



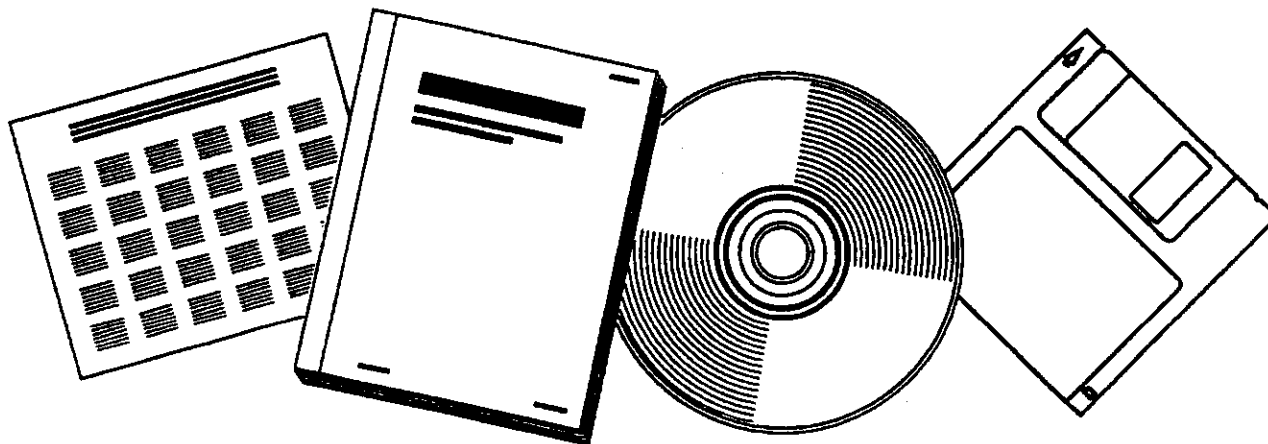
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**LIQUID HYDROCARBON FUELS FROM SNYGAS.
THIRTEENTH QUARTERLY PROGRESS REPORT,
MARCH-MAY 1984**

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

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Thirteenth Quarterly Report
March - May 1984

LIQUID HYDROCARBON FUELS FROM SYNGAS

Molecular Sieve Department
Catalysts and Process Systems Division

Union Carbide Corporation
Tarrytown Technical Center
Tarrytown, New York 10591

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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, essentially 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 the surface effects and reaction intermediates present on various catalysts during the hydrogenation of carbon monoxide 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

The work during the period March through May 1984 was in pursuit of two objectives: 1. To explore variations on the most promising catalyst developed to date (Catalyst 6, Co/Th/X₄/UCC-103+UCC-101, Run 11677-11 of the Third Annual Report) with the aim of improving on its effectiveness and stability still further. 2. To try to develop a water gas shift catalyst which would function effectively in combination with a Fischer-Tropsch catalyst.

Twelve catalysts were tested, of which four were thorium-promoted cobalt Fischer-Tropsch catalysts combined with intimately mixed Molecular Sieves as the shape selective components. Eight were water gas shift catalysts, three tested alone and five tested in combination with Fischer-Tropsch components.

The Fischer-Tropsch catalysts, all thorium-promoted cobalt, differed mainly in method of preparation, the intimately mixed Molecular Sieve component, reduction temperature, and cobalt loading level. One was further promoted with X₄. All four for-

mulations included UCC-101 as a physically mixed component.

The water gas shift catalysts were zinc-promoted copper in combination with either alumina or one of two Molecular Sieves. Three were tested alone, and five in combination with thorium-promoted cobalt Fischer-Tropsch catalysts. Zeolite A was also incorporated to test whether it might shield the water gas shift components from deactivation, presumably from some of the Fischer-Tropsch products or their intermediates.

For a detailed description of the composition and preparation of each catalyst tested, and details of the test results, see the Appendix.

Tables of results from the individual runs have been refined to include three new data items: feed H_2/CO from effluent, specific activity, and residual H_2/CO ratio. See Appendix Section I, Introduction.

Fischer-Tropsch Test Results

None of the Fischer-Tropsch catalysts tested approached Third Annual Report Catalyst 6 in conversion, selectivity or stability. The results did, however, shed light on some factors which may have contributed to its effectiveness.

When the X_4 was omitted, and the reduction temperature was 400C (Catalyst 1, Run 11723-10), the stability decreased to a level comparable to that of cobalt catalysts without the physically mixed UCC-101. Reducing the same catalyst at 350C (Catalyst 2, Run 11677-14) produced some improvement in selectivity. When the UCC-101 was substituted for UCC-103 as the intimately

mixed Molecular Sieve component (Catalyst 3, Run 11723-14), there was almost no water gas shift activity and the conversion and selectivity deactivated more slowly--in contrast to the greater stability found earlier for a Co/Th/UCC-103 catalyst (Run 7, Eleventh Quarterly Report) over that of a Co/Th/UCC-101 catalyst (Run 1, Third Annual Report). And when the X₄ was taken from a different source, which turned out to contain deleterious volatiles, the high calcination temperature required to remove the volatiles seriously impaired both the conversion and the selectivity.

These findings, when compared with themselves and with similar past runs, suggest (a) that X₄ is essential to the stability of Third Annual Report Catalyst 6; (b) that additional, physically mixed UCC-101 is not; and (c) that the X₄ must be obtained from a source which is free of known catalyst poisons or can be rendered free of such components without destroying the cobalt's Fischer-Tropsch activity.

Water Gas Shift Test Results

All of the eight tests for an improved copper-zinc water gas shift catalyst, which would function effectively in combination with a Fischer-Tropsch catalyst, resulted in failure.

One test of a water gas shift catalyst alone (Catalyst 5, Run 11677-13, Cu/Zn/Al+UCC-101) showed some initial promise although it deactivated rapidly. But when the UCC-101 was replaced by LZ-105-6, an acidic zeolite which resists coking and is used for the conversion of small olefins, the water gas shift activity disappeared almost entirely. This was true both when the LZ-105-6

was loaded in one step with the copper and zinc (Catalyst 8, Run 11677-20) and when the LZ-105-6 was zinc-ion exchanged before being loaded with copper (Catalyst 9, Run 11677-21).

Five trials were run of a water gas shift catalyst in combination with a Fischer-Tropsch catalyst; these were equally fruitless. The water gas shift catalysts were again copper and zinc with either alumina, zeolite LZ-105-6, or zeolite A.

In Catalyst 6 (Run 11723-11, Co/Th/Cu+UCC-101+Cu/Zn/Al) the cobalt-thorium was further promoted with copper in order to lower its reduction temperature, although it is known that copper impairs a catalyst's stability. The objective was to test the initial activity of the water gas shift component, which had demonstrated a fair degree of activity in an earlier run, when used with a Fischer-Tropsch catalyst. While there was some water gas shift activity, it was inferior to that of other similar catalysts which lacked both the copper and the water gas shift component.

Catalyst 7 (Run 11723-12) contained a Fischer-Tropsch component in combination with the water gas shift catalyst Cu/Zn/Al as a separate extrudate. But its water gas shift activity was not significantly better than that of the Fischer-Tropsch component alone in Catalyst 1.

The same was true of Catalyst 10 (Run 11677-18, Co/Th/UCC-103+Cu/Zn/LZ-105-6), in which the Fischer-Tropsch component was similar to Catalyst 7 (Run 10225-16) of the Eleventh Quarterly Report. However, the conversion, specific activity and selec-

tivity of this catalyst all improved with time, albeit slowly; another few hundred hours on stream, assuming the same rate of increase, would bring its effectiveness up to substantial levels.

Catalysts 11 and 12 (Co/Th/UCC-103+UCC-101+Cu/Zn/A) incorporated zeolite A to test whether the small size of the zeolite pores might shield the copper and zinc from some of the Fischer-Tropsch intermediates and products, while allowing these water gas shift components to react with carbon monoxide and water. In Catalyst 11 (Run 11723-13) the copper and zinc were loaded into the zeolite A together; in Catalyst 12 (Run 11677-19) the zinc was ion-exchanged into the zeolite A before loading the copper. There was no water gas shift activity with either catalyst.

These trials have produced the paradoxical result that when a water gas shift catalyst was combined with a Fischer-Tropsch catalyst--both of which have independently demonstrated water gas shift activity--the water gas shift activity of both was sharply curtailed or eliminated entirely. Each, in short, appeared to deactivate the other.

One useful insight derived from these test is the response of the specific activity term to different temperatures and to different ratios of hydrogen and carbon monoxide in the feed. See Appendix Section XII, Run 11, for a discussion of this finding.

V. CHANGES

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

VI. FUTURE WORK

Efforts during the next 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.



A. C. Frost

APPENDIX

Appendix. CATALYST TESTING

P. K. Coughlin, C. L. Yang, G. N. Long and L. F. Elek

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I. INTRODUCTION

This report presents the results of twelve tests conducted during the Thirteenth Quarter of the contract, February through April, 1984. The first four were with cobalt Fischer-Tropsch catalysts, three of which were directly related to the most stable catalyst reported thus far--Catalyst 6 (Run 11677-11) of the Third Annual Report (Co/Th/X₄/UCC-103+UCC-101). Runs 1 and 2 were with a similar catalyst except omitting the X₄. Run 3 was with a catalyst like that in Runs 1 and 2 except that the UCC-103 was replaced by UCC-101 as the intimately mixed component. Run 4 was with a catalyst containing X₄ from a different source.

The eight other runs were with copper-zinc water gas shift catalysts, either alone in Runs 5, 8 and 9, or in combination with Fischer-Tropsch active components in the remaining runs. This also is a continuation of work reported in the Third Annual Report.

The tables of results have been modified slightly to incorporate three new items of data. One is the feed H₂/CO from effluent. This is the ratio of hydrogen to carbon monoxide in the feed based on a material balance of the products, and is a check on the assumed feed ratio.

Another is the specific activity, a measure of the catalyst's intrinsic activity based on a model for the conversion of syngas

calculated from previous data; the model, and the regression analysis used to calculate it, will be reported later. For the present, the specific activity provides a way to compare catalysts tested at different temperatures and at different H₂:CO ratios inside the Bertly reactor. It was found, during the modeling, that conversion is very much a function of both the hydrogen and the carbon monoxide pressures, the carbon monoxide pressure having a negative exponent.

The third new number is the residual H₂/CO ratio, the ratio of hydrogen to carbon monoxide inside the Bertly reactor. This has been discussed in previous reports, but not reported explicitly in the tables. With the results of the modeling, and the importance of maintaining catalyst stability in a low hydrogen environment, this measure has become more significant.

II. Run 1 (11723-10) with Catalyst 1 (Co/Th/UCC-103+UCC-101)

This catalyst is a modified version of Third Annual Report Catalyst 6 (Run 11677-11)--an exceptionally stable catalyst which did not measurably deactivate during the last 200 hours of its run. It differs from that catalyst in containing no X₄ and nearly twice as much cobalt.

The thorium-promoted cobalt metal component was formed in contact with UCC-103. The metal-loaded UCC-103 was combined with UCC-101 in a ratio of 9:8, bonded with 15 weight percent SiO₂, and formed as an extrudate. The final catalyst contained approximately 8 percent cobalt, and was activated at 400C under H₂ instead of the usual 350C.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. 1-4. Simulated distillations of the C₅⁺ product are plotted in Figs. 5-10. Carbon number product distributions are plotted in Figs. 11-21. Detailed material balances appear in Tables 1-4.

All but the last two samples were tested at 262-265C. Both conversion and selectivity were fairly steady throughout the test. The syngas conversion was 70 percent at the beginning of the run, and after 214 hours on stream had decreased only to 61 percent. By linear least squares analysis, the deactivation rate

was 0.04 percent per hour on stream, or a little less than one percent per day. A correlation coefficient of -0.92 assured that at a confidence level of 99.9 percent, this deactivation rate was real. During the last 100 hours on stream, however, the correlation coefficient was so much lower (-0.30) as to suggest that the deactivation in this period was small compared to the scatter in the data. The overall deactivation rate is similar to that of Catalyst 7 (Run 10225-16) from the Eleventh Quarterly Report, which also contained Co/Th/UCC-103 but no UCC-101 and a higher level of cobalt (about 10 percent). The addition of physically mixed UCC-101 has previously been shown to have little effect on selectivity; evidently it contributes little if anything to stability as well.

Production of methane was less than 12 percent initially, which is low for a cobalt catalyst, but increased steadily, at 0.016 percent per hour or one percent every 62.5 hours, to exceed 15 percent after 200 hours on stream. The methane production of Catalyst 6 from the Third Annual Report, in comparison, was steady at more than 13 percent. Since the C₂-C₄ fraction was almost constant throughout the run, the production of C₅⁺ varied inversely with that of methane, from 76 percent initially to about 71 percent after 200 hours on stream. The C₅⁺ product, meanwhile, grew heavier with time: the 700+F fraction increased one percent every 51 hours, and the ratio of diesel fuel to gasoline grew steadily higher (see Figs. 5-10, the C₅⁺ distillation curves).