Application of Hypothesis

According to the above hypothesis, when synthesis gas is passed through a given amount of catalyst of given activity at a given space velocity, three things can happen.

1. The "catalyst equilibrium" can be reached and primary reactions cease early in the bed so that only secondary reactions proceed throughout the remainder of the bed. In such cases the proportion of secondary products such as methane, to primary products such as C_3+ will be high.

2. The reactants use up practically the whole bed before reaching "catalyst equilibrium". In such cases the product distribution can be called normal.

3. The reactants leave the bed before catalyst equilibrium is reached at all.

It is the fact that these three possibilities exist that complicates the entire picture. Before this complexity can be resolved some fundamental data must be obtained on the effect of space velocity with various catalysts and feed compositions.

It is indicated however that with good catalysts the "catalyst equilibrium" is reached and the primary reactions cease only when the concentration of the reactants H_2, CO, CO_2 and H_2O is such that the water-gas-shift is somewhere near to equilibrium. Therefore although the deviation from this rule may be very broad, the degree of approach to the water-gas-shift equilibrium can be used as an index of the approach to "catalyst equilibrium" until some more accurate index is developed. This same index does not apply when a catalyst is poor.

From the above hypothesis it is possible to predict the qualitative effect of various changes in feed composition and other operating variables as follows:

Effect of Catalyst Activity:

A catalyst may be inactive relatively for three reasons:

1. The "catalyst equilibrium" may be reached while the CO and H_2 Conversion are still low.

2. The catalyst may activate the primary reactions so little that equilibrium is not reached before the reactants leave the bed.

3. The catalyst may be effective for some of the reactions involved but not for others.

In the Beacon runs with special catalysts, the C.I. Powder catalyst may have been an example of the second case because, although the CO and H_2 conversion was very low, the distribution of product was not materially out of line with that expected from the correlations.

The unreduced CM&S catalyst was apparently an example of the third case. Here again catalyst equilibrium may not have been reached (water-gas-shift equilibrium ratio was only 5 to 16) and all reactions were slower than with reduced catalyst but the gas shift and primary methane forming reactions were apparently slower compared to the basic synthesis reaction because the methane and CO_2 yields were low while the C_3+ and water yields were high.

The Limonite and the iron synthetic ammonia type catalysts prepared at Beacon may have been examples of case 1 to varying degrees. Here the "catalyst equilibrium" may have been reached early while there was still plenty of CO left for the continuation of the methane reactions or these catalyst may selectively speed up the methane reactions.

Effect of Temperature

Lowering temperature slows up all reactions as well as the cracking reactions so that at low temperature more of the bed will be used before "catalyst equilibrium" is reached. Under such conditions less methane will be made because of the slowness of the primary methane forming reactions and the reduced tendency for hydrogenation-cracking. More wax will be formed because of the latter.

Effect of Space Velocity in Once Through Operations

There are no once through data where space velocity was changed while all other conditions were maintained equal but a comparison of once through data obtained at different space velocities but with slightly different H_2/CO ratios and a comparison of Beacon recycling data indicated that space velocities of 20 to 60 SCFH/# Cat. had no effect. This is consistent with the theory presented above and confirms that reactions stop after "catalyst equilibrium" is reached otherwise a greater H_2 and CO conversion would have been obtained at the lower space velocity. It indicates further that permissable space velocities can be more than 60 before "catalyst equilibrium" is not reached.

The space velocity at which "catalyst equilibrium" will just be reached should be determined since this will establish how much catalyst is required. Any surplus catalyst or any lower space velocity is apparently of no value and may be undesirable from the standpoint of allowing secondary reactions.

With this critical amount of catalyst present, if the space velocity is further increased the CO conversion will be reduced until a point will be reached where no oxygenated compounds will be produced and the ratio of H_2/CO consumed will be one. The yield of oil then will be about 33% of the CO in the Fresh Feed or about 41.2% of the CO converted.

Effect of Adding CO_2 to the Feed in Once Through Operations

From the above theory of the process it would be reasoned that adding CO_2 to the feed would have the following effects.

1. Less CO would be consumed by the shift before "catalyst equilibrium" was reached and the reactions stopped.

2. The average rate of the water gas shift would be reduced because its driving potential, distance from equilibrium, would be less at the start.

3. During the period of reaction, more CO would be available for the faster basic synthesis reaction and more oil would be formed.

4. The "catalyst equilibrium" would be reached sooner in the bed so that less methane would be formed through the primary methane forming reactions before the primary reactions ceased.

5. The critical CO_2 concentration would be reached sooner and more oxygenated compounds would be formed. This would show a higher yield of C_3+ (by carbon balance) even though the oil yield were not increased.

6. Because of item 5 the H_2 conversion might be the same or somewhat greater than before in spite of a lower CO Conversion.

7. CO_2 yields would be materially reduced proportional to the amount of CO_2 added to the feed.

8. H_2O yield would increase, consistent with the increase in yield of C_3+ and oxygenated compounds.

A glance at the various plots of Beacon data will show that in general all of these effects occurred. The net CO_2 yield was reduced in direct proportion to the CO_2 added, and with some allowance for inaccuracies in the data, the H_2 Conversion , % Contraction and yield of C_3^+ increased in proportion to CO_2 added. The CO Conversion decreased.

It is indicated that "catalyst equilibrium" was reached in all cases (Sp.Vel. was 20 to 40) and these results show that when CO_2 is added to the feed in once through operations it produces a higher yield of C_3^+ (by carbon balance) and H_2O. Further data are necessary to determine what part of this increase in C_3^+ was oil and what part oxygenated compounds. It appears quite conclusive however that oxygenated compound yield can be increased without reducing oil yield and methane and CO_2 yield can be reduced by adding CO_2 to the feed. This can only be accomplished at the expense of a reduction in CO Conversion and in commercial application it will require a reduction in space velocity. More quantitative data and an economical study will be required to establish whether this is desirable or not.

Effect of Recycling

Compared to the concentration in the reactor effluent when running once through, recycling reduces the concentration of CO_2, H_2O and $(=CH_2)$ and increases the concentration of H_2 & CO. As a result, recycling upsets the "catalyst equilibrium" and causes the further conversion of CO and H_2 than that attainable once through.

On the other hand if the recycle ratio is raised too much, a longer period of time is required in the reactor before reaching "catalyst equilibrium" leaving more time for the slower methane reactions to proceed causing a higher ultimate yield of methane. There appears to be no justification for a recycle ratio higher than 1.5 to 2.0.

The methane reactions are apparently irreversible because recycling increases methane concentration in the reactor and yet methane yield is higher at high recycle rates.

Recycling also increases the concentration of components other than CH_4, CO_2, CO and H_2. Among these components is a large percentage of oxygenated compounds and since the oxygenated compound reactions are reversible a high recycle ratio tends to reduce the yield of oxygenated compounds.