2.0 OBJECTIVES

The major goal of this project was to thoroughly investigate the preparation, characterization and performance of cobalt and ruthenium carbonyl cluster-based catalysts for use in slurry phase F-T technology. Using the knowledge obtained in pursuing this goal, improved catalysts were to be designed and process concepts developed toward increasing catalyst activity, lifetime and selective production of liquid fuel product. The objectives were addressed by the following three tasks.

2.1 Development of Improved Supported Catalyst Compositions

The starting point for this contract was based on the initial development, during the aforementioned previous contract of cobalt and ruthenium carbonyl cluster derived catalysts for a slurry phase F-T process. Part of the overall objective of the current project was to further develop these catalysts to improve their activity, stability and selectivity to liquid fields, particularly for use in a slurry phase F-T process. Through a more in depth study of the preparation, characterization and performance, the catalyst development effort focused on identifying the key properties and parameters that resulted in improved supported cobalt and ruthenium carbonyl-based catalysts. Specific objectives were the following:

- Increasing catalyst activity.

- Improving product selectivity for liquid fuels and reducing the yield of methane.

- Developing catalyst systems active at high $CO:H_2$ ratios.

- Improving catalyst activity maintenance.

In achieving these objectives catalysts were tested and evaluated for their potential to convert synthesis gas into liquid hydrocarbon fuels. Catalysts were studied by a combination of tests in slurry and fixed-bed reactors and were evaluated on the basis of activity, selectivity, stability and aging. In addition, catalysts were characterized by surface and bulk analyses. The detailed areas of catalyst development were as follows:

1. Develop reproducible syntheses of the alumina-supported cobalt and ruthenium carbonyl-based catalysts, which were initially developed in the prior contract.

2. Perform gas-phase and slurry-phase tests on these baseline catalyst compositions and establish that the slurry reactors do not operate in a diffusion limited regime.

3. Establish a baseline performance for Co/Zr catalysts prepared from conventional cobalt salts for comparison with the cobalt carbonyl-derived catalyst.

4. Determine the effect of catalyst activation procedure on subsequent catalyst performance.

5. Investigate the effect of metal to promoter ratio on catalyst activity and selectivity.

6. Study the effect of metal loading on catalyst performance and relate this to the metal dispersion.

7. Examine alternate catalyst promoters and compare their effectiveness to that of the promoter (Zr) used in the basecase composition.

8. Evaluate other metal carbonyl catalyst precursors as sources for making mixed-metal catalyst systems in combination with the basecase catalyst.

9. Investigate supports other than alumina for the Co/Zr catalyst system.

10. Incorporate water-gas shift (WGS) activity into the cobalt and ruthenium catalyst systems, either directly in the catalysts or indirectly by using a mixture containing a known WGS catalyst.

11. Develop relationships between catalyst properties and performance by characterizing the catalysts with respect to bulk elemental analysis, surface area, metal surface area and

dispersion, and porosity. Specific surface characterization techniques such as ESCA were used to determine surface composition and metal oxidation states.

2.2 Slurry Reactor Kinetic Studies

Determination of kinetic parameters and studies of reaction mechanisms were the focus of this part of the research program. The specific objectives were to:

- Test mechanistic concepts, such as olefin re-incorporation, by appropriate experiments in the slurry reactor.

- Derive slurry reactor rate equations, rate constants and activation energies for the most promising metal carbonyl-based catalysts.

- Obtain kinetics in terms of rates of formation of individual product components and/or fractions.

- Utilize a backmixed reactor model and bubble column model to predict space time yields in commercial scale units.

While working on these objectives other aspects were to be addressed, as well. In determining the kinetic parameters, test conditions were held constant long enough to ensure steady state in the reactor. In doing so, information was provided on variations in product selectivity over extended periods of slurry phase operation and on rates of deactivation of the improved catalyst compositions.

2.3 Fuel Product Characterization

The final part of the program involved determination of the fuel properties of the liquid hydrocarbon product from the slurry reactor tests. Hydrocarbon product fractions, accumulated from the extended slurry test of the improved catalyst, were collected under constant process conditions and subjected to ASTM testing to evaluate their properties and suitability for use as a diesel fuel.