Appendix B. THE NEW REPORTING FORMAT

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Additional features, derived from the results of the correlation work on reaction rates and product selectivities, have been incorporated in the new reporting format. A power law rate expression on CO conversion and an Arrhenius temperature function have been derived from the data of Run 10011-14, Eighth Quarterly Report, which tested a simple cobalt-loaded UCC-101 catalyst, as follows:

$$R_{CO} = 0.01515617 \times \frac{(pH_2)^{1.6515671}}{(pCO)^{0.466108}} \times \frac{TCOEF}{1000.0} \quad \frac{\text{gm moles CO}}{\text{hr, gm catalyst}}$$

$$TCOEF = \exp\left[\frac{30114.78 \times (tc - 250)}{1.98726 \times 523.15 \times (tc + 273.15)}\right]$$

where R_{CO} = rate of CO conversion, gm mole CO/hr, gm catalyst
pH_2 = partial pressure of hydrogen, psia
pCO = partial pressure of carbon monoxide, psia
TCOEF = Arrhenius temperature coefficient with 250C as reference
tc = temperature, deg. C

During each sampling period an experimental CO conversion rate is computed from the CO feed rate, the CO conversion, and the weight of the catalyst. This is compared with the expected CO conversion rate from the correlation, as indicated above. The

ratio is defined as Specific Activity, SA, and reported in the tabulated result. Thus,

$$\text{Specific Activity, SA} = \frac{\text{experimental CO conversion rate}}{\text{CO conversion rate from the correlation}}$$

This serves as a measure of the intrinsic activity of any new catalyst composition under test as compared with a reference catalyst under the same partial pressures of hydrogen and carbon monoxide and the same temperature.

The hydrocarbon product distribution has been reasonably well represented by Schulz-Flory distribution for Fischer-Tropsch products. The theory assumes that the hydrocarbon chain grows one carbon atom by one carbon atom. At each growth stage, the chain can either terminate or grow one more carbon atom. Furthermore, the growth rate and the termination rates remain the same regardless of the carbon number. Based on these assumptions, the following relationship holds:

$$Wn = n \times (1 - \text{alpha})^2 \times \text{alpha}^{(n-1)}$$

where Wn = wt. fraction of hydrocarbon fraction of carbon number n
alpha = chain growth probability
= exp(slope) of Ln(Wn/n) vs. n plot (Schulz-Flory plot)

The validity of this relationship is shown by a straight line relationship if we plot the logarithm of (Wn/n) vs. carbon number n. The product distribution does conform to this general scheme with the exception of methane. When cobalt is used as catalyst, the methane make is usually much higher than it would have been

with the Schulz-Flory distribution. Therefore methane would have to be handled separately, such as by a methane factor, FCH_4.

$$FCH_4 = \frac{\text{Wt. Fr. } CH_4}{(1-\text{alpha})^2}$$

Since the Thirteenth Quarterly Report, the alpha value and the methane factor have been a regular feature of the test result tabulations.

The correlation effort was extended to the product distribution as represented by the alpha value and $Wt\%CH_4$. These two variables are correlated as a function of the H_2/CO ratio and temperature as follows:

$$\text{alpha} = 0.78124 - 0.048725 \times \text{Ln}\left[\frac{pH_2}{pCO}\right] + 0.031305 \times \frac{1000.0}{1.98726 \times (tc+273.15)}$$

$$Wt\%CH_4 = 147.791 + 15.1143 \times \text{Ln}\left[\frac{pH_2}{pCO}\right] - 128.4976 \times \frac{1000.0}{1.98726 \times (tc+273.15)}$$

The correlation is based on data from five runs of cobalt- and cobalt/thoria-promoted catalyst systems (Runs 10011-14, 10112-14, 10112-15, 10225-06, 11677-07, Eighth, Tenth and Eleventh Quarterly Reports).

Again, in the new reporting format, the experimental values of alpha and $Wt\%CH_4$, their expected values from the correlation, and the ratios of the experimental to the expected, are all reported in the tabulation. A further refinement was incorporated in computing the experimental alpha value. Previously the alpha

value was evaluated from the best fitting slope of the C_2-C_{28} Schulz-Flory plot. This has been revised to use the data points of C_3-C_6 and C_9-C_{28}. The data points of C_2, C_7 and C_8 have been left out of the fitting due to known inaccuracies. C_2 is known to deviate from the straight line (part of which appeared as ethanol in the aqueous layer), and C_7 and C_8 suffered from evaporation loss of the oil samples.