

#### 4.0 CONCLUSIONS AND RECOMMENDATIONS

##### 4.1 Catalyst Studies

As a result of this project, the understanding of the performance and behavior of cobalt and ruthenium carbonyl-based catalysts in slurry-phase F-T processing has been greatly enhanced. The data obtained from this in-depth study of catalyst preparation, activation and processing parameters have enabled the design of a Co/Zr/SiO<sub>2</sub> catalyst that performs at least as well as conventional Co-based catalysts but with a more desirable production of fuel range product, as opposed to large amounts of wax. The diesel fuel product produced by this catalyst was high quality, meeting 9 of 11 specifications for No. 1-D diesel fuel oil. Catalyst lifetime was also good as demonstrated by a continuous 6-month run.

These cobalt catalysts have been optimized to some extent during this study but more work must be done especially with the higher Co loading catalysts where the potential for very high bulk activity exists. More detailed catalyst characterization would be warranted for this optimization, especially the use of a reaction chamber on the ESCA instrument. A method for increasing dispersion at higher metal loadings would be desirable.

The Co and Ru catalysts showed low activity for the WGS reaction and consequently performed poorly when CO-rich feeds were used. Attempts to incorporate WGS activity were unsuccessful. It would appear that

CO-rich feed, like that produced by state of the art coal gasifiers, will have to be shifted prior to F-T processing with these catalysts. The costs for adding such a process step would not be prohibitive(27), especially when improved product yields and quality would result compared to that from "conventional" iron catalysts.

The Ru-based catalysts showed very high activity in the fixed-bed reactor but consistently deactivated when used in the slurry-phase reactor. Pore blockage by the heavy wax produced by these catalysts may be more of a problem in the slurry reactor where, unlike the downflow fixed-bed reactor, product is not readily drained from the pores.

#### 4.2 Kinetics

Analysis of the data obtained from laboratory Fischer-Tropsch reactors yielded kinetic constants for the following functionality:

$$-r_{CO + H_2} = \frac{k C_{H_2}}{1 + K C_{H_2O} / (C_{CO} C_{H_2})}$$

While other kinetic models resulted in adequate representations of the data, the above model was chosen as best for a variety of physical reasons, as discussed in Section 3.2.3 of this report. The most significant reasons are that this model represents the data quite well over the entire range of collected data and has been shown by other investigators to effectively describe data with high water

concentrations (such as is the case here due to the low WGS activity of the catalyst).

While there is a physical basis for selection of this model, it is not possible, with the current data, to statistically discriminate among the rival models. A Bartlett's F-test revealed that it would require sixty data points (with data at the same degree of error as those already reported) to justifiably perform such a discrimination. With tighter error control, through refined analytical measurements, this number of experiments could be reduced significantly. Better analytical techniques would also be required if the model were to be extended to predict component fraction yields instead of reactant depletion as it is currently formulated.

The current study has, therefore, resulted in identification of the most likely kinetic functionality and evaluation of the associated kinetic constants. If the model were to be used for scaleup purposes, additional experiments would be required to ensure that the kinetic parameters were sufficiently accurate. Experimental design techniques could be used in order to minimize the number of runs and to maximize the informative power of the data. The most beneficial experiments would be:

- Runs with steam added to the feed stream to allow quantification of the water inhibition effects.

- Runs at a wider range of reactor temperatures to allow better quantification of the activation energies.
- Runs at higher space velocities to more fully explore the lower end of the conversion map.
- Runs with fresh catalyst to separate kinetic effects from deactivation phenomena (see paragraph below).
- In general, runs over a wider, more well defined experimental grid to allow the statistical discrimination discussed above.

In the analysis of the kinetic data, catalyst deactivation was assumed to proceed linearly between baseline experiments at fixed temperature. As discussed in Section 3.2.3 of this report, this linear decay assumption proved to be approximately true and allowed elucidation of the intrinsic rate phenomena. The underlying causes of the deactivation are not fully understood. Additional studies are required to determine if the decay is caused by thermal or process effects and the extent to which the decay is reversible. Such studies would ultimately result in the definition of regeneration procedures. Also, with a clear understanding of the deactivation phenomena, future studies could easily separate kinetic effects from those caused by deactivation.