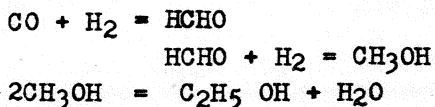


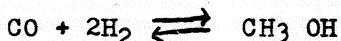
under the conditions of hydrocarbon synthesis with which we are concerned.

They state that all oxygenated compounds may stem from methanol by the process of stepwise condensation. The methanol being produced through formaldehyde as an intermediate thus:



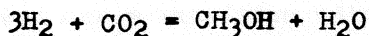
It is stated that to produce higher alcohols the water concentration must be reasonably low otherwise the water will saturate the catalyst and condensation cease.

Throughout the papers it is taken for granted that the reaction,



is completely reversible.

Smith & Hirst, (p. 1037) suggest that the formation of methanol may not proceed directly from CO at all, but may proceed through the water-gas-shift and the resulting CO₂ stage thus:



Equilibrium constants for this and other similar equations are presented.

"Catalyst Equilibrium"

When most of the CO has disappeared, usually over 85% the primary reactions mentioned above appear to stop. Some kind of equilibrium has been reached and further disappearance of H₂ and CO can only be accomplished by upsetting that equilibrium through recycling or by adding some reactant to the fresh feed.

Why the reactions should stop cannot be deduced for sure from the data presented here but, it is conjectured that the catalyst acts as an intermediate in all the reactions involved and apparent equilibrium is reached when the partial pressure of the components in the medium surrounding the catalyst is such that the catalyst surface or catalyst composition itself has reached equilibrium with the medium and is therefore no longer effective. This idea is consistent with what Mr. C.W. Watson has been contending all the time.

There is no doubt that such an equilibrium is reached and it is evident that this phenomenon is related to the relative partial pressures of the various components at the time. What that partial pressure relationship is, has not been established. It may be influenced by the amount of product which has not yet desorbed from the catalyst but this is not the only factor involved by any means. The ratio at the moment of those components in the reactor or catalyst surrounding medium which tend to carbide the catalyst to those which tend to oxidize and those which tend to reduce the catalyst are also influential and "catalyst equilibrium" may be reached when the oxidizing tendency is equal to some combination of the reducing plus carbiding tendency.

The degree of conversion of CO and H₂ and the liquid hydrocarbon yield that can be attained before this "catalyst equilibrium" is reached can be influenced by many factors such as space velocity, temperature pressure, catalyst activity and principally feed composition as will be explained below.

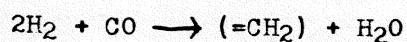
Water-Gas-Shift Equilibrium

This is not an equilibrium process but instead it is a series of competing reactions. As a result, the reversal of the gas shift can occur at anytime depending upon the effect of the other reactions on the partial pressure of any one of the components involved in the shift. In other words the shift can start reversing before it has reached its theoretical equilibrium or it can proceed to the right beyond its theoretical equilibrium. When "catalyst equilibrium" is reached and the reactions stop, the water-gas-shift equilibrium ratio may vary anywhere from 10 to 60 thus:

$$\frac{(H_2) (CO_2)}{(H_2O) (CO)} = 10 \text{ to } 60 \text{ compared with about } 22 \text{ at temperatures involved.}$$

Gas Production:

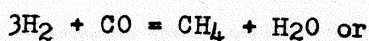
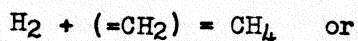
The production of unsaturated gas components such as ethylene, propylene, etc., can, for all practical purposes, be considered to result directly from the basic synthesis reactions thus:



The methane, ethane and other light paraffins are apparently produced predominantly through hydrogenation-cracking as suggested by Craxford.

The basic synthesis reaction apparently proceeds on the surface of the catalyst and some of the unsaturated chains apparently grow to heavy wax proportions before being detached. These when once formed are slow to desorb and since they crack quite easily it is reasonable to believe that a large percentage of paraffins are produced as a result of the hydrogenation cracking of these heavier molecules. This would account for the fact that wax is not found in the product at high temperatures whereas the methane production is then high.

Methane and other light paraffins may also be formed directly by primary reactions such as the following:



These primary reactions normally are slow compared to the basic synthesis reaction and the gas shift and they occur to an appreciable extent only when conditions are such that the basic synthesis and the water-gas-shift are slow or "catalyst equilibrium" is reached slowly thereby leaving the CO concentration high a longer period of reaction time. These reactions apparently stop at the same time the other primary reactions stop, when "catalyst equilibrium" is reached.

Other Reactions

In addition to those mentioned above there are other secondary or trace reactions which may proceed involving the products themselves such as polymerization, aromatization, naphthenization, dehydrogenation, etc. It is known, for example, that the hydrocarbon liquid does contain some aromatics. No consideration will be given to such secondary reactions at this time, but they probably continue even after "catalyst equilibrium" is reached.

Carbon or coke formation reactions will not be considered in this report.