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LIQUID HYDROCARBON FUELS FROM SYNGAS

Molecular Sieves      ment, Engineering Products Division  
Carbide Corporation  
Tarrytown Technical Center  
Tarrytown, New York

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## I. CONTRACT OBJECTIVE

The objective of the contract is to develop a catalyst and to select 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 is planned for a thirty-six month period, which started March 6, 1981. The work on the program is divided into four tasks. In Task 1, shape-selective catalysts (SSC's) are being evaluated for converting low molecular weight liquids such as methanol and propylene to desired products including gasoline, turbine and diesel fuel. In Task 2, the feed is syngas ( $\text{CO} + \text{H}_2$ ), and the catalyst is a combination of transition metal component (MC) and SSC. Task 3 is a study of surface effects and reaction intermediates during the hydrogenation of carbon monoxide, carried out as a subcontract under the direction of Dr. Gabor A. Somorjai, of U.C. Berkeley. Task 4 is a series of management and technical reports.

## III. ORGANIZATION

"Liquid Hydrocarbon Fuels from Syngas" is the goal of a research and development program on catalysts carried out by the Molecular Sieve Technology Department of the Engineering Products Division, Union Carbide Corporation at their Tarrytown Laboratories. Principal investigator is Dr. Jule A. Rabo. Program manager is Dr. Richard C. Eschenbach.

#### IV. PROGRESS SUMMARY

##### TASK 1

Initial Task 1 tests used methanol as the feed. It was found that catalysts of interest tended to make highly methylated aromatics in the Bertly reactor. Although a simulated distillation showed that these products boiled in the gasoline and diesel range, most were solid at room temperature. Aromatic products frequently are desirable constituents of gasoline, but highly methylated aromatics which precipitate at the concentrations found are undesirable. Since small olefins are products and intermediates in reactions over Fischer-Tropsch catalysts, propylene was chosen as feedstock to replace methanol. Hydrogen and water were used in conjunction with propylene to aid in maintaining system pressure and to reduce deactivation rates, respectively.

A standard test was developed, feeding a mix of  $H_2$ ,  $C_3H_6$  and  $H_2O$  at proportions of 1:1:2, a pressure of 150 psig and temperatures of 280°C and 340°C. At these conditions, LZ-105-6 and Tarrytown synthesized "ZSM-5" catalysts were quite active and selective to gasoline range products. Deactivation was low. UCC-101 and UCC-109, proprietary molecular sieves, have larger pores than LZ-105-6 and ZSM-5; both are less active in propylene oligomerization than the first two. It was discovered that two related new molecular sieves, UCC-104 and 108, were even more selective to gasoline range products than "ZSM-5" or LZ-105, with over 95% of the product in the gasoline range. A classic faujasite-type zeolite, LZ-Y-82, was found to deactivate quite rapidly in propylene oligomerization. Another faujasite, Y-62, was somewhat better. Table 1 below shows results at nearly comparable conditions.

Additional details on Task 1 results, and data from such runs in the most recent quarter, are presented in Appendix C.

# TASK 1

## TEST SUMMARY

$H_2:C_3H_6:H_2O$  @ 0.5 hr.<sup>-1</sup> WHSV on  $C_3H_6$ , 150 psig, 280°C, 24 Hours on Stream

| <u>CATALYST</u> | <u>UCC-</u>     |                 |                |             |             |             |             |             |             |             |
|-----------------|-----------------|-----------------|----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
|                 | <u>LZ-105-6</u> | <u>H-ZSM-5*</u> | <u>ZSM-5**</u> | <u>UCC-</u> | <u>UCC-</u> | <u>UCC-</u> | <u>UCC-</u> | <u>UCC-</u> | <u>UCC-</u> | <u>UCC-</u> |
|                 |                 |                 |                | <u>101</u>  | <u>109</u>  | <u>104</u>  | <u>108</u>  | <u>Y-82</u> | <u>Y-62</u> |             |

|                   |       |       |       |       |       |       |       |       |       |       |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $H_2:C_3H_6:H_2O$ | 1:1:2 | 1:1:2 | 1:1:2 | 1:1:3 | 1:1:2 | 2:1:1 | 1:1:2 | 1:1:2 | 1:1:2 | 1:1:2 |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|

|                       |    |    |    |   |   |    |    |   |    |  |
|-----------------------|----|----|----|---|---|----|----|---|----|--|
| Average Conversion, % | 94 | 91 | 68 | 7 | 9 | 62 | 68 | 5 | 11 |  |
|-----------------------|----|----|----|---|---|----|----|---|----|--|

Total Converted

Hydrocarbons:

%  $C_5^+$

% 420-700°F

|    |    |    |    |    |    |    |    |    |  |
|----|----|----|----|----|----|----|----|----|--|
| 89 | 88 | 86 | 52 | 77 | 90 | 96 | 66 | 82 |  |
| 6  | 10 | 5  | 4  | 10 | .8 | 3  | 0  | 2  |  |

|         |         |         |         |        |             |        |         |         |             |
|---------|---------|---------|---------|--------|-------------|--------|---------|---------|-------------|
| Run No. | 9972-13 | 9972-20 | 9972-18 | 9972-4 | 10112<br>-1 | 9972-7 | 9972-22 | 9972-19 | 10112<br>-3 |
|---------|---------|---------|---------|--------|-------------|--------|---------|---------|-------------|

\*  $SiO_2/Al_2O_3$  about 35

\*\*  $SiO_2/Al_2O_3$  about 85

## TASK 2

Catalysts for syngas feed have a metal component (MC) and a shape-selective component (SSC). Four techniques have been used in synthesizing our bi-functional catalysts. Appendix A summarizes recent synthesis work. Physical mixtures (e.g. Fe+UCC-101) have usually worked quite well. Metal pore-filled or precipitated on an SSC has worked in some cases, but not in others. To date, we have had little success with carbonyl deposition, although additional work is planned.

An extensive run with a reference potassium-promoted iron catalyst helped to choose conditions appropriate for our "standard" test. A number of runs were made with iron, potassium-promoted iron or cobalt loaded SSC's, (and one with  $\alpha$ -alumina). Detailed results are given in Appendix C. Progress in analytical techniques is summarized in Appendix B.

The data presented show that catalysts and conditions have been found which enable converting 1:1 H<sub>2</sub>/CO syngas feed at reasonable conversions in one step to motor fuel range products with quite acceptable selectivity to C<sub>5</sub><sup>+</sup> products. Table 2 below shows the results after 72 hours of operation with four catalysts. Achievement of quasi steady-state conditions in the "standard test" takes about three days because the heavier hydrocarbons formed tend to build up in the reactor for two to three days before emerging at their true concentration in the product stream.

Two effects should be noted. The molecular sieves used reduced the high boiling (wax) component of the product as compared to physical mixture with the relatively inert  $\alpha$ -alumina. Also the quality of the gasoline range product with the molecular sieve is much better than with the F-T type catalyst.

One run was made with a catalyst made with UCC-108 (shown in Task 1 tests to be more active than UCC-104 and similarly selective). However, the catalyst was made by precipitation of iron and potassium on the UCC-108, rather than by being physically mixed. It was found that the precipitation technique resulted in an almost inactive catalyst. Other methods of combining MC with UCC-108 will be tried.

TABLE 2  
SYNGAS OPERATION

(12L/hr. H<sub>2</sub>, 12L/hr. CO, ~300 psig, ~250°C)

Iron Catalysts Were Physical Mixtures, Cobalt was Pore-Filled

| <u>Run No. 10011-</u>              | <u>15</u>                                | <u>8</u> | <u>9</u> | <u>14</u> | <u>10</u> |
|------------------------------------|--|----------|----------|-----------|-----------|
| MC                                 | Fe/K                                     | Fe/K     | Fe/K     | Co        | Fe/K      |
| SSC                                | $\alpha$ -Al <sub>2</sub> O <sub>3</sub> | UCC-101  | UCC-101  | UCC-101   | UCC-104   |
| Hours on Stream                    | 75                                       | 72       | 75       | 68*       | 73        |
| Conversion, % (CO+H <sub>2</sub> ) | 64                                       | 78       | 31       | 42        | 76        |
| Hydrocarbon Product:               |  |          |          |           |           |
| Wt. % C <sub>5</sub> -420°F        | 36                                       | 37       | 38       | 44        | 34        |
| Wt. % 420-700°F                    | 21                                       | 8        | 14       | 24        | 7         |
| Wt. % 700°F-end pt.                | 11                                       | 3        | 5        | 7         | 2         |
| Comments on Chromatogram           | (1)                                      | (2)      | (2)      | (2)       | (3)       |

(1) Only n-alkanes and n-alkenes

(2) Partly n-alkanes, part n-alkenes, part iso-alkanes and alkenes

(3) Highly isomerized alkanes and alkenes.

\* Run 14 had 75 hours at 220°C, then 68 hours at 250°C.

### TASK 3

At the University of California, Berkeley, three researchers have been using the techniques of surface science to study catalysts of interest in syngas conversion, working under the direction of Professor Gabor Somorjai. To date, the work has concentrated on several fundamental aspects of Fischer-Tropsch catalysts (see Appendix D).


In work with rhodium compounds, the oxidation state of rhodium at the active sites was correlated with the observed product distribution. Methane was a major product in all cases, but the distribution of the balance varied among alkanes, alkenes and oxygenates. Promoted thorium compounds were found to produce methanol at high rates. Effects of potassium promotion in CO hydrogenation over iron are explained in terms of co-adsorption. The last part of Appendix D describes work with CO hydrogenation on model Re, Fe, Pt and Pd catalysts.

### V. CHANGES

During this second year of the contract, two modifications were implemented, increasing the obligation to the fully funded level.

### VI. FUTURE WORK

Work during the third and last year of the contract will focus on optimizing Task 2 catalysts and on measuring the quality of the LHF's produced.

  
R. C. Eschenbach

RCE/eh