

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. Summary of Progress

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, L2-105, 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 not on the external surface or on the binder. This in turn, yielded catalysts with significantly lower deactivation rates.

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 active 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 thorium 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 % thorium, 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.

Section B: Technical Report

I. Abstract

Commercial Fischer-Tropsch (F-T) processes are limited by deficiencies intrinsic to the metal catalysts used (Fe and Co). These are (1) the predominance of normal paraffins in the product, (2) a small liquid motor fuel fraction formed in the total product, and (3) the formation of oxygenated compounds which cause separation and corrosion problems. Union Carbide believed that substantial improvements could be made based upon recent discoveries of new molecular sieves. It was believed that the combination of the new molecular sieves with the classical F-T catalysts could eliminate these deficiencies.

The initial effort focused on studies of the molecular sieve component alone (Task 1). This resulted in the identification of UCC-108 and UCC-101 (and their variations) as candidates for the production of fuel range hydrocarbons with Fischer-Tropsch catalysts.

The next step (Task 2) was the study of these materials in conjunction with Fischer-Tropsch catalysts to generate fuel hydrocarbons from syngas. A few outstanding candidates were discovered that provided significantly better product yields and quality as well as an improved catalyst stability.

This report summarizes the results of the program.

II. Introduction

The objective of Contract DE-AC22-81PC40077, under which the work described here was performed, was to develop a cost effective catalytic process for converting syngas ($H_2 + CO$) to liquid hydrocarbon fuels (LHF) including gasoline, turbine and diesel fuel. The catalytic process was to use microporous crystalline catalysts - also known as Shape Selective Catalysts (S.S.C.) or "Molecular Sieves" - in combination with metal catalysts (M.C.) from the Group VIII transition metals.

As a result of the upheavals in the petroleum economy during the 1970's, and the simultaneous growing pressure on the available petroleum reserves for use in non-fuel applications, the search for alternatives to petroleum based energy became a major national priority. Against this background, and to draw on Union Carbide's special expertise in the catalytic chemistry of hydrocarbons and in molecular sieve catalysis, the present contract was started in 1981.

The original term of 30 months, from the starting date of March 1981, was extended by agreement, first to 36 months, and again to 42 months. Development work was completed in September 1984.

Most of the first twelve months was occupied by preparatory work. This included:

- Assembly of staff,
- Allocation and remodeling of laboratory facilities,
- Specification, procurement, installation, testing, and calibration of experimental apparatus,
- Design of preliminary test protocols,
- Design, preparation, installation, and debugging of analytical techniques and computer software,
- Shake-down runs from which the final test protocols were derived.

Task 1

The objective of Task 1 was to select one or more of the promising microporous molecular sieve crystal catalysts from Union Carbide's product portfolio, as candidates for initial testing in Task 2. To identify the capabilities of these materials for synthesizing the desired higher molecular weight liquid hydrocarbons from light intermediates, they were to be tested without the use of metal components.

Two series of tests were to be carried out on the selected catalysts. One set would employ methanol as the feed and the other would employ propylene.

Work on Task 1 began in June 1981 and was completed in February 1983.

Task 2

The objective of Task 2, which was the main thrust of the contract, was to develop a catalyst and process for the most cost-effective synthesis of liquid hydrocarbon fuels from syngas.

The catalytic systems contemplated were combinations of one or more SSC's (identified as the best candidates from Task 1 results) with one or more of the MC's of known effectiveness in catalyzing the synthesis of light intermediates from syngas.

The first tests in Task 2 were conducted in June 1982 and the work continued through the remaining term of the contract.

Task 3

Task 3 was a fundamental study of surface effects and reaction intermediates during the hydrogenation of carbon monoxide on transition metal catalysts. The objective was to support Task 2 efforts in two respects:

First, to characterize the surface structure and chemical intermediates of several important MC catalyst candidates using the most advanced scientific techniques and skills available.

Second, to determine the primary hydrocarbon (or alcohol) products obtained on a few selected MC catalysts.

These findings were to be fed continuously into the work on Task 2.

Because of their expertise in surface studies and in the design and construction of appropriate test apparatus, Task 3 was conducted by Professor G. A. Somorjai, University of California at Berkeley, under a subcontract. The subcontract was started in June 1981 and completed in February 1984.

The Final Technical Report for Task 3 was delivered as Appendix B of the Third Annual Report, for the period March 1983 to February 1984, and will not be repeated here.

Task 4

Task 4 comprised the tasks of program management and the preparation of technical reports.

III. EXPERIMENTAL APPARATUS

Two over-riding considerations dictated the choice of reactors for the catalyst test runs. Firstly, because Fischer-Tropsch reactions are highly exothermic, a reliable and precise means of controlling the reaction temperature was required. Secondly, because techno-economic evaluations would eventually be required, run data had to be correlatable for use in a computer simulation of a large commercial reactor.

The Berty reactor was selected as the best means to meet both requirements. Its high internal recirculation rate provides an accurate control of the reaction temperature. In addition, since the discharge conditions are nearly the same as those of an ideal, perfectly mixed Continuous-Flow Stirred Tank Reactor, the data can be easily correlated into rate expressions for the computer simulation.

Over 200 Berty reactors have been used in the chemical industry for routine catalyst testing and kinetic modeling since their introduction in the middle of the 1960's. Union Carbide's experience with over 40 Berty reactors has shown them to be relatively free of technical problems, to give reliable rate data, and to have small internal temperature gradients with even highly exothermic reactions.

The Berty Reactor

The reactor proper (Figure 1) is a stainless steel cylinder nominally five inches high and five inches in

diameter. The internal chamber is 4 1/2 inches high and 4 7/8 inches in diameter, with a convex domed upper surface. In the center of the chamber is a solid, doughnut shaped, stainless steel toroid, 3 1/4 inches high, with a 2 inch inside diameter and a 4 3/8 inch outside diameter. With the toroid in place the void volume of the chamber is about 750 cc.

In the center of the toroid is placed a stainless steel open mesh basket, 3 inches high and 2 inches in diameter. This holds the catalyst that is being tested. Vertical draft tubes between the basket and the inside of the toroid keep the basket centered.

Below the basket is a horizontally rotating down-draft impeller, mounted on a shaft which extends down to the base of the reactor, where it is magnetically driven by a variable speed motor.

Liquid feed is introduced through a horizontal channel in the side of the vessel, at the level of the impeller. Gas feed is introduced up through the magnetic drive shaft. Both liquid and gaseous products are withdrawn through a channel at the bottom of the vessel.

The impeller draws gases down through the catalyst bed and propels them centrifugally outward. The shape of the chamber forces them around the toroid to recirculate through the basket before discharge. The recirculation ratio, which is controlled by the impeller speed, can be set to an experimentally determined level at which catalyst performance becomes

insensitive to small changes, closely approaching a gradientless reactor.

Two thermowells provide for continuous monitoring of the reaction temperature. One is positioned just below the catalyst bed, and the other just above it.

The catalyst basket described above held 80 cc of undiluted catalyst, the amount that was used for most of the Task 1 and Task 2 runs. A larger basket, with a correspondingly smaller toroid, held 250 cc of undiluted catalyst and was used for the other runs.

The Complete System

Figure 2 presents a schematic diagram of the complete system. The system has the capability to deliver either liquid or gaseous feed stocks to the reactor.

Liquid feed, such as methanol or propylene, is drawn from a tank reservoir equipped with a graduated level gauge. A positive displacement pump introduces the liquid into the reactor where it is vaporized.

The CO and H₂ feed gases are drawn from their own high pressure feed line or storage cylinder. The flow rate of each gas is controlled by a Linde mass-flow controller, which is stable and reliable. The gases mix and enter the reactor through the magnetic drive shaft of the reactor.

The desired temperature is obtained by the use of electrical resistance heating elements, which are mounted above and around the sides of the reactor and are controlled by two independent temperature

controllers.

The product leaving the reactor passes through a pressure control valve which is operated by a pneumatic pressure controller with a Bourdon tube sensing element. The now depressurized and cooled product enters a 500 cc. glass receiver where the condensable fraction separates out. The non-condensable fraction passes out of the receiver to an on-line chromatograph, then to a back-up separator, a dry gas meter, and finally to the vent.

The reactor was also fitted with a by-pass line and a 1000 psig relief valve.

Three complete systems were installed, each in an individual bay, in a manner that allowed easy servicing of the reactors.