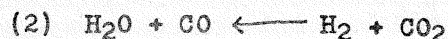




It is also agreed that the oxygenated compound reactions such as the above are completely reversible.

Reversal of Water Gas Shift:

The above primary reactions (three) proceed simultaneously, each at its own relative rate with the continued production of CO_2 and consumption of CO and H_2 until a point is reached where the relative concentration of the reactants dictates that the water-gas shift starts reversing to the left and CO_2 starts to disappear thus:



This occurs only if there is enough H_2 left in the system at the time the reversal would normally start. The point where reversal begins does not necessarily coincide with the reaching of the water-gas shift equilibrium. The reversal may start when the ratio $(\text{H}_2)(\text{CO}_2)/(\text{H}_2\text{O})(\text{CO})$ is equal to 10 or 60 compared with an equilibrium value of about 22. The point of reversal is dependent not on the concentration of the reactants alone, but on the relative rate of production or consumption of these reactants by the other reactions which are proceeding simultaneously.

Reversal of Oxygenated Compound Reactions:

As the consumption of H_2 , CO and CO_2 proceeds still further with the continued production of hydrocarbons and H_2O the concentration of H_2O or oxygenated compounds becomes so great that the oxygenated compound reactions also start to reverse.

Ultimate Product:

Theoretically, the process proceeds as though it were trying to make only $(=\text{CH}_2)$ and H_2O . The CO_2 and oxygenated compound production are only the result of reversible side reactions and both of these products would disappear if the reactions could be carried to completion.

Gas Production:

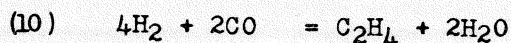
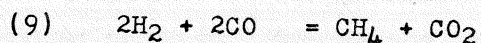
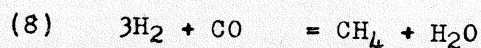
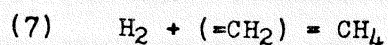
It is believed that the basic synthesis reaction proceeds on the catalyst surface in a manner something like that described by the "carbiding theory" proposed in the literature. That is, unsaturated molecules (multiples of $=\text{CH}_2$) continue to grow on the surface until they are detached, probably by hydrogen. According to this theory, unsaturated molecules of

any length may be formed depending to a large extent upon laws of probability and relative concentration at any instant of the active components involved in this mechanism.

It is probable that all the light unsaturated hydrocarbons such as ethylene, propylene and butylene are formed in this manner, as a direct result of primary reactions.

The methane and other light paraffin gases such as ethane, propane and butane on the other hand can be formed in two ways:

A. Directly by primary reactions such as:



etc.

These primary reactions are slow compared to the basic synthesis reaction and the water-gas shift and occur only under conditions where the CO concentration stays high throughout the reaction time which in turn only happens when the basic and shift reactions are slow.

B. Methane and other light paraffins are formed as a result of secondary hydrogenation-cracking reactions.

According to the carbiding theory the unsaturated primary product molecule may grow to waxlike proportions before being detached from the surface. Such large molecules are slow to desorb and are relatively easy to crack. It is reasonable to believe therefore that a large percentage of the light paraffin gases are produced in this manner. This satisfactorily explains the fact that wax yield is only high when the reaction temperature is low and the methane yield is always relatively high when the reaction temperature is high. This also accounts for the fact that a good cracking catalyst makes a poor synthesis catalyst and vice versa.

Other Secondary Reactions:

There are probably proceeding in varying degrees throughout the reaction zone other secondary reactions involving the products themselves such as polymerization, dehydrogenation, hydrogenation, cracking, etc., which are responsible for the fact that aromatics are found in the liquid