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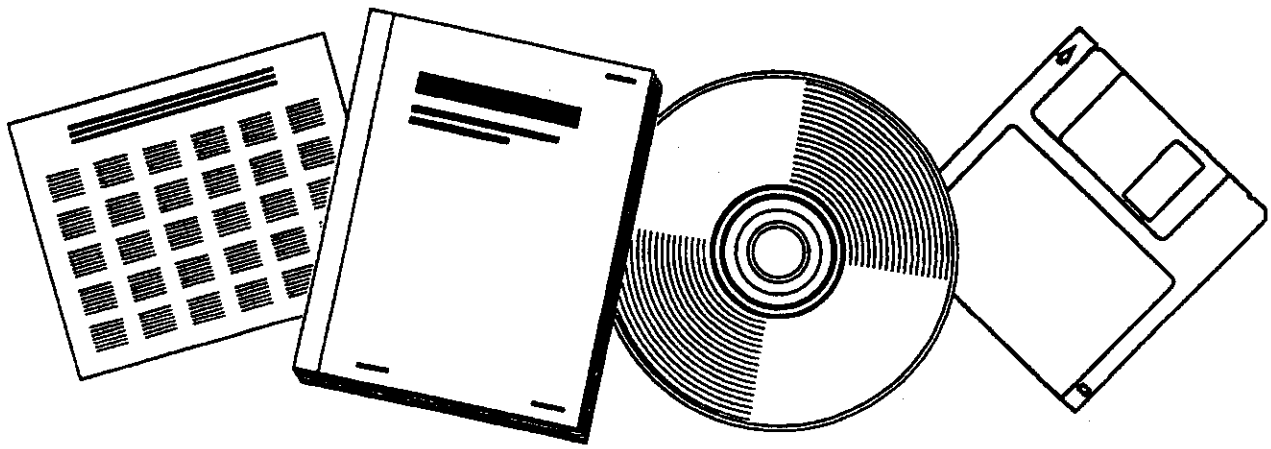
# IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS: NINTH QUARTERLY TECHNICAL PROGRESS REPORT, OCTOBER-DECEMBER 1986

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

1987



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TECHNICAL PROGRESS REPORT
DE-AC22-84PC70028

Ninth Quarterly Report
October-December 1986

# IMPROVED CATALYSTS FOR LIQUID HYDROCARBON FUELS FROM SYNGAS



Molecular Sieve Department
Catalysts and Services Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

Contents



Appendixes

## 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 initially planned for the twenty-eight month period beginning September 18, 1984. The completion date has since been extended to January 17, 1988.

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 is conducting on an updated version of their previously 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 entire duration 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 entire duration 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 entire duration 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 Thirteenth 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. A. 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 an updated version of their previously 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, C23-C30 carbon cutoff, overall conversion, feed H2: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 simulated process operating curves to readily obtain an conomic worth for each tested catalyst for any set of envisioned parameters.

C. Tasks 3 and 4

The catalyst testing effort during this quarter was focused primarily on further developing the Co/X11/X9/TC-123 catalyst system (run 55, Seventh Quarterly Report, Appendix B) previously reported.

Five of the six experiments screened the effects of varying the formulation procedure. Runs # 68, 70, and 73 not only tested a new variation in the formulation procedure, but they also examined the effect of increasing the promoted cobalt oxide loading. Preliminary results showed that the new formulation procedure gave a catalyst which performed slightly better than catalyst # 55 in both activity and selectivity. The initial stability was found to be inferior, but it improved with time to a level that was superior. Increasing the cobalt oxide levels by 1.24 % and 1.5 % with the new formulation procedure demonstrated little or no performance benefits. Runs # 69 and 72 further tested the effect of the calcination procedure used during the catalyst formulation. These results, combined with the results of run # 67 (described in Appendix B), showed that the original calcination procedure used in run # 55 was the best.

A new additive, X14, was evaluated as a cobalt oxide promoter (run # 71), but it was found to be inferior to the X11 promoted catalysts.

D. Task 5

This Quarter's Task 5 work centered on detailing how the rate and selectivity correlations, used in the calculation of the technical data sent to Mitre for their ongoing economic evaluation, were determined from run # 45 data. This work is described in Appendix C.

E. Task 6

The economic evaluation of Catalyst 45 under various sets of operating conditions will begin when Mitre has completed the sensitivity curves which are to compliment their soon-to-be-completed base case study of Catalyst 45.

## V. CHANGES

The contract completion date has been extended by twelve (12) months to January 17, 1988. This extension shall not increase the total $ 2,399,683 cost of the contract.

## VI. FUTURE WORK

Tasks 3 and 4 will continue to be devoted to developing new catalyst formulations which will have higher stabilities or resistance to regenerations than do the present UCC catalysts.

Task 5 will continue to be devoted to examining various operating conditions for Catalyst 45.

Albert C. Frost

## APPENDIX A. CATALYST TESTING: SUMMARY OF RUNS REPORTED DURING THIS QUARTER

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J. G. Miller, C-L Yang, and K. N. Beale

This report is organized around the six (6) catalyst tests conducted from October through December 1986, the ninth quarter of the contract.

A list of the catalysts tested, a description of their preparation, and a brief statement of each test's objective are shown in Table A1. All the catalysts tested this quarter involved promoted cobalt oxide intimately contacted with the molecular sieve support TC-123.

Three of the runs (68, 70, 73) investigated a variation in the formulation procedure used for catalyst # 55 described in the Eighth Quartely Report. These runs also tested the effect of the cobalt oxide loading on catalyst performance. Catalyst runs # 69 and # 72 examined the effect of calcining on the performance of catalyst # 55 (discussed in Appendix B of this report for catalyst # 67), and run # 71 examined the effect of a new promoter, X14.

An abbreviated table of results for these catalyst runs is shown in Table A2. The conversion, weight percent methane, weight percent C5 plus, specific activity and methane ratio, as well as qualitative estimates of stability, are listed for each catalyst. A more complete report of the results and analyses of these runs will be presented in the Tenth Quartely Report.

Table A1. Description of catalysts tested during the ninth quarter

| Run | Catalyst | Catalyst preparation | Objective |
|---|---|---|---|
| 68 | Co/X11/X9/ TC-123 (12570-07) | The X11,X9 promoted cobalt oxide catalyst was prepared using a new formulation procedure. The theoretical cobalt and promoter were the same as those for Catalyst # 55, Co = 8.2 %, X11 = 1.6 %, X9 = 1.1 % | To test the effect of a new formulation procedure. |
| 69 | Co/X11/X9/ TC-123 (12561-12) | The X11,X9 promoted cobalt oxide catalyst was formulated similarly to Catalyst # 55, except that the calcination procedure was varied. Cobalt and promoter levels were as in Catalyst # 55 (see above). | To test the effect of the calcination procedure. |
| 70 | Co/X11/X9/ TC-123 (12570-08) | The X11,X9 promoted cobalt oxide catalyst was prepared using a formulation procedure similar to that used for Catalyst # 68. The theoretical Co = 10.3 %, X11 = 2.0 %, and X14 = 1.4 %. | To test the effect of increased metal loading for this formulation |
| 71 | Co/X14/ TC-123 | The X14 promoted cobalt oxide catalyst was prepared similarly to Catalyst # 37, except that X14 was substituted in place of X9. Theoretical Co = 8.2 %, X14 = 1.4. | To test the effect of the X14 promoter on catalyst performance |
| 72 | Co/X11/X9/ TC-123 (12561-14) | The X11, X9 promoted cobalt oxide catalyst was formulated similarly to Catalysts # 55 and 67, except that the calcination procedure was varied. Theoretical Co = 8.0 %, X11 = 1.6 %, X9 = 1.1 %. | To test the effect of the calcination procedure. |
| 73 | Co/X11/X9/ TC-123 (11617-14) | The X11,X9 promoted cobalt oxide catalyst was prepared using the the formulation procedure used for Catalysts # 68 and 70. Theoretical Co = 12.0, X11 = 2.4 %, X9 = 1.7 %. | To test the effect of increasing the cobalt metal for this type of catalyst formulation. |

TABLE A2: Preliminary Test Results for Catalyst Runs Made During the Ninth Quarter

| Run No. | Catalyst | Hours on | Total Cnvrsn. | CH4 wt% | C5+ wt% | Spcfc. Actvty (1) | CH4 Ratio (2) | Condi-tions | Stab-ility |
|---|---|---|---|---|---|---|---|---|---|
| 68 | Co/X11/X9 TC-123 (12570-07) | 116.5 | 46.5 | 2.4 | 89.8 | 0.95 | 0.91 | (3) | Good |
| | | 332.0 | 41.8 | 2.8 | 88.7 | 0.80 | 0.86 | | |
| | | 356.0 | 75.0 | 11.3 | 77.1 | 0.57 | 2.10 | (4) | Good |
| | | 735.5 | 68.2 | 10.8 | 78.2 | 0.45 | 2.05 | | (5) |
| 69 | Co/X11/X9 TC-123 | 121.0 | 42.1 | 4.7 | 86.5 | 0.93 | 0.88 | (3) | |
| | | 169.0 | 41.4 | 4.6 | 85.3 | 0.92 | 0.87 | | |
| | | | (mechanical failure ended run) | | | | | | |
| 70 | Co/X11/X9 TC-123 (12570-8) | 46.0 | 40.6 | 4.0 | 85.9 | 0.94 | 1.22 | (3) | Exclt |
| | | 241.0 | 39.9 | 3.9 | 84.8 | 0.85 | 1.00 | | |
| | | 261.0 | 71.6 | 8.8 | 80.8 | 0.82 | 1.66 | (4) | Good |
| | | 431.0 | 74.1 | 11.7 | 76.2 | 0.61 | 1.89 | | |
| 71 | Co/X14/ TC-123 | 42.5 | 32.8 | 7.9 | 83.1 | 0.48 | 1.15 | (3) | Poor |
| | | 187.0 | 21.0 | 11.4 | 75.4 | 0.32 | 1.54 | | |
| 72 | Co/X11/X9 TC-123 (12561-14) | 114.5 | 44.6 | 4.4 | 85.9 | 0.98 | 0.98 | (3) | Exclt |
| | | 259.0 | 42.4 | 5.1 | 84.8 | 0.92 | 1.05 | | |
| | | 477.5 | 37.7 | 5.6 | 83.3 | 0.88 | 1.16 | (3a) | Exclt |
| | | 600.0 | 37.8 | 5.5 | 84.5 | 0.87 | 1.19 | | |
| 73 | Co/X11/X9 TC-123 (11617-14) | 68.0 | 44.0 | 3.7 | 89.3 | 1.01 | 0.88 | (3) | Good |
| | | 309.0 | 38.0 | 4.2 | 87.9 | 0.86 | 0.93 | | |
| | | 410.0 | 76.5 | 13.3 | 74.8 | 0.62 | 1.83 | (4) | |

Conditions: (1) Ratio of the actual syngas consumption of the tested catalyst to the calculated syngas consumption of Catalyst No. 45 at the same operating conditions.
(2) Ratio of the actual methane make of the tested catalyst to the calculated methane make of Catalyst No. 45 at the same operating conditions.
(3) 240 C, 300 psig, 1:1 H2:CO (3a-small H2 upset)
(4) 260 C, 500 psig, 1.5:1 H2:CO
(5) Demonstrated excellent stability for the last 140 hours of the test.

## APPENDIX B. CATALYST TESTING: DETAILS OF RUNS INITIALLY REPORTED DURING LAST QUARTER

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Contents

## I. INTRODUCTION

Presented in this report are detailed analyses of the six catalyst test runs summerized previously in Appendix A of the Eighth Quarterly Report, which constituted the major thrust of the work during that quarter.

All six of the catalysts contained promoted cobalt metal in close contact with a molecular sieve support, and were formulated by the method first used in Catalyst No. 11 (Run No. 12185-07 of the Third Quarterly Report).

Three of the runs, numbers 62, 64, and 66, examined the utility of the new molecular sieves TC-201, TC-211 and TC-12365 as promoted cobalt Fischer-Tropsch metal supports.

The remaining catalysts utilized molecular sieve TC-123 as the catalyst support and probed the effects of the previously reported promoters X11 and X9 (run no. 65), variations in the calcination procedure (run no. 67), and variations in the testing conditions (run no. 63).