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IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS. SIXTH QUARTERLY TECHNICAL PROGRESS REPORT, JANUARY-MARCH 1986

UNION CARBIDE CORP., TARRYTOWN, NY.
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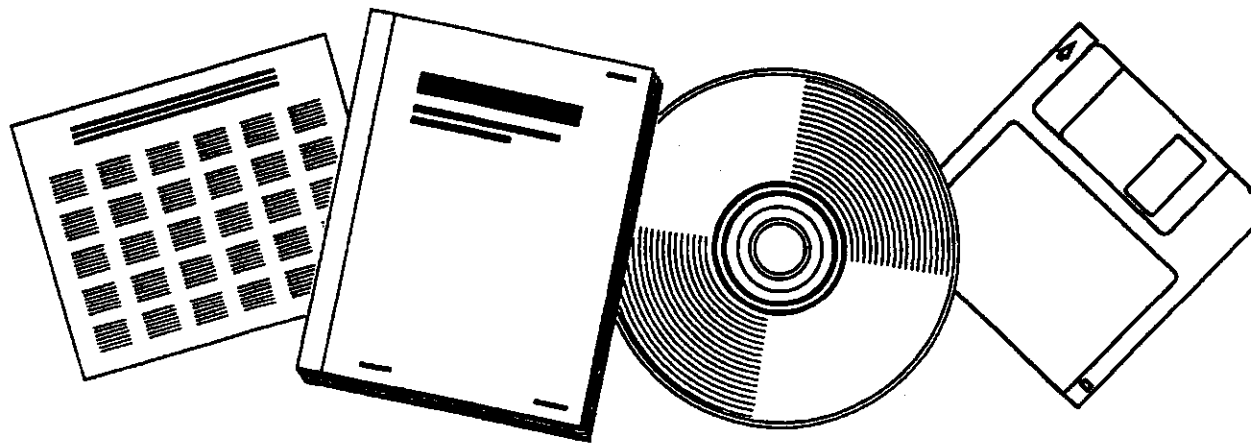

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TECHNICAL PROGRESS REPORT
DE-AC22-84PC70028

Sixth Quarterly Report
January - March 1986

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LIQUID HYDROCARBON FUELS FROM SYNGAS

Molecular Sieve Department
Catalysts and Services Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

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B. Catalyst Testing: Details of Runs Initially Reported During Last Quarter B1

I. CONTRACT OBJECTIVE

The objective of the contract is to consolidate the advances made during the previous contract in the conversion of syngas to motor fuels using Molecular Sieve-containing catalysts and to demonstrate the practical utility and economic value of the new catalyst/process systems with appropriate laboratory runs.

II. SCHEDULE

The contract work was planned for the twenty-eight month period beginning September 18, 1984.

Work on the program is divided into six tasks.

Task 1 consists of the preparation of a detailed, non-proprietary work plan covering the entire performance of the contract. This work plan was completed in November, 1984.

Task 2 consists of a preliminary techno-economic assessment of the UCC catalyst/process system. This assessment, as well as the final techno-economic evaluation planned for Task 6, will be based on a sensitivity analysis which MITRE will conduct on their recently completed economic evaluation of the Union Carbide Corporation (UCC) system.

Task 3 consists of the optimization of the most promising catalysts developed under prior contract DE-AC22-81PC40077 toward goals defined by the MITRE and Task 2 studies. This work will run through the first 24 months of the contract.

Task 4 consists of the optimization of the UCC catalyst system in a manner which will give it the longest possible service life. This work will run through the first 24 months of the contract.

Task 5 consists of the optimization of a UCC process/catalyst system based upon a tubular reactor with a recycle loop

(i.e., the Arge reactor) containing the most promising catalysts developed under the Tasks 3 and 4 studies. This optimal performance will be estimated from a mathematical model of the tubular reactor which incorporates reaction rate constants determined from appropriate Berty reactor runs. This effort will run through the first 24 months of the contract.

Task 6 consists of an economic evaluation of the optimal performance found under Task 5 for the UCC process/catalyst system. This effort will be based on the MITRE sensitivity analysis referred to in the description of Task 2.

The final four months of the contract will be devoted exclusively to the writing of the Eighth Quarterly Report and the Final Technical Report.

III. ORGANIZATION

This contract is being carried out by the Catalyst Research and Development Group of the Molecular Sieve Technology Department, Catalysts and Services Division, Union Carbide Corporation, Tarrytown, New York.

The principal investigator is Dr. Jule A. Rabo.

The program manager is Dr. Albert C. Frost.

IV. SUMMARY OF PROGRESS

A. Task 1

Task 1, a detailing of the work planned for the other tasks in the contract, has been completed.

B. Task 2

Task 2, a preliminary techno-economic assessment of the UCC catalyst/process system, will be based on a sensitivity analysis which MITRE is conducting on their recently completed economic evaluation of the UCC system.

This sensitivity study is expected to graphically show the differential cost (around the base case cost), expressed as differential cents per gallon of motor fuels, for changes in each of the operating parameters of space velocity, catalyst life, methane make, alpha, C_{25}-C_{30} carbon cutoff, overall conversion, feed H_2:CO ratio, reactor temperature, and reactor pressure.

These differential cost-operating parameter curves will not only strikingly illuminate which of those operating parameters have the greatest effect on product cost (for Task 2), but they will also be used with catalyst performance data and the existing tubular reactor design curves to readily obtain an economic worth for each tested catalyst for any set of envisioned process conditions (for Task 6).

C. Tasks 3 and 4

The catalyst testing for this quarter was focused on further understanding and developing the X_{11} promoted cobalt oxide component intimately contacted with the Molecular Sieve TC-123. Furthermore, the addition of new promoters, the addition of a water gas shift component, and the substitution of TC-123 with a new Molecular Sieve TC-121 and with γ-alumina was also studied.

The use of the additional promoter X_{13} was found to increase the water gas shift acitivity of the X_{11} promoted Co/TC-123 catalyst. While the catalyst demonstrated excellent stability at 240C, it did, however, show considerable deactivation at 260C.

The use of the additive X_9, geared towards improving the Co/X_{11}/TC-123 catalyst's stability at higher temperatures, appeared partially successful. The catalyst demonstrated high activity (about 75 percent $CO+H_2$ conversion at 260C, 500 psig, and a 1.5:1 H_2:CO) with a deactivation rate of only about one percentage point every 150 hours. The selectivity, however, remained excellent with about 9 percent CH_4 being produced throughout the 800 hour test period.

Attempts to improve the water gas shift activity of the system by the simple addition of a separate water gas shift catalyst (K/Ni/Mo-γ-alumina) were unsuccessful. Similarly, the testing of the new Molecular Sieve TC-121 demonstrated inferior performance in both activity and selectivity when compared with the analogous TC-123 supported catalyst.

The preliminary test results for these catalysts are summa-

rized in Appendix A. The detailed test results for the catalysts first reported in last quarter's report (Appendix A of that report) are given in Appendix B.

D. Task 5

There were no Task 5 studies carried out during the Sixth Quarter. Manpower remained temporarily diverted to converting non-DOE computer programs over to the new CAS computer system.

This delay was considered justifiable in view of the rapid progress that has recently been made in the catalyst development effort, and the attendant need to wait until these improvements have somewhat plateaued before process studies are initiated.

E. Task 6

The final techno-economic evaluation will begin when some of the more promising catalysts that have recently been developed demonstrate a plateau of improved performance, particularly in respect to stability. The Berty (CSTR) rate data will then be used with our mathematical simulation of the tubular reactor to generate a wide range of possible process operating conditions. These conditions, in turn, will be costed with the forthcoming results of the MITRE sensitivity studies to define the optimum set of conditions that will give the lowest cost/bbl of F-T product.

V. CHANGES

There were no contract changes during the Fifth Quarter.

VI. FUTURE WORK

Tasks 3 and 4 will continue to be devoted to developing new, stable catalyst formulations which will have higher specific activities and lower methane makes than do our present catalysts.

Task 5 will be devoted to examining the space velocity-methane make trade-off with correlated data for the more promising catalysts developed under Tasks 3 and 4.

Albert C. Frost