Obviously the water-gas-shift equilibrium was not reached.

If a third equation is added to form methane and still retain the H_2/CO consumed at one to one; thus:

$$2H_2 + 2CO = CH_4 + CO_2$$

and the methane is assumed to be produced at about 1/6 the rate of production of CH_2 as in the once through runs cited above then we have the following combination.

$$\begin{array}{l} 12H_2 + 6CO = 6CH_2 + 6H_2O \\ 3H_2O + 3CO = 3CO_2 + 3H_2 \\ \underline{2H_2 + 2CO = CH_4 + CO_2} \\ 11H_2 + 11CO = 6CH_2 + CH_4 + 4CO_2 + 3H_2O \end{array}$$

or for 40% H_2 converted and 80% CO converted we have

$$200\ H_2 + 100\ CO = 120\ H_2 + 20\ CO + 43.6\ CH_2 + 7.26\ CH_4 + 29.1\ CO_2 + 21.8\ H_2O$$

and the water-gas-shift ratio although a little higher is still too low as follows:

$$\frac{(H_2)(CO_2)}{(H_2O)(CO)} = \frac{(120)(29.1)}{(21.8)(20)} = 8.0$$

The data of the once through runs cited above do not justify a further material increase in the assumed methane yield.

From the graphs themselves at 40% H_2 Conversion the following products are indicated:

% CO Converted	=	80%
% CO Unconverted	=	20
% CO to CO_2	=	25
% H_2 Unconverted	=	60.0
% H_2 to H_2O		11.8

$$\frac{(H_2)(CO_2)}{(H_2O)(CO)} = \frac{(120)(25)}{(23.6)(20)} = 6.35 \quad \text{still too low}$$

From this analysis it was concluded that this break point in the CO Conversion curve (Fig. II) was not caused by the reaching of the water-gas-shift equilibrium at this particular point.

Beginning of Oxygenated Compound Reactions

Instead, from a comparison of the above overall reactions and those written for the once through runs reported above it is indicated that at this break point the concentration of one of the primary products has become great enough so that some other reaction sets in which causes a much higher ratio of consumption of H_2/CO (2.5 to 1) than before as well as the production of appreciable water. It will be noted from Fig. XIII that to some extent the data indicate a similar break point in the water yield curve.

It is indicated that the component whose effective concentration has been reached at this point is CO_2 because its concentration does not change materially from this point on until the equilibrium is reached and all reactions cease. Note that this concentration of CO_2 amounts to about 18% of the total reactants at this time and the ratio of CO_2/CO is 1.2 to 1.33.

What reaction is promoted by the reaching of this particular CO_2 concentration is not at all clear. It is certain that it involves a relatively high consumption ratio of H_2 and CO and it produces H_2O as the by product. It could easily be the methane reaction such as

$$3H_2 + CO = CH_4 + H_2O$$

or the ethane reaction such as

$$5H_2 + 2CO = C_2H_6 + 2H_2O$$

but these are apparently produced even at low CO_2 concentration and in the C.I. Powder run where the CO_2 concentration was very low the ratio of ethane yield to methane yield was even higher than in the runs of high CO_2 concentration.

It is suggested that perhaps this is the point where the production of oxygenated compounds begins through reactions such as the following:

Alcohols) $2n\ H_2 + nCO \longrightarrow C_n H_{2n+2} O + n-1\ H_2O$

Ketones & Aldehydes) $2n-1\ H_2 + nCO \longrightarrow C_n H_{2n} O + n-1\ H_2O$

Acids) $2n-2\ H_2 + nCO \longrightarrow C_n H_{2n} O_2 + n-2\ H_2O$

Why these reactions should wait until the CO_2 concentration is high before they occur is not clear when the oxygenated compound reactions are written in this manner. Perhaps they should be written with CO_2 as the starting component as follows:

$$3H_2 + CO_2 = CH_3OH + H_2O$$

$$2H_2 + CO_2 = HCHO + H_2O$$

$$4H_2 + 2CO_2 = CH_3COOH + 2H_2O$$

This theory accounts very well for the increased rate of H_2 disappearance and H_2O production after a certain CO_2 concentration has been reached.