Section A: Contract Protocol

I. Contract Objective

The objective of this contract was to develop a catalyst and operating conditions for the direct conversion of syngas to liquid hydrocarbon fuels, using microporous crystals ("Molecular Sieves") in combination with transition metals.

II. Schedule

The contract work was planned for a 30 month period beginning March 6, 1981 and extended, at no additional cost, to September 5, 1987.

Work on the program was divided into four tasks.

Task 1 was a study of the conversion of low molecular weight liquids, such as methanol or propylene, to gasoline and diesel fuel, with catalysts consisting of molecular sieves only. The molecular sieves are commonly designated as the shape selective component (SSC).

Task 2 was a study of the conversion of syngas (carbon monoxide and hydrogen) to gasoline and diesel fuel, using catalysts consisting of both a SSC and a transition metal component (MC).

Task 3 was a study of surface effects by Professor Gabor A. Somorjai of the University of California. This work was reported in the Third Annual Report.

Task 4 comprised the management of the program and the preparation of the technical reports for the contract which, with this report, have been completed.

III. Organization

Synthesizing "Liquid Hydrocarbon Fuels From Syngas" is the goal of a research and development program on catalysis conducted by the Molecular Sieve Department, Catalyst and Process Systems Division, Union Carbide Corporation.

The work was performed at Union Carbide Corporation's Tarrytown Technical Center, Tarrytown, New York.

The Technical Director was Dr. Jule A. Rabo.

The Principal Investigators were Dr. Peter J. Coughlin and Dr. James G. Miller.

The Program Managers were Dr. Richard C. Eschenbach, initially, and subsequently Dr. Albert C. Frost.

IV. <u>Summary of Progress</u>

This report is the Final Technical Report and summarizes all of the experimental work performed at the Union Carbide Laboratories in Tarrytown during the period of the contract between March 6, 1981 and September 17, 1984. All of the tasks were successfully completed.

The two major steps of indirect coal liquefaction are the gasification of the coal into syngas and the subsequent conversion of the syngas into liquid hydrocarbon fuels with Fischer-Tropsch (F-T) catalysts. The work under this contract was aimed at developing a F-T catalyst of superior performance, suitable for the present state of the art coal gasification technology.

It was believed that the combination of molecular sieves with F-T catalyst components would tighten its usual widely spread hydrocarbon product distribution towards the liquid fuel range. This was considered possible because of the "shape selective" phenomena associated with molecular sieves.

The contract's effort towards evaluating the efficacy of selected molecular sieves as a F-T catalyst component was divided into two tasks. Task 1 examined the effectiveness of various molecular sieves as shape selective components (SSC) without any metal component (MC). These studies used either methanol or propylene as feed. Task 2 examined the effectiveness of various molecular sieves in combination with various metals and catalyst additives. These studies used simulated syngas having a 1/1 H2/CO ratio as their

usual feed. This ratio was considered reasonable for a coal gasifier effluent undergoing an economically acceptable amount of subsequent water gas shifting.

In regards to Task 1 testing, the technique of performing experiments with only a component of the catalyst, in this case the SSC, and a model feedstock, in this case propylene, is a useful research technique for catalyst screening. While the F-T feed is simple, the product is a very complex mixture. The composition of the product depends upon many properties of the catalyst. Combination of the classical F-T MC catalyst (whose operating characteristics are well documented) with a SSC in the initial phase of this study, would make the evaluation of the contribution of this component upon the results too difficult, if not impossible. Thus, the ability to isolate and test the SSC separately provides vital insight into the characteristics of that portion of the catalyst. In addition, if the catalytic behavior of the SSC component is not understood, then interactive affects, which may occur upon the combination of the SSC and the MC, could go unrecognized.

There are some risks involved in this approach. The first is that the feed must be a good model for the intermediates upon which the catalyst component being studied has to act. Methanol proved to be unsuitable as a feed. Propylene proved to be a good model feed which yielded results that provided an understanding of the catalyst properties of the SSC materials in a reaction environment simulating the secondary chemical reactions in the F-T synthesis. These results were valuable in helping to explain the results

obtained in the Task 2 testing.

The Task 1 studies identified two molecular sieves as having properties which could be useful in a final F-T catalyst. These were:

- UCC-108 (SAPO-11, a moderately acidic, medium pore size molecular sieve) which oligomerized the propylene to make iso-olefins without converting significant amounts of the propylene to propane. The latter is the usual byproduct of aromatics-rich oligomers produced with a ZSM-5 catalyst.

- UCC-101 (hydrophobic Y zeolite, a moderately acidic, large pore molecular sieve) which produced hydrocarbon products heavier than gasoline and did not deactivate as rapidly as do the strongly acidic, large pore molecular sieves.

The objective of Task 2 was to evaluate the most promising SSC catalysts, discovered during Task 1, as an additive or a support for Fischer-Tropsch catalysts. Ninety runs were made involving eleven different molecular sieves (UCC-101, -103, -104, -107, -108, -109, -110, -111, LZ-105, Y-52, and Y-82) and two non-molecular sieve materials (alpha-alumina and silica-alumina). Combinations of two molecular sieves and ion exchanged forms of molecular sieves were also tested. Iron and cobalt were selected as F-T catalyst components and ruthenium was rejected due to cost factors. Nine different metals were tested as catalyst additives to improve the stability and/or the selectivity of the catalysts. In addition, three water gas shift (WGS) catalyst components were tested to determine if their use as

catalyst additives would enhance catalyst performance.

Of the SSC materials tested, UCC-101, LZ-105, Y-52, and Y-82 have been commercially produced. UCC-103 is a modification of UCC-101 which uses techniques which have been employed commercially to manufacture other catalyst materials. Thus, no problems are anticipated in the manufacture of this material. The other materials have only been prepared in lab scale quantities.

Before summarizing the key findings of the Task 2 effort, it is important to review some key issues which arose during the course of the work and which were subsequently resolved.

The method used to combine the SSC and the MC had a major effect upon both catalyst activity and stability. Five methods were used: (1) physical mixing, (2) precipitation of the MC onto the SSC, (3) occlusion of a metal carbonyl into the pores of the SSC, (4) pore filling of an SSC extrudate with an MC salt solution, and (5) pore filling of the SSC powder using a solvent, drying to remove the solvent, and then bonding. The latter method resulted in the occlusion of the MC into the SSC crystallites and <u>not</u> on the external surface or on the binder. This in turn, yielded catalysts with <u>significantly lower deactivation rates</u>.

A number of methods were used to bind the catalysts used in Task 2. Pressing into tablets was adequate in some cases, but usually, binders were added for strength. Most of the bound catalysts employed gelled silica as the binder (neutral pH) and were formed as extrudates. Alumina, which

is peptized with acid, was also tested on a few occasions.

As with any research and development program, reproducibility of the results is vital. Without reproducibility in catalyst synthesis and testing, good catalysts may be overlooked and program direction can go astray. There are three sources of reproducibility problems in catalyst development: (1) catalyst preparation, (2) catalyst testing, and (3) hydrocarbon product analysis. Product analysis was a major problem that had to be resolved during Task 1. The wide breadth of the product distribution required the development of new analytical techniques to allow for accurate and reproducible characterization of the product. Catalyst testing can also cause problems. Irregularities in process control during testing can cloud results and make reproducibility questionable. However, modern instrumentation applied in this program substantially reduced this source of error to a relatively small value. Catalyst preparation can be a serious threat to reproducibility, especially with new compositions and crystal structures. Techniques which have been successful in the past may provide guidelines, but, may not be applicable. Therefore, attention must be given to assure that reproducibility has been achieved. Generally, reproducibility from catalyst synthesis to catalyst evaluation was high based upon duplicate test runs. As work progressed, the consistency of the observed effects of the additional and different components added to the catalysts provided increasing confidence in the reproducibility of the catalyst preparations. Finally, identical F-T performance results

obtained from different preparations of the same catalyst
demonstrated the ability to prepare reproducible catalysts.

The Schulz-Flory model provides a good, but not perfect
method to evaluate F-T product distribution. Testing of a
commercial iron catalyst showed a double alpha distribution,
as if there were two active sites, each exhibiting its own
distribution. Some SSC containing catalysts also yielded a
mild double alpha behavior with, however, less than the
reference Fe amount of heavies in the product. In some
cases this was due to a slight carbon number cutoff and in
others due to an anomaly associated with Berty reactor
dynamics. Typically, the cobalt catalysts yielded a product
distribution which followed the Schulz-Flory distribution
with two exceptions: (1) the methane was higher and (2) the
C2-C4 fraction was lower than indicated by the S-F plot.
The cobalt catalysts were also much more active than the
iron catalysts. The catalysts with 20 % cobalt were more
acive than catalysts containing 50 % iron. Since higher
catalyst activity relates to lower capital investment, the
cobalt catalyst was judged to be superior to iron. In
addition, selectivity is very important, with a premium for
a product providing a heavier boiling range product. With
SSC catalysts, a cobalt MC exhibited a much higher
selectivity for heavier products and less C2-C4 gaseous
products than did the iron catalysts. Finally, the cobalt
catalysts had excellent stability, deactivating only slowly
even at the destabilizing, low H2/CO ratio in syngas feed.

While the Task 2 studies did not succeed in finding a
catalyst that would significantly alter the Schulz-Flory

distribution experienced with F-T catalysts, they did identify a promising molecular sieve component and they did identify two effective additives for the cobalt metal catalyst. Specifically:

- UCC-103, the acid-extracted version of UCC-101, was found to be an excellent and unique support for the metal component, particularly for cobalt. Because of the unique, high dispersion of the metal in this support, this catalyst required a far lower metal content than did the unsupported F-T catalysts.

- X4 (molybdenum), applied as a dopant in minor quantities, greatly increased the stability of the cobalt catalyst and, additionally, increased the selectivity towards olefins in the liquid and gaseous products by approximately 7 %. The higher olefin content not only improves the octane number of the gasoline product, but would also make the gasoline product more amenable to product quality improvements by subsequent processing.

- X6 (gold), applied as a dopant in minor quantities, lowered the methane production rate of the cobalt catalyst by about 25 %.

- A catalyst containing a physical mixture of UCC-103 and UCC-101, in which the UCC-103 supported a thoria promoted cobalt which was also doped with X4 produced the best results of any product tested during this program. This catalyst contained only 4.5 % cobalt, 0.7 % thoria, and 0.9 % of the X4 additive. The 50/50 UCC-101/UCC-103 mixture was bonded with 15 %

silica binder and formed into 1/8 inch pellets. This product displayed extraordinary stability with nearly immeasurably low deactivation rate, estimated to be as little as 1 % per 1100 hours on stream. A typical reference catalyst shows a 1 % loss about every nine hours on stream at comparable process conditions. The product distribution and yield were stable as well. The C5+ hydrocarbon yield was 69.7 % at the beginning of the run and dropped by only 1 % at the end. The methane make remained constant at about 13 %, as did the C2-C4 fraction (18 %). This was one of the few catalysts to produce more C2-C4 than methane. Results are reviewed on page 69 of this report and on page 224 of the Third Annual Report.

- Berty process data for Co/ThO2/UCC-101 catalysts were used to develop a kinetic model to predict catalyst performance in a commercial tubular reactor. The resulting design parameters were used as the basis for a techno-economic study of the process/catalyst system by an independent evaluator.

The advances made during this contract revealed new areas where further gains could be expected. The potential gains would include even higher activities, lower methane makes, and greater C5 + selectivities.

The attainment of these potential gains are the subject of a sequential contract with the Department of Energy, Contract No. DE-AC-22-84PC70028.