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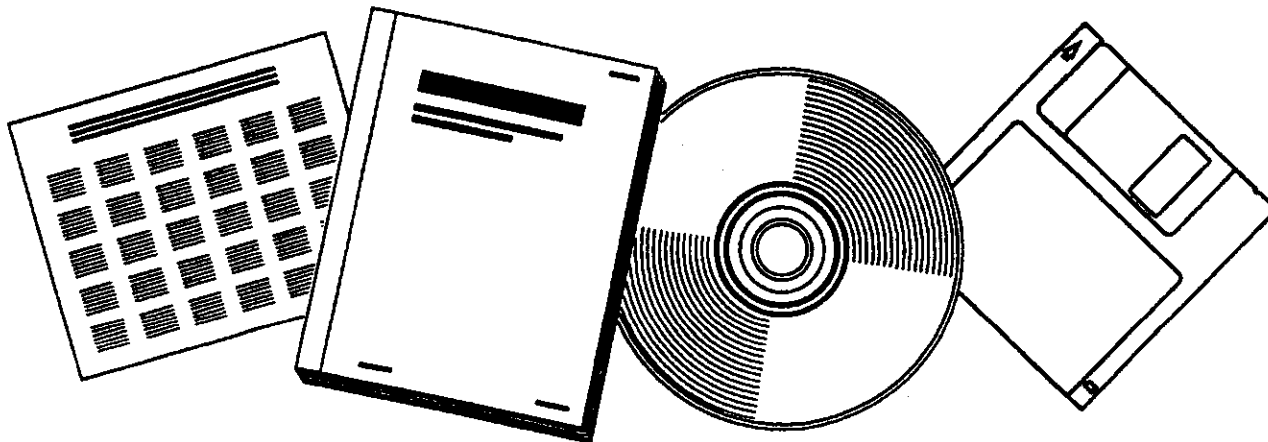
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**LIQUID HYDROCARBON FUELS FROM SYNGAS.  
FOURTEENTH QUARTERLY PROGRESS REPORT,  
JUNE-AUGUST 1984**

UNION CARBIDE CORP., TARRYTOWN, NY.  
MOLECULAR SIEVE DEPT

1985



U.S. DEPARTMENT OF COMMERCE  
National Technical Information Service

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DOE/PC/40077--T9

DE85 017394

TECHNICAL PROGRESS REPORT  
DE-AC22-81PC40077

Fourteenth Quarterly Report  
June - August 1984

LIQUID HYDROCARBON FUELS FROM SYNGAS

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**MASTER**

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## I. CONTRACT OBJECTIVE

The objective of the contract is 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 the 36-month period beginning March 6, 1981.

Work on the program is divided into four tasks.

Task 1, completed, was the conversion of low molecular weight liquids, such as methanol and propylene, to gasoline and diesel fuel, with catalysts consisting of only a Molecular-Sieve component, commonly designated as the shape-selective component (SSC).

Task 2 is 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, a study of surface effects by Professor Gabor A. Somorjai of the University of California, has been completed and was reported in the Third Annual Report.

Task 4 comprises the management and technical reports for the contract.

### 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, Catalysts and Process Systems Division, Union Carbide Corporation.

The work is performed at Union Carbide Corporation's Tarrytown Technical Center, Tarrytown NY 10591.

Principal investigator is Dr. Jule A. Rabo.

Program manager is Dr. Albert C. Frost.

#### IV. SUMMARY OF PROGRESS

##### A. Task 1

Task 1 has been essentially completed. Only minimal work, if any, is contemplated in future.

##### B. Task 2

All of the eight catalysts reported for May through July 1984 contained cobalt intimately mixed with the shape-selective component UCC-103, and in seven of these the cobalt was promoted with thorium. All but one also contained physically mixed shape-selective component UCC-101, which, in this form, has been found to be practically inert.

The additives  $X_4$ ,  $X_8$  and potassium were tested in varying combinations and concentrations-- $X_4$  alone in one run,  $X_8$  alone in two runs,  $X_4$  and  $X_8$  together in four runs, and  $X_4$  with potassium in one run. The  $X_4$  in two of the catalysts was obtained from the same source as that used for Third Annual Report Catalyst 6 (Run 11677-11), the most stable catalyst developed to date; in four others it was obtained from a source containing catalyst poisons which had to be removed before the catalysts were prepared. The additive  $X_8$ , new to this program, is chemically similar to  $X_6$ , which was effective in a physically mixed catalyst but not in an intimately mixed one;  $X_8$  was prepared to be more compatible than

X<sub>6</sub> with the intimately mixed formulation.

Two data items, described below, have been added to the tables of material balances beginning with this report. They provide comparisons of the test catalyst against a reference catalyst under similar process conditions.

#### Catalyst Test Results

No other catalyst has yet been developed to equal Third Annual Report Catalyst 6 (Run 11677-11), which throughout the twelve days of its run delivered a product of higher than average quality with no measurable deactivation. One of this quarter's catalysts, however, ran a fairly close second during a large part of its run, and most of the eight runs yielded much valuable information on the synergistic actions, both positive and negative, of the constituents being tested.

Catalyst 7 (Run 11885-02), due to its great stability, was maintained on stream for an unusually long run of one month; during 60 percent of that time its deactivation rate was only one percentage point every 200 hours. It contained about 7 percent cobalt, 15 percent as much X<sub>4</sub> as cobalt, and 2 percent as much X<sub>8</sub> as cobalt. In contrast, Catalyst 4 (Run 11885-01), with the same components but at much lower levels of X<sub>4</sub> and X<sub>8</sub>, was largely ineffective. The catalyst of Run 11677-11, for reference, contained 4.5 percent cobalt, 20 percent as much X<sub>4</sub> as cobalt, and no X<sub>8</sub>.

After nearly 300 hours under uniform conditions, the run of Catalyst 1 (Run 11723-17) was continued more than 300 hours long-



er, in five stages, to test the effects of changes in temperature and pressure. The results indicated, in a preliminary way, that stability is considerably greater at 300 than at 500 psig, and that still lower pressures might be worth investigating.

The effects of additive X<sub>8</sub> were varied--some useful, others less so. Despite its chemical resemblance to X<sub>6</sub>, it acted very differently in these cobalt Fischer-Tropsch catalysts. It lowered the production of methane but not the water gas shift activity. In combination with X<sub>4</sub> it performed poorly at low concentrations, but at moderately high concentrations it produced one of the most stable catalysts found so far (Catalyst 7).

The poor performance of Catalyst 8, which was identical to Catalyst 7 except for the omission of thorium, demonstrates that, at least with the cobalt/X<sub>4</sub>/X<sub>8</sub> combination, thorium is essential. In this environment it substantially enhances both the activity and the selectivity of the catalyst, although without reducing the production of methane.

The substitution of potassium for X<sub>8</sub> in Catalyst 6 (Run 11723-18), also produced mixed results. The conversion was exceptionally high at first, but deactivated very rapidly. The water gas shift activity was somewhat improved. Unlike its function in iron catalysts, however, the potassium did not contribute either to the growth of hydrocarbon chains or to the olefinic content of the product.

For test details see Appendix A.

### The New Reporting Format

Beginning with this report, two new data items have been added to the tables of material balances for each run.

One is the specific activity (SA) of the catalyst at each sampling point. This is the ratio of the measured CO conversion rate of the catalyst under test, to the expected conversion rate calculated from a model based on the performance of a typical cobalt loaded UCC-101 catalyst. The SA provides a comparison of the catalyst's intrinsic activity against that of a reference catalyst under the same partial pressures of hydrogen and carbon monoxide and the same temperature.

The other is a comparison of the weight percent of methane being produced by the catalyst under test against the weight percent predicted by another mathematical model. This is especially useful in comparing two catalysts with different usage ratios or activity levels, as well as in explaining selectivity changes which accompany deactivation.

Both mathematical models are fully explicated in Appendix B.


V. CHANGES

The period of performance was changed from forty-two months to forty-seven months, without any increase in the total estimated cost of the contract.

## VI. FUTURE WORK

The catalyst development effort during the next, final quarter will continue to be directed at examining the cobalt catalysts at various thorium levels, with various metal additives, and with various other Molecular Sieves.

The catalyst development effort for the next quarter will finalize the design package requested by the Department of Energy for MITRE's techno-economic evaluation of Union Carbide Corporation's Catalyst/Process System.



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A. C. Frost