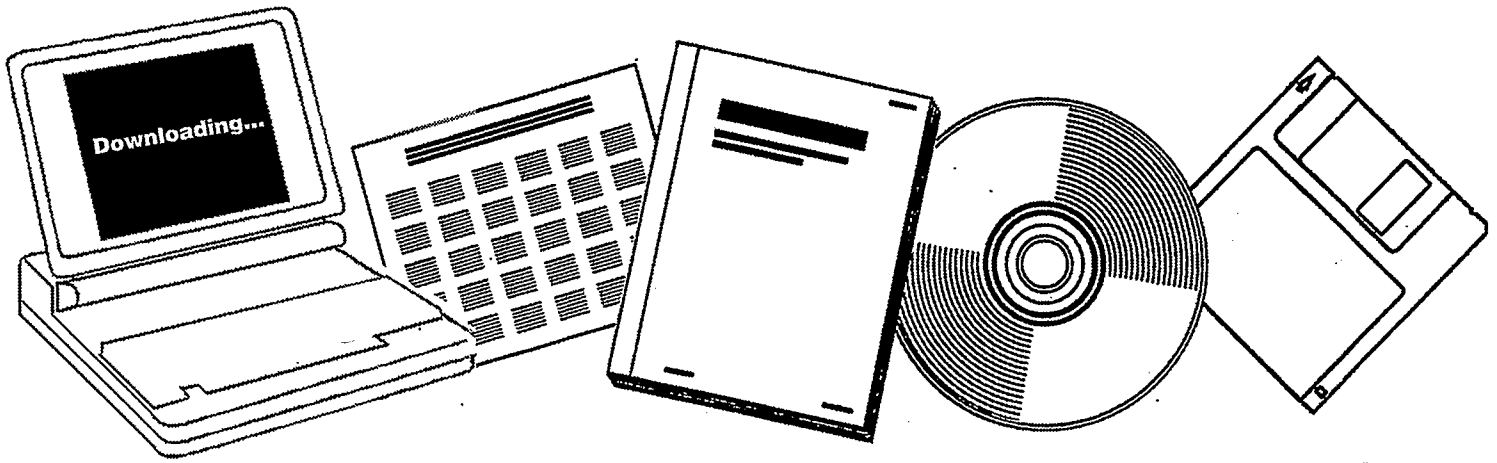
IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS. FIRST QUARTERLY TECHNICAL PROGRESS REPORT, SEPTEMBER-DECEMBER 1984

UNION CARBIDE CORP., TARRYTOWN, NY.
TARRYTOWN TECHNICAL CENTER

1984



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TECHNICAL PROGRESS REPORT
DE-AC22-84PC70028

First Quarterly Report
September - December 1984

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Molecular Sieve Department
Catalysts and Process Systems Division

Union Carbide Corporation
Tarrytown Technical Center
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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 is to be completed by mid-October.

Task 2 consists of techno-economic studies that will supplement those that are presently being carried out by MITRE. These studies are tentatively scheduled to be completed by April, 1985.

Task 3 consists of the optimization of the most promising catalysts developed under prior contract DE-AC22-81PC40077 towards 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 that 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 catalyst 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 run from the eighteenth through the twenty-fourth month of the contract.

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 Process Systems Division, Union Carbide Corporation, in 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

The first draft of Task 1 was submitted in November for review by DOE.

B. Task 2

In conformance with the program schedule, no Task 2 work was done this Quarter.

C. Tasks 3 and 4

A description of the nine catalysts tested this Quarter and their preliminary test results are detailed in Appendix A. Seven of these catalysts were based on intimately mixed Co/UCC-103 and the remaining two catalysts were based on intimately mixed X_3/UCC-103.

The most promising catalyst, Catalyst No. 4, was loaded with an unusually high level of cobalt, and had an initial specific activity of 8, as opposed to the usual 1-3 stabilized specific activities obtained from past catalysts containing less cobalt. However, this high initial specific activity was short-lived, which was not unexpected since the catalyst contained no additives to increase its stability.

Other catalysts were less promising. An attempt at improving gasoline quality by using silicalite as a second shape-selective

component in the Catalyst No. 8 formulation proved unsuccessful. Similarly, an unusually good initial selectivity to C_5^+ products for the X_3 containing Catalyst No. 2 was only transient, and the specific activity for the X_7 containing Catalyst No. 3 was far below average.

Details of all of these runs will be presented in the next Quarterly Report.

D. Task 5

Documentation of the FIXBD7 and BERTY1 computer programs for calculating the performance of an isothermal reactor incorporating reaction rates derived from the Berty reactor data and having a recycle stream with all and none, respectively, of its water and C_5^+ hydrocarbons removed with a condenser/separator, was sent to MITRE for their evaluation of this approach for carrying out the future Task 5 process/catalyst optimization.

MITRE was also sent additional tubular reactor design curves covering catalysts having specific activities as high as 7.0 and usage ratios between 1.4 and 2.0 when operated under conditions limiting the CH_4 production to 9 and 11 weight percent of the total hydrocarbon product.

E. Task 6

Since this final techno-economic evaluation is scheduled to begin in fiscal year 1986, no work was done on it this quarter.

V. CHANGES

There were no contract changes during the First Quarter.

VI. FUTURE WORK

Task 1 will be rewritten to reflect the results of the MITRE study, which has tentatively indicated that the present UCC catalyst/process system is on a par with the existing Arge system. Since a considerably superior performance over that of the existing Arge system is desired, the emphasis will now be on further developing a superior catalyst instead of optimizing the present one.

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

A recommendation will also be made to have MITRE carry out a sequential sensitivity study which will graphically represent 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, α, C_{25}-C_{30} carbon cut-off, over-all conversion, feed H_2/CO ratio, reactor temperature, and reactor pressure.

These differential cost-operating parameter curves could then be used with catalyst performance data and the existing tubular reactor design curve to readily obtain an economic worth for each tested catalyst for any set of process conditions.

Since such an economic quantification would more than meet the objectives of Tasks 2 and 6, these tasks would no longer be needed.

Work on Task 5 will be directed towards incorporating heat generation and heat transfer terms into the presently isothermal mathematical model, and then using it to define upper space velocity limits for different operating pressures.

Albert C. Frost
Program Manager

APPENDIX

Appendix A. CATALYST TESTING

J. G. Miller, L. F. Elek, C-L Yang and P. K. Coughlin

This report is organized around the nine catalytic tests conducted from September 18th through December 1984, the first quarter of this contract.

A list of the catalysts tested and a description of their preparation are shown in Table 1. All but two of the runs (Runs 2 and 9) involve catalysts which have cobalt oxide intimately contacted with UCC-103, and were developed in the previous three-year contract (DE-AC22-81PC40077). The catalysts used in Runs 2 and 9 involve X_3 intimately contacted with UCC-103.

An abbreviated table of results for these catalyst runs is shown in Table 2. The conversion, weight percent CH_4, weight percent C_5^+, specific activity, the methane factor and a qualitative estimate of stability are listed for each catalyst. A more complete report of results and analyses for these runs will be presented in the Second Quarterly Report.

Table 1. Descriptions of the catalysts tested during the first quarter.

Run no.	Catalyst	Catalyst preparation
1	Co/UCC-103+UCC-107 (12185-01)	Cobalt oxide was formed in close contact with UCC-103, the resulting powder was mixed with UCC-107 in a weight ratio of 1.125/1, and the mixture, after bonding with 15% silica, was extruded as 1/8" pellets. Final catalyst contained 6.75% Co.
2	X_3/K/UCC-103+UCC-101 (12200-01)	X_3 and K were formed in close contact with UCC-103, the resulting powder was mixed with UCC-101 in a weight ratio of 1.125/1, and the mixture, after bonding with 15% silica, was extruded as 1/8" pellets. Pct X_3=1.1, pct K=0.45.
3	Co/X_7/UCC-103+UCC-101 (12185-02)	X_7-promoted cobalt oxide was formed in close contact with UCC-103. The resulting powder was mixed with UCC-101 in a weight ratio of 1.125/1, and the mixture, after bonding with 15% silica, was extruded as 1/8" pellets. Pct Co=6.5, pct X_7=1.3.
4	Co/UCC-103 (12185-03)	Cobalt oxide was formed in close contact with UCC-103, after bonding with 15% silica the mixture was extruded as 1/8" pellets. Pct Co=17.0.
5	Co/UCC-103 (12200-02)	Same catalyst as in Run 12185-03 but activated under higher pressure.
6	Co/UCC-103 (12200-03)	Repeat of Run 5 (12200-02).
7	Co/UCC-103 (12185-04)	Same catalyst as Run 4 (12185-03) after attempted regeneration using 5% O_2 in N_2.
8	Co/Th/X_4/UCC-103+S115 (12200-04)	The thorium-promoted cobalt oxide was formed in close contact with UCC-103, then further promoted with X_4. The resulting powder was mixed with S115 in a weight ratio of 1.125/1, and the mixture, after bonding with 15% silica, was extruded as 1/8" pellets. Pct Co=4.4, pct Th=0.6, pct X_4=0.4.
9	X_3/K/UCC-103+UCC-101 (12200-05)	Same procedure as Run 2 (12200-01).

Table 2. Preliminary catalyst test results for the runs made during the first quarter.

Run no.	Catalyst	Hours on stream	Total conversion ($CO+H_2$)	CH_4 wt %	C_5^+ wt %	Specific activity	Methane factor(1)	Stability
1	Co/UCC-103+UCC-101 (12185-01)	- - - - - - - - - - - Inactive - - - - - - - - - - -						
2	X_3/K/UCC-103+UCC-101 (12200-01)	43.5*	15.6	21.4	56.4	.38	3.13	Poor
		164.5	20.3	10.7	68.1	.18	5.32	
3	Co/X_7/UCC-103+UCC-101 (12185-02)	41.1	35.6	19.2	61.7	.40	3.61	Fair
		89.5	32.1	21.1	58.0	.36	4.52	
4	Co/UCC-103 (12185-03)	43.3*	71.7	19.2	65.7	15.34(2)	5.51	Fair
		234.5	56.5	20.2	66.4	1.82	6.70	
5	Co/UCC-103 (12200-02)	- - - - - - - - - - Inactive - - - - - - - - - -						
6	Co/UCC-103 (12200-03)	- - - - - - - - - - Inactive - - - - - - - - - -						
7	Co/UCC-103 (12185-04)	46.0	31.8	19.5	63.3	.35	4.52	---
8	Co/Th/X_4/UCC-103+S115 (12200-04)	42.5	53.3	10.1	75.9	1.06	2.92	Good
		306.5	49.2	13.4	72.0	.71	4.15	
9	X_3/K/UCC-103+UCC-101 (12200-05)	22.0**	14.0	12.9	69.5	.56	5.85	Poor

Conditions: 300 psig, 260C, 300 GHSV, except as noted below.
*100 psig, 260C, 300 GHSV.
**100 psig, 250C, 300 GHSV.
(1) The ratio of the amount of CH_4 actually produced to the amount of CH_4 predicted from the Schulz-Flory equation $[CH_4/(1-\alpha)^2]$.
(2) Equivalent to ~8 when adjusted to a 300 psig pressure.

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