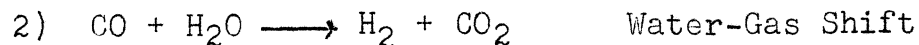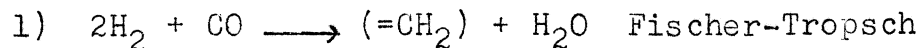## Discussion

As discussed extensively in the correlation report of 1947, the water gas shift and the Fischer-Tropsch reaction go on simultaneously both using up CO as the reactants proceed up the reactor thus:

1)  $2H_2 + CO \longrightarrow (=CH_2) + H_2O$  Fischer-Tropsch
2)  $CO + H_2O \longrightarrow H_2 + CO_2$      Water-Gas Shift

Since the feed to the reactor, total feed in this case, is relatively dry it is far removed from equilibrium and should proceed quite rapidly as soon as water is made by the Fischer-Tropsch reaction. Normally as these two reactions proceed simultaneously the CO disappears rapidly, part of it going quickly to $CO_2$ until the concentration of $CO_2$ has been built up and the CO concentration reduced to the point where the water gas shift reverses thereby converting the $CO_2$ back to CO by reaction with the remain-

ing $H_2$ thus:

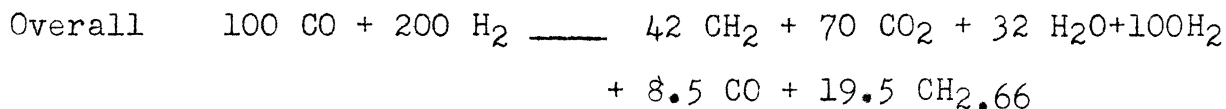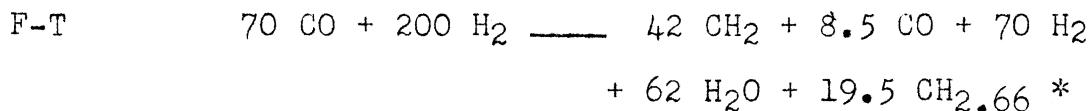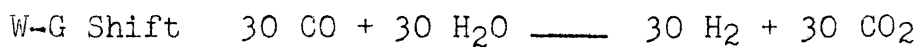$$CO + H_2O \longleftarrow H_2 + CO_2$$
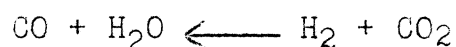
This reversal of the water gas shift is of course what accounts for the humped shape of the $CO_2$ base line in Fig. 3. When the shift reaction is occurring at normal speed this reversal <u>must</u> take place if one wishes to exceed an $H_2$ conversion of 50 to 60% (for $H_2/CO$ ratio feed of 2) otherwise the reactions would stop simply because practically all the CO has been used up. If the water gas shift is slow however and doesn't use up the CO so rapidly, the $H_2$ conversion can exceed this figure of 50 to 60% materially but never can it get up to the level of conversion we want, of the water gas shift is occurring at all, because the water gas shift inevitably uses up part of the CO and if it is too slow to reach a point of reversal it never gives the CO back.

The 1947 Correlation shows that about 30% of the CO is initially consumed by the water gas shift before it's reversal occurs. At that time most of the rest of the CO has been consumed simultaneously by the F-T reaction.

Consider for example the case for 50% $H_2$ conversion. From the base lines for 2/1 gas we get the following:

| | |
|---|---|
| $H_2$ Conv. | 50% |
| CO Conv. | 92.5% |
| CO to $CH_2$ | 42% |
| CO to $CO_2$ | 30% |
| $H_2$ to $H_2O$ | 16% |

The equations can be written as follows:

W-G Shift    $30\ CO + 30\ H_2O \longrightarrow 30\ H_2 + 30\ CO_2$

F-T    $70\ CO + 200\ H_2 \longrightarrow 42\ CH_2 + 8.5\ CO + 70\ H_2$
$$+ 62\ H_2O + 19.5\ CH_{2.66}\ *$$

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Overall    $100\ CO + 200\ H_2 \longrightarrow 42\ CH_2 + 70\ CO_2 + 32\ H_2O + 100\ H_2$
$$+ 8.5\ CO + 19.5\ CH_{2.66}$$

The water gas shift ratio at this point is

$$\frac{(H_2)\ (CO_2)}{(H_2O)\ (CO)} = 11$$ and shortly thereafter the water gas

shift starts reversing to convert $CO_2$ back to $CO$.

If on the other hand an average line is drawn thru the Brownsville data on Figs. 1, 2 & 3 however the same approach shows that at 50% $H_2$ conversion the amount of $CO$ used up by the water gas shift is only 22.5% of the total, some 25% less than normal, thus:

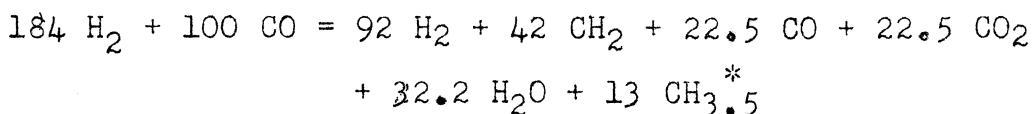For Brownsville data $H_2/CO$ in FF = 1.84

$H_2$ Conv.  =  50%

CO Conv.  =  77.5%

CO to $CO_2$ = 22.5

CO to $CH_2$ = 42

$H_2$ to $H_2O$ = 17.5

$184\ H_2 + 100\ CO = 92\ H_2 + 42\ CH_2 + 22.5\ CO + 22.5\ CO_2$
$$+ 32.2\ H_2O + 13\ CH_{3.5}^{*}$$

Water Gas Shift ratio = $\dfrac{(92)\ (22.5)}{(22.5)\ (72.2)} = 2.9$

*Found by C & H Balance

Precisely the same effect is evident at 80% $H_2$ conversion level from a similar comparison of the 1947 correlation base lines and an average line thru the pilot unit data on Mill Scale. It is suspected that the same _kind_ of thing is true also in the Beacon Runs with Mill Scale but in this case, at the high levels of conversion attained, the differences are too small to notice.

This characteristic of Mill Scale catalyst (slow water-gas shift) and it's relationship to the fact that lower conversions are obtained at Brownsville than on Pilot units could stand some further thought and development. It is felt however that the facts are already sufficiently developed to permit drawing conclusions and therefore, in the interest of getting this report out, indulgence in further discussion will be left until later.