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.

Subsequently, Contract DE-AC22-81PC40077 was undertaken to identify molecular sieve candidates that showed improved F-T performance in conjunction with conventional F-T catalyst base metals (Fe and Co). That work identified a few outstanding candidates that provided significantly better yields and product quality and, in addition, exhibited improved catalyst stability when compared with currently available commercial catalysts.

Consequently, the present contract (DE-AC22-84PC70028) was initiated to capitalize upon the leads generated by the previous work. The objective included a demonstration of the economic value of a combined catalyst process system.

II. INTRODUCTION

The objective of Contract DE-AC22-84PC70028, under which the work described here was performed, was to consolidate the advances made during the previous contract in the conversion of syngas to motor fuels using Molecular Sieve containing catalysts. In addition, the practical utility and economic value of the new catalyst/process system was to be demonstrated with appropriate laboratory studies.

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 catalytic chemistry of hydrocarbons and in molecular sieve catalysis, the previous contract was started in 1981. The present contract was started in September 1984. This final report represents the completion of the contract.

III. EXPERIMENTAL APPARATUS

Two overriding 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 into rate constant data 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 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 could be varied to hold from 80 cc of catalyst to as much as 250 cc (with a correspondingly smaller toroid).

The Complete System

The system has the capability to deliver either liquid or gaseous feed stocks to the reactor.

Liquid feeds were used during the previous contract. Syngas feedstocks were used for this study.

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.

IV. ANALYTICAL PROCEDURES

A major effort was expended during the first contract (DE-AC22-8IPC40077) to develop accurate product analysis techniques that were fast enough to provide "on-line" results. These techniques provided a major cost controlling benefit in two ways; 1) the results were available without additional sample handling and subsequent analysis in separate facilities, and 2) the immediacy of the results allowed for more accurate planning of subsequent runs, thus eliminating "shot-in-the-dark" experiments.

The details of the evolution of the analytical techniques were reported fully in the Final Technical Report of the previous contract. A summary of the ultimate techniques used are presented here for the sake of completeness.

A. Gaseous Product

A Carle Model 530 gas chromatograph was used for on-line analysis of the non-condensable gaseous product. This instrument is capable of analyzing saturated and unsaturated hydrocarbons through hexane, polar compounds (methanol,water, dimethyl ether) and fixed gases (hydrogen, carbon monoxide, carbon dioxide, nitrogen). The unit performed satisfactorily for the duration of the contract.

B. Liquid Product

The liquid product consists of two phases (aqueous and hydrocarbon). These were separated by centifugation. The aqueous phase was analyzed by standard gas chromatographic methods.

The hydrocarbon phase was separated by the use of an Envirochem Unacon Model 810B concentrating purge and trap system chromatograph. This allowed separation of the C5+ fraction from the butanes and lighter fraction. The light fraction was analyzed by conventional chromatography. The C5+ fraction was analyzed by carbon number by glass capillary chromatography, using a Perkin-Elmer Model 910 gas chromatograph.

C. Reporting

Analytical results for each run, including detailed material balances were reported in a table which included (a) data relating to the run as a whole, and (b) data for each sample analyzed during the course of the run.

Supplementing each table were four series of displays:

1. Four graphs in which the performance of the catalyst during the course of the run was plotted against time on stream showing:

- Conversion of syngas, hydrogen, and carbon monoxide to hydrocarbons.

- Hydrocarbon product selectivity by carbon number groups.

- Isomerization of the pentane fraction.

- Percent olefins in the C4 fraction.

2. A graph for each sample which plotted the Schulz-Flory hydrocarbon product distribution.

3. A graph for each sample which presented the simulated distillation curve (boiling point vs. percent distilled).

4. The chromatograph of the C5+ fraction for each sample.