited by Perrin (457) showing that sufficient dilution of the incoming gases will prevent the preliminary formation of methane. He stipulates that the formation of methane is due to overheating of the catalyst bed and proposes that dilution (or any other method of preventing this temperature rise) will suffice to get the hydrocarbon synthesis started without the formation of excess methane. For the polymerization of the CH_2-groups, they must be able to migrate freely on the catalyst surface. Hamai (448) cites evidence supporting this fact. In subsequent studies, Hamai, Hayashi, Shimamura and Igarashi (449) made experimental studies to verify the theory which was postulated.

P. Robinet (459) proposed that the reaction mechanism of the Fischer-Tropsch process be called hydropolymerization, signifying that the reaction is one comprising both hydrogenation and polymerization. He postulated three types of hydrogenation:

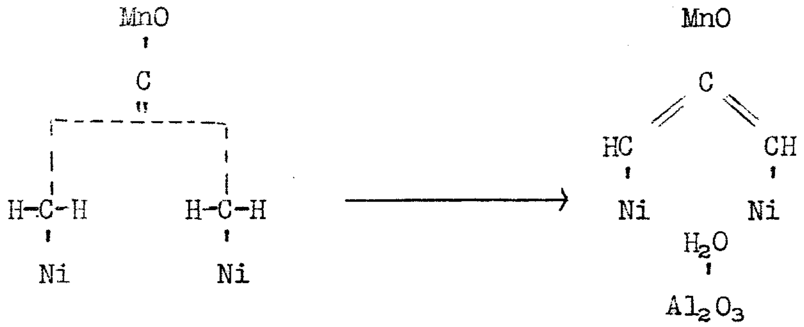
(a) additive $CO + H_2 \longrightarrow HCHO \xrightarrow{H_2} CH_3OH$

(b) dehydrating $CO + 3H_2 \longrightarrow CH_4 + H_2O$

(c) decarboxylating $2CO + 2H_2 \longrightarrow CH_4 + CO_2$.

A cobalt catalyst favors reaction (b), and its action may be improved by the addition of hydrogenation activators and dehydrating components. An iron catalyst favors reaction (c). Nickel catalysts can react according to both (b) and (c) and its properties may be modified by the addition of suitable promoting agents.

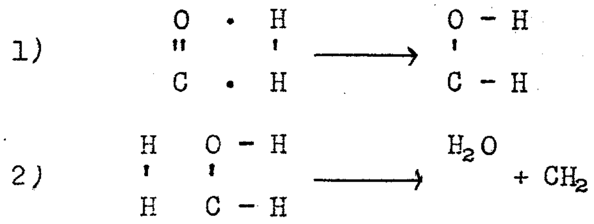
In order to explain the necessity of a mixed catalyst, Pobakin and Karzhavin (452) arrived at the following scheme for the synthesis of the hydrocarbon chain on the interphase boundary of a mixed catalyst:



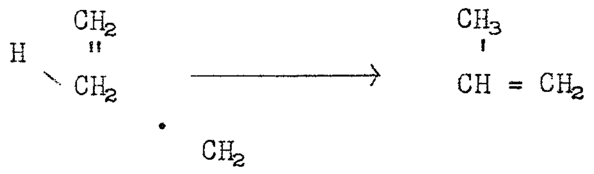
This scheme is entirely possible from the energy standpoint and it explains the roles of the separate components.

Pospekhov (458) proposed that the primary process was the hydration of CO and also its condensation with the formation of the lower oxides. This article was not available for a detailed study.

Other investigators have proposed oxygen-containing compounds as intermediate formations (440, 441). However, no direct proof was available and this proposal was based mainly upon the fact that oxygenated compounds were present in the final product. Smith, Hawk and Golden (461) found that by adding ethylene to the reaction mixture, the amount of oxygenated compounds increased. They proposed that the primary reaction was one involving CO and ethylene. Eidus and Pusitzkii (442) carried out an investigation with a Co-Cu-MnO catalyst, adding ethylene to the synthesis gas. They found that liquid hydrocarbons were obtained with a mixture of C_2H_4, CO and H_2 under conditions which gave no liquid products with a mixture of C_2H_4 with CO or H_2 alone. Although the yield of oxygenated products was high, the main part of the reaction products were found to be hydrocarbons. The authors propose the following scheme for the hydrocarbon formation:



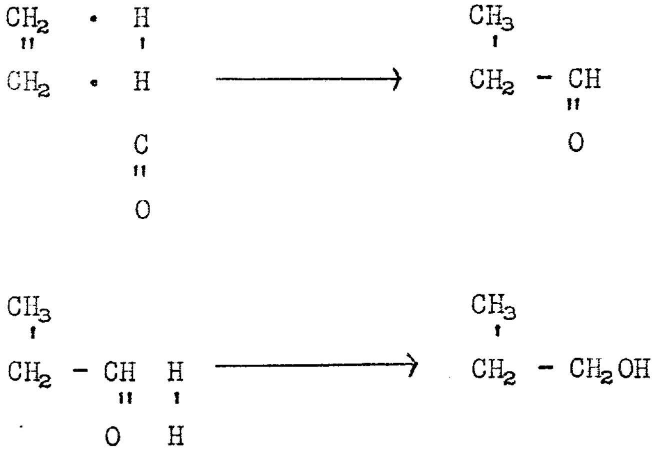
3)



$$H \cdot \overset{CH_2}{\underset{CH_2}{\|}} \cdot CH_2 \longrightarrow \overset{CH_3}{\underset{}{|}}\; CH = CH_2$$

They suggested that the hydropolymerization to form oxygen compounds might proceed according to either of the following schemes:

1)
2)

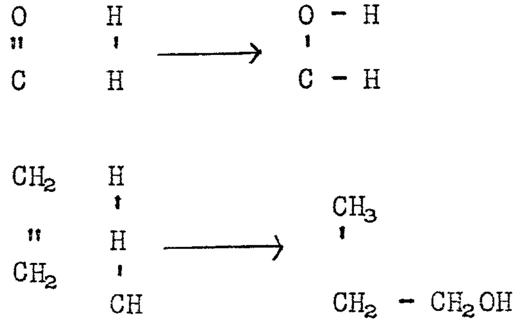


$$1)\quad \begin{matrix} CH_2 & \cdot & H \\ \| & & | \\ CH_2 & \cdot & H \\ & & C \\ & & \| \\ & & O \end{matrix} \longrightarrow \begin{matrix} CH_3 & & \\ | & & \\ CH_2 & - & CH \\ & & \| \\ & & O \end{matrix}$$

$$2)\quad \begin{matrix} CH_3 & & & \\ | & & & \\ CH_2 & - & CH & H \\ & & \| & | \\ & & O & H \end{matrix} \longrightarrow \begin{matrix} CH_3 & & \\ | & & \\ CH_2 & - & CH_2OH \end{matrix}$$

or

1)
2)



$$1)\quad \begin{matrix} O & & H \\ \| & & | \\ C & & H \end{matrix} \longrightarrow \begin{matrix} O & - & H \\ | & & \\ C & - & H \end{matrix}$$

$$2)\quad \begin{matrix} CH_2 & H \\ & | \\ \| & H \\ CH_2 & | \\ & CH \end{matrix} \longrightarrow \begin{matrix} CH_3 & & \\ | & & \\ CH_2 & - & CH_2OH \end{matrix}$$

These processes are in agreement with Balandin's "multiplet theory".

In order to show the presence of free methylene radicals, Eidus and Zelinskii (443) added benzene, which is not usually found among the reaction products of the Fischer-Tropsch Synthesis, to the inlet gas. They attribute the presence of small amounts of xylene and toluene in the reaction products to the action of free methylene radicals upon the benzene.

Warner, Derrig and Montgomery (463) found that ketene in the presence of H_2 on a Co-ThO_2-kieselguhr catalyst produced hydrocarbons and oxygenated compounds which are similar to those obtained by the Fischer-Tropsch reaction. They suggested that the first reaction might be the decomposition of the ketene according to the reaction:

$$CH_2CO \longrightarrow CO + CH_2$$

with a subsequent reaction of the methylene radical with a molecule of ketene according to the equation

$$CH_2 + CH_2CO \longrightarrow CH_3 - CH = C = O.$$

Therefore, they propose that in the Fischer-Tropsch reaction, the preliminary step might be the formation of ketene as an intermediate product.

Herington and Woodward proposed that the reaction took place on two different types of centers. The type A, which they considered to be a carbide was responsible for the formation of the methylene radicals. Type B, probably pure metal, was said to be responsible for the liberation of the observed products through the agency of hydrogen.

Craxford and Rideal (438) proposed that the methylene groups polymerized first to form giant molecules which were in turn cracked and hydrogenated. This is in apparent contradiction to the work of Karzhavin who found that the cracking of large, paraffin hydrocarbons does not take place on the surface of the catalyst under the conditions of the Fischer-Tropsch synthesis (452).

Weller (464) suggested that the methylene radicals might react in three ways: (a) remain on the surface and increase in length, (b) be desorbed as an olefin, (c) react with hydrogen and be desorbed as a saturated hydrocarbon. He added that the possibility of (a) occurring was enhanced by any factor which increased the surface concentration of reactants or which decreased the rate of desorption of the products.

Kling (453) contends that the CH_2 groups polymerize according to the laws of probability, thus accounting for the variance in the reaction products.

Craxford (437), by a study of the ortho-para conversion of hydrogen, showed that the formation of methane takes place in the presence of atomic hydrogen, whereas the formation of oils requires molecular hydrogen.

In a mathematical analysis of the Fischer-Tropsch Process, Herington (450) found that the probability of termination as a paraffin, compared with the probability of propagation, increased slightly with chain length.

IX - KINETICS

The kinetics of the Fischer-Tropsch process have not been investigated in any great detail. Although many general papers have been published on the kinetics of heterogeneous reactions (466, 468, 471, 473, 474) there are relatively few which deal specifically with the Fischer-Tropsch process.

One of the more extensive studies of the kinetics of this process was recently published by Anderson, Krieg and Friedel (465). These authors have presented differential reaction data for the Fischer-Tropsch process with cobalt catalysts at atmospheric pressure. These authors found that the reaction rate was highest at the beginning of the catalyst bed and lower (and nearly constant) throughout a large portion of the catalyst bed. These authors expressed the belief that the rate of the Fischer-Tropsch synthesis could not be expressed by a simple rate equation due to the complexity of the reaction and the variance in the nature of the catalyst surface. Erofeev and his coworkers (467), as well as Anderson, found that the Fischer-Tropsch reaction was of a zero order. Erofeev has developed an empirical equation which fits the data very well. Gol'denskii (469) and Grekhnev and Eroshevskii (470) studied the relationship between the amount of catalyst used and the rate of the heterogeneous reaction. As the amount of catalyst is increased, it has the same effect as decreasing the space velocity in liters of synthesis gas per liter of catalyst per hour. Both of these investigations found that as the amount of catalyst is increased, the rate of the reaction attains a maximum and then decreases.

In connection with the Fischer-Tropsch synthesis, the investigators in Russia have studied the polymerization of olefins. Pshezhetzkii and Gladyshev (472) studied the rate of dimerization of ethylene. They found that the polymerization rate was a linear function of the amount of ethylene which is adsorbed on the catalyst surface.

It is, thus, apparent that there is a lack of basic research on the question of the Fischer-Tropsch reaction. It can be said that it has a zero order of reaction and an activation energy of about 25 Kcal. per mole. There has been only a cursory study made of the kinetics of the reaction.