

TECHNICAL AND RESEARCH DIVISION  
ENGINEERING DEVELOPMENT GROUP (NY. OFFICE)

REPORT NO. 1

HYDROGENATION OF CARBON MONOXIDE  
CORRELATION OF SYNTHESIS DATA

SUMMARY

The results of several runs on the Beacon synthesis units #7 and #8 which were made at various operation conditions with many different catalysts have been compared graphically in considerable detail with similar data supplied by Hydrocarbon Research Inc.

**Correlation:**

The correlations obtained are summarized on the following Fig. S. From these graphs, if the fresh feed composition and % contraction are known, it is possible to estimate the degree of conversion attained, the yields of CO<sub>2</sub>, light hydrocarbon components, liquid hydrocarbons, oxygenated compounds and the degree of unsaturation of the light hydrocarbon fractions.

**Measure of Process Efficiency:**

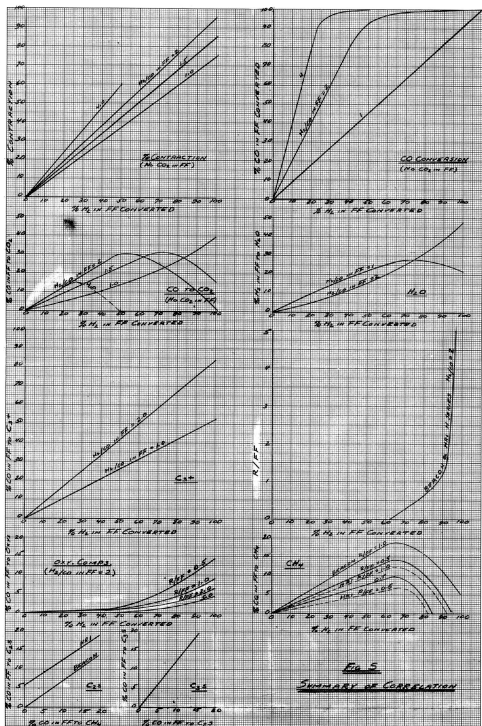
It has been established that CO conversion is a very poor measure of process efficiency. Contraction and disappearance of H<sub>2</sub> in the Fresh Feed are much more significant.

**Process Mechanism:**

From these correlations it has been deduced that the reactions and mechanism involved in the process are similar to those proposed by Craxford\* for fixed bed operation with cobalt catalysts. In the present case however, with a fluidized bed, the catalyst particles whether carbided, oxidized or uncombined are all mixed together so that the reactions proceed more or less simultaneously instead of stepwise as proposed by Craxford.

Notwithstanding this complication, the process appears to be relatively simple and quite inflexible. Although more study and further

\* "On the mechanism of the Fischer-Tropsch Reaction", S.R. Craxford -  
Proc. of Faraday Soc. August, 1946

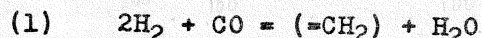


quantitative data are required, there are certain deductions which seem well founded at this time and a working hypothesis based on these deductions is proposed.

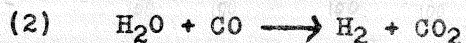
The process is not one of equilibrium. Instead it involves a series of competing reactions of different rates. Some of the reactions are reversible at these conditions but some are not.

#### Basic Reactions:

When  $H_2$  and CO are first contacted with a suitable catalyst the two most important reactions are the basic synthesis reaction:



and the water-gas shift to the right:

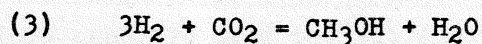


The basic synthesis reaction is about twice as fast as the shift so that, at first, the ratio of consumption of  $H_2$  and CO is about one to one. This is true regardless of the ratio of  $H_2/CO$  in the reactor feed.

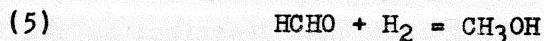
After these reactions have proceeded far enough to consume most of the CO they both slow down because of the reduced partial pressure of the CO. The shift slows down still further because it is nearer to equilibrium than before as a result of the increase in  $CO_2$  concentration.

#### Oxygenated Compounds:

At this point the ratio of  $H_2/CO$  consumption increases and a third slower reaction begins to manifest itself. This is the reaction or reactions responsible for the production of oxygenated compounds. The exact nature of this reaction has not been established. Furthermore the literature on methanol synthesis is not entirely conclusive. Some authors suggest that the oxygenated compounds are formed through  $CO_2$  thus:



while others believe that the all oxygenated compounds are produced through CO and the formaldehyde step thus:



It seems to be agreed however that the higher alcohols and other oxygenated compounds all stem from methanol through condensation and other similar secondary reactions thus: