

It must be remembered that the effect of recycling or of increasing recycle ratio will be different under two different sets of conditions:

- A. When conditions are such that "catalyst equilibrium" was reached before the recycle ratio was increased.
- B. When the "catalyst equilibrium" was not reached.

In the latter case recycling is detrimental.

Effect of H_2/CO Ratio in Reactor Feed

As pointed out above, the H_2/CO ratio in the reactor feed does not effect the relative rate of the basic synthesis reaction and the water-gas-shift. It has a profound effect however on the time required to reach "catalyst equilibrium" and cessation of primary reactions.

When the ratio in the feed is 2/1 with no CO_2 or CH_4 in the feed "catalyst equilibrium" occurs when the H_2 conversion is about 62.5% and the CO Conversion about 98%. The product distribution then is as shown below under "Once Through Operations".

When the H_2/CO ratio is reduced to one to one the "catalyst equilibrium is evidently reached sooner and more recycling is necessary to effect a high conversion of CO. This may account for the high recycle ratios consistently used in the Laboratory A runs. Of course a high yield of CO_2 is a mathematical consequence of low H_2/CO ratios in the FF.

When the H_2/CO ratio is high, catalyst equilibrium may never be reached at all because the reducing tendency is always high so that high CO Conversions can probably be obtained once through or at low recycle rates with high H_2/CO ratios but only at the expense of a waste in H_2 . If CO_2 is added to a high H_2/CO feed to use up the extra H_2 it acts then as just though CO had been added. The wax yield should be lower with high H_2/CO in the feed but the methane yield need not necessarily be higher. It is unfortunate that no data are available on high H_2/CO ratio feeds with no CO_2 in the feed.

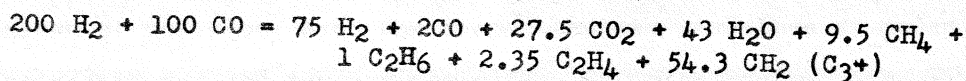
Since the CO_2 disappears rapidly when the $H_2/CO + CO_2$ is high a lower oxygenated compound yield is to be expected with this type of feed.

Once Through Operations

With an active reduced CM&S catalyst and a pure $2H_2$ plus 1 CO feed operating once through at $650^\circ F.$ and 200# the reactions do not stop until the water-gas-shift equilibrium has been reached or soon after, at which time 98% of the CO has disappeared, 62.5% of the H_2 and the contraction is 58 to 59%. The product is about as follows:

% CO in FF Unconverted	2.0
% CO in FF to CO_2	27.5
% CO in FF to CH_4	9.5
% CO in FF to C_2S	6.7
% CO in FF to C_3^+	54.3
% CO in FF to Oxy. Comps.	Small
% H_2 in FF Unconverted	37.5
% H_2 to H_2O	21.5
% H_2 to CH_4	9.5
% H_2 to C_2S	4.0
% H_2 to Hydrocarbons	27.5
% Unsats. in C_2S	70.0
% Unsats. in C_3S	90.0
% Unsats. in C_4S	85.0
Ratio H/C in C_3^+	2.0
Ratio H_2/CO consumed	1.28

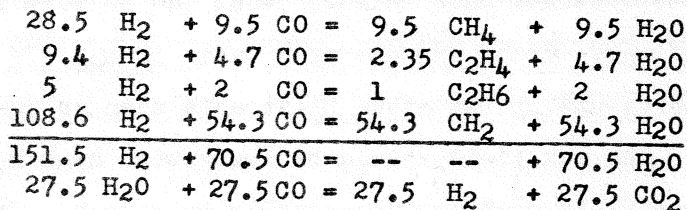
The overall reaction can be written roughly as follows:



The water-gas-shift equilibrium ratio was as follows:

$$\frac{(H_2)(CO_2)}{(H_2O)(CO)} = \frac{(75)(27.5)}{(43)(2)} = 24 \text{ compared with the theoretical of } 22 \text{ at } 650^\circ F.$$

As a matter of interest the overall reaction may be broken down into the following:



It will be noted that twice as much CO went to oil via the basic synthesis reactions as to CO_2 by the water-gas-shift and about half as much went to methane, ethane and propane.

Water Gas Shift Equilibrium - Quantitative Data

If the water-gas-shift were extremely fast compared to the other reactions then at conditions of low CO conversion either the water or the CO₂ formed by the other reactions would be used up by the water-gas-shift as rapidly as formed in its effort to reach equilibrium.

This is not the case. In the Beacon once through runs with the relatively inactive C.I. Powder as the catalyst, the water-gas-shift equilibrium was not reached at all but even so the water and CO₂ yields were substantial. The CO conversion was less than 40% and H₂ conversion less than 20% but the product distribution including C₃+ yield was very much as would be expected if all reactions involved were slowed up equally, except that there was definitely a higher yield of methane and other light saturated hydrocarbons as pointed out before.

It is pointed out that when starting with a pure H₂ and CO feed with no H₂O or CO₂ initially present, it is clear that some of the other reactions must proceed to make H₂O or CO₂ before the water-gas-shift can begin. Whether the CO₂ or H₂O is formed first is not particularly important but it appears that water is the first by product and the water-gas-shift proceeds to the right.

To check the question as to whether the reaching of the water-gas-shift equilibrium coincides with the point at which all reactions stop we can work backwards along the graphs starting from the point represented by the once through yields reported above, where the H₂ conversion was 62.5%.

Suppose we start with H₂ conversion = 55% then the graphs show the following pertinent yields:

	<u>%</u>	<u>Mols</u>
CO Converted	= 95.2	
CO Unconverted	= 4.8	4.8
CO to CO ₂	= 30.5	30.5
H ₂ Unconverted	= 45	90
H ₂ to H ₂ O	= 17.5	35

$$\frac{(H_2)(CO_2)}{(H_2O)(CO)} = \frac{(90)(30.5)}{(35)(4.8)} = 16.3$$

At H₂ conversion = 60% the corresponding figures are

$$\frac{(80)(29.5)}{(40)(3)} = 19.8$$

Obviously it seems safe to assume that the reactions do not stop until the water-gas-shift equilibrium is reached.

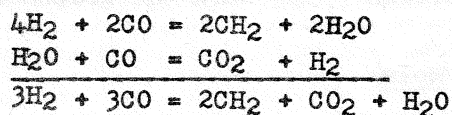
Ratio of H₂/CO Consumption - Quantitative Data

The graphs of H₂ Conversion vs. CO Conversion (Group II) indicates that when there is nothing but H₂ and CO in the feed, the H₂ and CO disappear at first in the ratio of one to one regardless of the original concentration of H₂. That is, this appears to happen whether we start with a 2/1 feed, a 1/1 feed or a 4/1 feed. It seems to happen as well whether the catalyst is active or not.

This may be quite significant from the standpoint of mechanism. It will be noted that where the H₂/CO ratio in the feed is more than 1 a break in the curves occurs after a certain amount of CO has disappeared. For a 2/1 feed this break apparently occurs when 80% of the CO and 40% of the H₂ have disappeared.

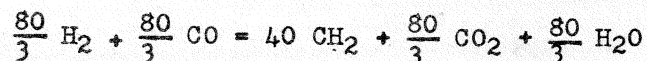
It was thought that perhaps this is the point at which the water-gas-shift equilibrium is first reached and the point from which continued reaction occurs through reversal of this reaction. This is not confirmed by the CO₂ plots (Group III) which indicate that reversal begins only when 50% of the H₂ has disappeared however, it was possible that these were in error and that the point of reversal should be moved to the left. To scout this possibility, the following analysis was made.

If the ratio of CH₄ and CO₂ production experienced in the above once through runs is used and it is assumed that no methane reaction occurred before this point was reached, then the reactions would be as follows:



and for this particular case:

	<u>Feed</u>		<u>Reacted</u>		<u>Unreacted</u>
	<u>Mols</u>	<u>%</u>	<u>Mols</u>	<u>%</u>	<u>Mols</u>
H ₂	200	40	80	60	120
CO	100	80	80	20	20



$$\text{water-gas-shift ratio} = \frac{(\text{H}_2)(\text{CO}_2)}{(\text{H}_2\text{O})(\text{CO})} = \frac{(120)(80/3)}{(20)(80/3)} = 6$$