Fluid Bed "Working Hypothesis"

The present process deals with a fluidized bed of iron catalyst where the catalyst particles, whether carbided, oxided or uncombined, are constantly agitated.

Therefore, the reaction steps that Craxford speaks of, oil synthesis, water-gas-shift and hydrogenation cracking all go on simultaneously instead of step wise. Furthermore it appears from the present data that methane and other light saturated hydrocarbons may be formed as the result of primary reactions as well as through hydrogenation-cracking.

The following is an overall statement of the "working hypothesis" proposed. Proof of some of the conclusions will be presented later.

In this process, judging from the graphs presented here, the reactions try to produce only unsaturates and water through a basic synthesis reactions such as the following:

1)
$$2H_2 + C0 = (= CH_2) + H_20$$
 or $2n H_2 + nC0 = C_nH_{2n} + nH_20$

If the H_2/CO ratio in the feed is less than two then CO_2 becomes an inevitable by-product until at a ratio of one to one the results will be as follows, and at least 33-1/3% of the CO will go to CO_2 :

2)
$$3H_2 + 3C0 = (=CH_2) + CO_2 + H_2O$$

When the ratio is less than one the H20 will decrease and C02 increase until at 0.5 to one the product will be:

3)
$$H_2 + 200 = (=CH_2) + CO_2$$

For ratios higher than two, the excess H_2 will appear in the product. For a ratio of four to one the following is the goal:

4)
$$4H_2 + CO = (=CH_2) + H_2O + 2H_2$$

In such cases where there is excess ${\rm H_2}$ in the feed, ${\rm CO_2}$ can be added to utilize the excess ${\rm H_2}$ thus:

5)
$$7H_2 + 2CO + CO_2 = 3(=CH_2) + 4H_2O$$

If only H2 and CO2 are charged the ultimate reaction becomes

6)
$$3H_2 + CO_2 = (=CH_2) + 2H_2O$$

These goals might be attained directly if it were not for side and secondary reactions which, in a fluidized bed, proceed simultaneously with the above. The most influential of the side reactions is the watergas-shift.

7)
$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

This reaction at first proceeds to the right competing with the synthesis reactions for the utilization of the important component, CO. Phases

The path of the process is divided into two major phases. In the first phase CO₂ is made and in the second phase it is consumed.

As will be proved later, when H_2 and CO are first contacted with an active catalyst there are only two important reactions; the basic synthesis reaction and the water-gas shift proceeding to the right. The basic synthesis reaction is, at the beginning, about twice as fast as the shift reaction so that H_2 and CO are consumed at a ratio of one to one and CO_2 and H_2O are formed thus:

$$4H_2 + 2CO = 2 (=CH_2) + 2H_2O$$

$$\frac{\text{H}_2\text{O} + \text{CO}}{3\text{H}_2 + 3\text{CO}} + \frac{\text{H}_2 + \text{CO}}{2} + \frac{\text{H}_2\text{O}}{2} + \frac{\text$$

This initial ratio of $\rm H_2/CO$ consumption is independent of the $\rm H_2/CO$ ratio in the feed.

The basic synthesis reaction apparently may produce unsaturates of any molecular weight although the boiling range of the product may be markedly affected by factors such as H₂ content or free Fe in the catalyst mixture which according to the carbiding theory of mechanism may control the length of the molecules before they are detached from the catalyst. The factors affecting quality of product are not considered in this report and for the present purpose it is assumed that unsaturates of all molecular weights may be formed simultaneously.

As CO concentration is reduced by the above reactions the rate of both reactions decreases. The rate of the gas shift is reduced still further by the fact that it is approaching equilibrium and the ratio of $\rm H_2$ to CO consumption increases.

Oxygenated Compounds

As a result of the reduced rate of the above reactions as well as the fact that CO₂ concentration in the reactor has been increased, a third primary but slower reaction begins to manifest itself. This, it is suggested, is that which produces oxygenated compounds.

The oxygenated compound production continues to increase until it reaches a maximum and then starts to decrease as the conversion of $\rm H_2$ and $\rm CO$ is continued. In this respect, the oxygenated compound reactions act in the same manner as the gas shift.

What reactions are involved in the formation of oxygenated compounds has not been established but the following is interesting in this connection.

In the October 1930 issue of Ind. & Engrg. Chem. there are presented a series of articles related to the so-called methanol synthesis.

The one by Frolich et al* contains some conclusions which may apply as well

^{*&}quot;Catalyst for the formation of alcohols from CO and H2". Frolich & Cryder p. 1051