Conclusions

It is concluded that Mill Scale is not a good Fischer-Tropsch catalyst. It changes activity up or down very rapidly depending upon the composition of the gases surrounding it and in addition it does not promote the water-gas shift as much as it should. A freshly reduced Mill Scale catalyst gives excellent results in the Beacon reactors where pure H_2 and CO and stable conditions are used, and altho there is even there a slight deactivation with time aggravated by the fact that the composition of the recycle gas is gradually changing, the catalyst appears quite stable.

On the pilot units, on the other hand, the synthesis gas is not so pure (it contains CO_2, CH_4 and some H_2O) the bed conditions are not as stable and as time goes on the catalyst continuously readjusts itself to the surrounding gases chemically and in effectiveness and deactivates much more rapidly than on the purer laboratory units. This again is aggravated by recycling and constantly changing recycle composition. This change occurs even though in the very beginning, say in the first hour, of the pilot unit runs the catalyst activity and results obtained are fully as good as those obtained under more ideal conditions on the laboratory units.

The same thing happens in the plant but to a greater extent. There operating conditions are still more unstable and the situation is apparently further aggravated by the fact that the gases contain poisons as well as the CO_2, CH_4 and H_2O also found in the pilot unit.*

The stability of the operating conditions is quite important. In the F-T reaction there tries to be a dynamic

* Poisons may come from the salt water used to wash the fresh feed, acid water used to wash the recycle or highly chlorinated city water used as trim on both.

equilibrium between the solid and gaseous phases. In recycling operations any momentary change in operating conditions and therefore conversions causes a change in recycle composition which in turn affects the solid phase and its activity thereby upsetting the equilibrium to create a vicious circle.

It appears therefore that the low conversions at Brownsville are caused by exactly the same factors that prevent the pilot units from maintaining continuously the same results as obtained on the laboratory units which are operating under more nearly perfect conditions.

Since Mill Scale catalyst deactivates rapidly when certain changes occur in its surrounding atmosphere it, conversely, reactivates rapidly when the atmosphereis favorable. That explains why a catalyst sample drawn from the Brownsville reactor at say 12 or 96 hrs. operation and which was giving poor results at Brownsville gave almost immediately good results under Beacon's condition.

The difference in results obtained at Beacon on the samples drawn from the Brownsville reactor at the 0, 12 & 96th hr. of Run #11 are quite significant in this respect. In spite of widely different chemical compositions the results obtained at Beacon on the three samples were all very high. The small differences obtained at Beacon were probably due to permanent poisoning which had occurred in even that very short period.

The X-Ray analyses of these three samples together with the relative yields were as follows. They are compared with the Brownsville, Pilot unit and other laboratory data on Fig. 1.

Age of Catalyst Hrs.	0	12	96
Beacon Run #	11143	11146	11144
Analysis			
% Fe	100	25	-
% Carbide	-	60	75
% Oxide	-	15	25
C_3+ Yields gms/cm	152.4	142.0	141.0

The solution to the problem is to use a catalyst which resist changes effected by the surrounding atmosphere. The fused catalysts such as spent CM&S catalyst are apparently much more stable in this respect. Even these however will show a drift in activity with time especially at Brownsville and a method must be developed to periodically reactivate the catalyst in place. Permanent poisons, whatever they may be, will have to be identified and removed from the fresh feed and recycle gases.

It might be argued that the Mill Scale activity could be maintained by periodic reactivation. This is probably true but with this catalyst reactivations would probably be required every 4 hrs. or so.

Another hypothetical solution to the problem is to build 600 - 11.5" I.D. units like Montebello but even then Mill Scale catalyst would probably have to be reactivated every 2 days or so.