I - HISTORICAL DEVELOPMENT

The first work in the field of synthetic fuels was done by F. Bergius in 1910 (22). He found that by heating coal with H_2 under pressure, an oil yield of 85% could be obtained. Sabatier (14) in 1902 was the first to find that a hydrocarbon, methane, could be produced catalytically from a mixture of carbon monoxide and hydrogen. In 1913, at the Badische Anilin und Soda-Fabrik, it was revealed that a mixture of higher hydrocarbons and oxygenated compounds could be produced catalytically from mixtures of carbon monoxide and hydrogen under high pressure (23).

Early in the 1920's, Franz Fischer became the first director of the new Kaiser Wilhelm Institute fur Kohleforschung in Muelheim/Ruhr (11). It was here that Hans Tropsch became his assistant. In 1923, Fischer and Tropsch (5) observed that an increase in the yield of hydrocarbons was obtained with a decrease in the pressure of the reaction. However, it was apparent that more active catalysts were required. Fischer and Tropsch (11), in 1925, found that it was possible to obtain ethane, ethylene and higher saturated and unsaturated hydrocarbons in the presence of the iron group metals at relatively low pressures and moderately elevated temperatures. They also found that the addition of certain oxides (e.g. zinc oxide) improved the catalysts. They found that even at atmospheric pressure, fair yields were obtained and that only a small amount of oxygenated compounds were present. The product was called Kogasin (6). Fischer and Tropsch (23) filed for a patent on the hydrocarbon synthesis July 21, 1925. At this time, their process was considered of little practical value as compared to the so-called liquefaction of coal by the Bergius method. In the period that followed, the most intensive work was done in finding better catalysts. The emphasis was on mixed catalysts whose active component was iron, cobalt or nickel. Elvins and Nash (3), in 1926-28, reported work with a mixed catalyst of $Co-MnO_2-Cu$. Smith, Davis and Reynolds of the United States Bureau of Mines reported work with the same catalyst. Catalysts which were immune to sulfur poisoning were developed by the I. G. Farbenindustrie A. G. In Japan, in 1932, Kodama and others (8, 9, 10, 13) published data on the relative efficiency of certain promoters, e.g., Cu, ThO_2, WO_3, MoO_3, and MgO for cobalt catalysts.

In the period from 1933 to 1939, there was an intensive development of more active catalysts. Finally, a mixed catalyst, $Co-ThO_2-MgO-kieselguhr$ (100:5:8:200, parts by weight), was selected as the best catalyst for industrial purposes (25).

The first full-scale plant for coal hydrogenation was built at Leuna, Germany, by the I. G. Farbenindustrie A. G. in 1927. Its annual capacity was 100,000 tons of petrol from brown coal (22). In 1933, Ruhrchemie A. G. erected a pilot plant at Oberhausen-Halten (4). It employed a $Ni-MnO-Al_2O_3-kieselguhr$ catalyst and had a capacity of 1000 tons a year. Its working temperature was 190 - 210°C. at atmospheric pressure. The main difficulties encountered were (16, 17): a) short catalyst life, b) expensive design of the converters, c) the loss of the catalyst metals in regeneration, and d) the conversion of kogasin to marketable products.

In the face of an imminent war, impetus was added to the development of synthetic fuels in Germany. The Fischer-Tropsch Process was put into commercial operation in 1936 (15).

From 1938-44, all of the German plants were operating according to the Ruhrchemie process. The catalyst used was $Co-ThO_2-MgO-kieselguhr$, and the plant was operated at a temperature of 180° - 200°C. and a pressure of 1 or 10 atmospheres. The operation was carried out in two or three stages with product recovery after each stage. The average yield was 150 gm. product per cu. m. of synthesis gas ($2H_2 + 1CO$). The products ranged from propane-propylene to waxes of high molecular weights. The space velocity was, in general, 60-100 volumes of feed gas per volume of catalyst (18). By 1940, the commercial operation in Germany showed a ten-fold increase, producing 1,000,000 tons of liquid fuel annually (1).

In England, the Imperial Chemical Industries built a pilot plant at Billingham, England in 1929. In 1935, a full-scale plant was constructed at Billingham with a total output of 150,000 tons per annum (22). By 1940, plants had been erected in France, Japan and Manchukuo (15).

Much investigation was devoted to the problem of obtaining marketable products in high yields. In 1928-29, Fischer, Tropsch and Koch (7), published the results of the analysis of the product from an iron-copper catalyst at 1 atmosphere and 250°C. Fraction I (b.p. 60 - 185°) was 70% olefinic and 30% saturated. It contained octane, nonane, isononane, and no diolefins or naphthenes. An analysis by Smith, Hawk and Reynolds (21) of the product from a Co-Cu-MnO catalyst showed that the product was similar to the one above. In 1930, Smith, Hawk and Golden (20) found that ethylene, when added to the synthesis gas, enters into the reaction on a Co-Cu-MnO catalyst, but not on an Fe-Cu catalyst. Later, 1939, Craxford verified these findings.

II - PREPARATION OF THE SYNTHESIS GAS

The synthesis gas for the Fischer-Tropsch process consists of a mixture of CO and H_2 and possibly a small amount of inert gases such as CO_2 or N_2. The ratio of hydrogen to carbon monoxide can vary from 2:1 to less than 1:1. For use with cobalt or nickel catalysts, a ratio of 2:1 is the most satisfactory, but with an iron catalyst, a ratio of 1:1 was sufficient, (45). The Fischer-Tropsch reaction will operate satisfactorily with a gas mixture containing from 10 - 12% of inert gases (57).

Theoretically, any carbonaceous material which can be decomposed to give CO and H_2 can be used as raw material. However, only coal and natural gas have been of commercial interest. In Europe, coal is used and, although at the present time natural gas is considered more economical than coal in the United States, coal must also be considered as the most likely raw material of the future.

The synthesis gas mixture is readily produced in the intermittent type water-gas generator, according to the equation

$$C + H_2O_{(steam)} \longrightarrow CO + H_2$$
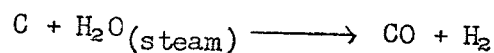
Theoretically, this reaction will produce a synthesis mixture with an $H_2:CO$ ratio of 1:1. In order to increase this ratio for use on a cobalt catalyst, the water-gas shift reaction is used

$$CO + H_2O \longrightarrow CO_2 + H_2 \,.$$
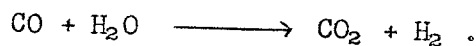
Usually, the CO_2 is not removed since it has no harmful effect and acts only as a diluent. The catalyst which is used for this reaction is ferric oxide promoted by the oxides of chromium, calcium and magnesium (27, 28). The hydrogen-rich mixture is then added to the water-gas in order to obtain the desired H_2:CO ratio.

At Wanne-Eickel, the Krupp-Lurgi process for the manufacture of low-temperature coke was used to produce a coke which, when used in the usual water-gas generator, gave blue water-gas with an H_2:CO ratio of 1.35:1. Another source of hydrogen-rich gas mixture was obtained by the cracking of coke-oven gas.

The use of the intermittent water-gas generator is limited because lower grade coals can not be used in it. However, methods which use oxygen in the steam blast can be used with all fuels. At the present time, the cost of producing sufficiently pure oxygen is the chief obstacle. There are four principle processes for the gasification of fuels using oxygen. The first is a process in which fine fuel is gasified in a fixed fluidized bed. The Winkler process (29, 45, 53) is an example of this type. The Winkler process was developed in Germany in 1921. The reaction in this process depends upon the interaction of a fixed fluidized bed of fine fuel with oxygen and steam. The fluidized bed acts as a liquid. The fuel which is used is brown coal which has been dried and ground. The gas which is produced has an H_2:CO ratio which ranges from 0.91 to 1.65. The oxygen which is used must have a purity of 98%.

The second type of process is one in which fine fuel is gasified in suspension in a single stage. The Koppers Process is of this type (29, 45). The fuels which are used are lignite, lean coal and lignite coke. The only requirement for the fuel is that it be readily ground. The action depends upon the reduction of steam by the fuel in the presence of oxygen. The amount of oxygen depends upon the H_2:CO ratio desired. The gas which is produced in the Kopper's process has an H_2:CO ratio of 1.28 – 1.43 from brown coal and 0.63 – 1.0 from bituminous coal. The Fuel Research Board Vortex chamber is also of this type.

The third type of process is gasification with recirculation. The Schmalfeldt-Wintershall Process (45, 53) is designed to gasify ground brown coal by means of recirculating gases. The oxygen is added to give additional heat. The chief disadvantage of this process is that the gas which is produced contains only 76% H_2 + CO. The Metallgesellschaft Dust-Gasification process is also of this type, but has not been used industrially.

The fourth type of process is one in which fuel is gasified in a fixed bed. The Lurgi-Pressure Gasification Process operates upon this principle (45). The fuel which is most commonly used is brown coal, although lignite and sub-bituminous coals may also be used. The purity requirement for the oxygen is 95%, and it is supplied under a pressure of 23 atmospheres. The gas which is produced is almost free from methane; however, as the temperature decreases, the amount of methane increases. It also increases with increasing pressure. The temperature depends upon the melting point of the ash and is controlled by the relative amounts of oxygen and steam admitted. The synthesis gas which is produced by the Lurgi-Pressure Gasification Method has an H_2:CO ratio of 2.66 – 3.12.

In the Standard Grate Operation (45) and Slagging-type Operation, lump

fuel is gasified in a stationery bed. In the former, the lump fuel is gasified by a mixture of air and steam. The use of oxygen can lead to clinker troubles. The gas which is produced has a $H_2:CO$ ratio of 1 - 1.75. In the Slagging-type Operation, a flux is added to the ash to keep it in a molten state. The $H_2:CO$ ratio of the gas which is produced is 0.33 - 0.38.

In the gasification of fine fuels, one of the main problems is that of dust carry-over. Wright and Barclay (59) tested the oxygen gasification of solid fuels in fixed-bed producer gas equipment. The problem of dust carry-over was not serious. The dust was readily removed in the regular scrubber. The construction and operation of equipment is simple and cost is relatively low.

The synthesis gas mixture may also be produced by the direct underground gasification of coal. This method has been studied extensively in Russia. Four methods have been used for the underground gasification of coal. They are: a) the chamber method, which is now obsolete due to the large amount of underground labor which is required, b) the percolator method, c) the crevice method, and d) the stream method. These differ principally in the methods for introducing air to the seam of coal and of removing the gas which is produced. These methods depend largely on the structure of the coal seam.
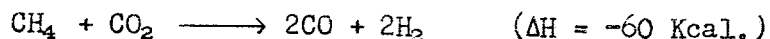
Recently, the University of Missouri School of Mines reported work on the electrocarbonization of coal. The coal was heated by inserting two electrodes into the coal seam. When the coal has become porous, air is admitted to the coal seam and the resulting gas may be used for the synthesis of liquid hydrocarbons (26).

Much work has been done in this country on the production of the synthesis gas mixture from light hydrocarbons, usually methane. As a starting material, natural gas, methane from coal seams, refinery gases or other gases which are rich in methane may be used. These gases may be converted to the synthesis gas by the three following methods (30, 35, 56):
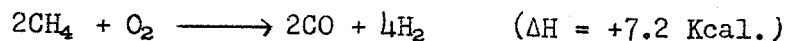
1. Reaction with steam according to the equation

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (\Delta H = -50.7 \text{ Kcal.})$$
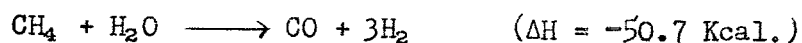
2. Reaction with CO_2 according to the equation

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \qquad (\Delta H = -60 \text{ Kcal.})$$

3. Controlled oxidation with air or oxygen according to the equation

$$2CH_4 + O_2 \longrightarrow 2CO + 4H_2 \qquad (\Delta H = +7.2 \text{ Kcal.})$$

The methane-steam reaction has been discussed in a number of articles (30, 31, 32, 34, 36, 37, 38, 41, 42, 43, 47, 48, 50, 60). The synthesis gas produced by this reaction is low in carbon monoxide, but it can be enriched by mixing with the product of the methane-carbon dioxide reaction. Both of these reactions may be carried out simultaneously over a nickel catalyst at a temperature of 1350°F. (56), according to the equation

$$3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2 \qquad \text{.}$$
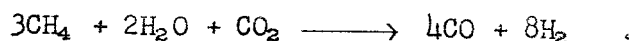
A study of the equilibrium relations for the methane-steam reaction shows that above 1500°F. and in the absence of excess steam, this reaction is confined to the production of H_2 and CO. However, with an excess of steam and at temperatures about 1200°F., the reaction tends to take place according to the equation (30, 51, 54):

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2 \quad .$$
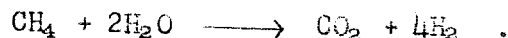
In the absence of catalysts, the methane steam reaction is slow becoming appreciable only at temperatures above 2370°F. (41).

Catalysts which have been suggested for this reaction include: $Ni-Al_2O_3-MgO$ on active carbon at 1200°F. (33), $Ni-ThO_2$, MgO, and nickel-iron at 1470°F. (40), $Ni-MgO$ (58) at 1500-1700°F. and $Ni-Al_2O_3$ on clay (47). Semi-industrial scale data on an intermittent, nickel-catalyzed process, showed that at temperatures of 860-900°C., the average composition of the gas produced from natural gas containing 87.5% methane was: CO_2 - 9%, CO - 22%, H_2 - 64%, CH_4 - 0.8% and N_2 - 4.2% (39).
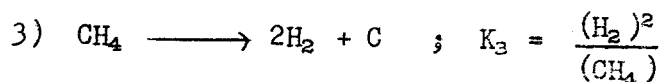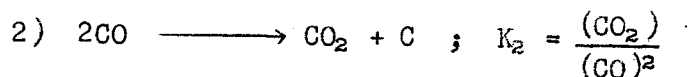
The methane-carbon dioxide reaction has not been studied extensively because it requires a reactant which is less available and because it is more endothermic than the methane-steam reaction. However, it produces a gas which is unusually high in carbon monoxide. Natta and Pontelli (44) have studied the production of synthesis gas from the ternary system, $CH_4-CO_2-O_2$ and $CH_4-H_2O-O_2$ and the quaternary system $CH_4-H_2O-CO_2-O_2$. Other references for this reaction are: (30, 35, 36, 46, 49, 60).

Since the last reaction (controlled oxidation) is endothermic, it would seem to be more economical than the other processes if inexpensive oxygen can be produced. Fischer and Pichler using two parts methane to one of oxygen at a temperature of 2550°F. and with a contact time of 0.01 sec. obtained a gas with the following composition: H_2 - 54%, CO - 26%, C_2H_2 - 9.4%, CH_4 - 4.8% and CO_2 - 3.0%.
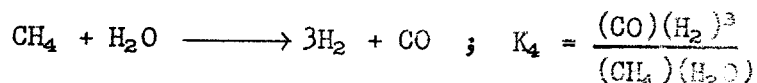
Reitmeier, Atwood, Bennett and Bough (52) made a study of the equilibria involved in the production of hydrogen and carbon monoxide from methane. Their purpose was to establish optimum conditions for producing synthesis gas mixtures having a $H_2:CO$ ratio which can be varied between 0.5 - 3.0. They calculated the equilibrium constants for the six reactions which follow:

1) $CO + H_2O \longrightarrow H_2 + CO_2$

$$K_1 = \frac{(CO_2)(H_2)}{(CO)(H_2O)}$$

2) $2CO \longrightarrow CO_2 + C$; $K_2 = \dfrac{(CO_2)}{(CO)^2}$

3) $CH_4 \longrightarrow 2H_2 + C$; $K_3 = \dfrac{(H_2)^2}{(CH_4)}$

4) (combination of equations 1, 2 and 3)

$CH_4 + H_2O \longrightarrow 3H_2 + CO$; $K_4 = \dfrac{(CO)(H_2)^3}{(CH_4)(H_2O)}$

5) (another combination of equations 1, 2 and 3)

$$CH_4 + 2H_2O \longrightarrow 4H_2 + CO_2 \quad ; \quad K_5 = \frac{(CO_2)(H_2)^4}{(H_2O)^2(CH_4)}$$

6) (a combination of 2 and 3)

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \quad ; \quad K_6 = \frac{(CO)^2(H_2)^2}{(CH_4)(CO_2)}$$
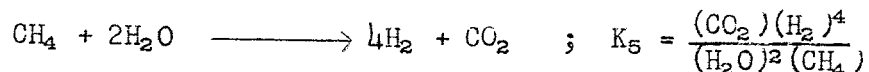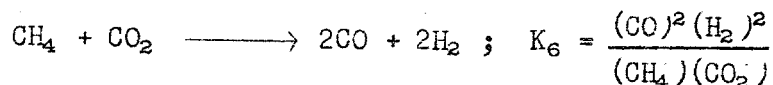
From the values of the equilibrium constants the authors have drawn curves which show below what composition carbon will deposit.

Another source of synthesis gas can be methanol. Eversole (61) has described a catalyst for the conversion of methanol. The catalyst is a mixture of copper and nickel oxides supported on Filtros. Seelig and Marschner (55) investigated this catalyst and found that its life averaged 200 hours. Upon regeneration by heating the catalyst in air, the activity of the catalyst is increased above its original value. These authors describe a service unit which produces a gas mixture with an H_2:CO ratio of 2.17. The authors express the opinion that this process would be advantageous for producing moderate quantities of synthesis gas of reasonably high purity.

III - PURIFICATION OF THE SYNTHESIS GAS

The two components of the synthesis gas required for the Fischer-Tropsch synthesis are carbon monoxide and hydrogen. Any other constituent of the gas may be considered an impurity. These impurities may be classified as inert or injurious. The inert constituents may include CO_2, CH_4 and N_2. These will not damage the catalyst but will only dilute the reaction. The presence of CO_2 is particularly noticeable with an iron catalyst, for in this reaction, it may be formed to the extent of 20% of the volume (83).

Among the impurities which are classified as injurious are tar, dust, gum formers, iron carbonyl, sulfur compounds, hydrogen cyanide, ammonia and naphthalene. A. E. Sands, H. W. Wainwright and L. D. Schmidt (83) have estimated the maximum amount of these impurities which are allowable.

Whether the inert impurities should be removed is usually determined by the relative cost of removal as compared to the cost due to a reduced reaction rate. Tsunaka and Fujimura (88) have found that the presence of N_2 or CO_2 in amounts less than 20% by volume show no marked effect on the synthesis rate. All liquid purification processes have proved effective in removing CO_2, HCN, NH_3 and much of the H_2S. In order to remove the dust and tar, several methods or combinations of methods may be used; e.g., water scrubbing, impingement on baffles, filtration and electrical precipitation (83).

Of greatest importance are the processes for removing organic sulfur compounds and hydrogen sulfide. All forms of sulfur are detrimental to the catalyst and the maximum content should not exceed 1.0 grains/1000 cu. ft. of synthesis gas (86). In general, rigid specifications have been prescribed for sulfur content (67, 70, 71, 72, 73, 78, 90).

When natural gas is the source material, it may be desulfurized before its conversion to synthesis gas. The Girbitol process (63, 69) may be useful

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in accomplishing this.

The removal of sulfur compounds is usually accomplished in two steps:
1) the removal of H_2S, 2) the removal of organic sulfur compounds. In the
German commercial plants, the H_2S was usually removed by the iron-oxide
method (65, 66, 77). However, at the Luetzkendorf plant, the "Alkazid"
process was used (80, 83). In this process an alkaline organic compound,
potassium-N-dimethylglycine (Dik) or potassium methyl alanine, absorbs the
H_2S and then is steam-stripped for reuse (65, 84). The latter compound
absorbs both H_2S and CO_2, whereas the former absorbs H_2S preferentially.
This process involved many difficulties, particularly that of corrosion (80).

In all of the German plants, the organic sulfur compounds were removed
by a process which consisted essentially of catalytic oxidation. The synthe-
sis gas was passed over a catalyst composed of ferric oxide and sodium car-
bonate at temperatures ranging from 350 to 535°F. depending upon the freshness
of the catalyst. It was necessary to add small amounts of oxygen to the synthe-
sis gas in order to convert all of the organic sulfur. The addition of oxygen
to the synthesis gas affected both the removal of H_2S as well as the removal
of organic sulfur. If the oxygen which was added before the gas was passed
through the tower containing beds of iron oxide for the removal of H_2S, amounted
to 0.012 volume percent, the H_2S removal was poor and the removal of organic
sulfur was not satisfactory. When the amount was increased to 0.117 - 0.205,
both were improved. (The overall optimum was in this range.) However, a
further increase of the oxygen to 0.822 - 0.903 volume percent, seriously de-
creased the removal of H_2S (66).

Several other processes have been proposed (82, 96, 100). One is a
multi-stage process in which the H_2S is first removed by moist iron oxide;
a part of the organic compounds are decomposed in the second stage by the
action of sulfurized iron and an alkali-metal carbonate at 570 - 840°F., the
H_2S being removed by the moist iron oxide; and in the last stage, the par-
tially purified gas is passed over a mixture of iron oxide and alkali-metal
carbonate at a temperature of 300 - 570°F.

The ferric oxide method for the removal is well-known. A plant using
a mixture of ferric oxide and wood shavings (for greater permeability) has
been described (81). Turner (89) has discussed the equipment and the de-
tailed advantages and disadvantages of this process.

For a synthesis gas which contains a high sulfur concentration, a pre-
liminary rough purification is often advisable. There are several processes
which are suitable for rough purification such as, the Seaboard process using
3.5% soda ash solution, the Koppers vacuum carbonate process and, the ammonia-
Thylox process. The latter process is said to reduce the H_2S content in coke-
oven gas from 2500 grains to less than 80 grains/1000 cu. ft. (64, 83).

Japanese investigators have done considerable experimental work on iron
oxide for the complete desulfurization of synthesis gas. Iron oxide was found
to be effective at 660°F. and at a space velocity of 330 volumes of gas/volume
of catalyst/hour (88). They also studied the effect of various promotors.
They found that the activity of the catalyst was greatly improved by such
additions as NaOH, ThO_2, $Cu(OH)_2$ and $Ni(OH)_2$ (74, 75).

The removals of both H_2S and organic sulfur by reaction over iron oxide

catalysts has been claimed by several investigators (94, 98, 101, 102). A preliminary treatment with active carbon is said to be effective in removing most of the organic sulfur compounds (76, 101).

Organic sulfur compounds may also be removed by reduction to H_2S which is removed in the customary manner. Processes of this nature are said to permit much higher space velocities than processes using an activated iron oxide-alkali catalyst (86). A pumice-supported catalyst containing uranium and cerium in a ratio of 4:1 by weight has been used at 660°F. (79). Catalysts for the reduction of organic sulfur to H_2S included such metals as lead, tin and copper mixed with inorganic bases or acid anhydrides, lead chromate, calcium plumbate, cupric oxide, or lead acetate (91), as well as precious metal catalysts, such as silver and gold (93, 95). Fischer has patented a process (92, 99) by which H_2S is removed with an alkaline solution of $K_3Fe(CN)_6$. The I. G. Farbenindustrie A. G. has claimed to have developed a process in which the organic sulfur compounds are decomposed to H_2S simultaneously with the water-gas shift reaction, the reaction with steam accomplishing both purposes (97).

Blohm and Chapin (68) have reported the use of ethanolamine and glyco-amine for the removal of sulfur compounds.

Since the purification of synthesis gas may involve many stages, each case requires a unique purification scheme. However, Sands, Wainwright and Schmidt have proposed two possible schemes which they have presented in tabular form, (83).

For a detailed bibliography of purification processes, Seil's (85) annotated bibliography may be used.