

I. CONTRACT OBJECTIVES

The objectives of this contract are to discover and evaluate the catalytic properties of novel homogeneous, heterogeneous, or combination catalytic systems for the production of alcohol fuel extenders from syngas, to evaluate analytically and on the bench scale novel reactor concepts for use in converting syngas to liquid fuel products, and to develop on the bench scale the best combination of chemistry, reactor, and total process configuration to achieve the minimum product cost for conversion of syngas to liquid fuel products.

II. SCHEDULE

This program is planned as a 33-month research and development effort, extending through September, 1989.

The contract work is composed of three tasks. Task 1, the preparation of a Project Work Plan, has been completed. Task 2 comprises the chemical investigation of novel and existing catalysts for the production of fuel alcohols from syngas, either directly or through a step-wise process. Task 3 consists of engineering activities which will support the chemical investigations, develop economic evaluations and process conceptualization, and evaluate catalysts in a bench-scale apparatus. Tasks 2 and 3 will proceed for the entire duration of the program.

During the first year of Task 2, research is being directed largely toward the homogeneous catalytic conversion of syngas to fuel alcohol products, including methanol homologation. Simultaneously, some research is being conducted on heterogeneous catalysts for the production of alcohol products from syngas.

During the second year of Task 2, catalyst systems which have been identified in earlier work as having the best characteristics will be investigated in more detail. These studies may include both homogeneous and heterogeneous systems. Chemical studies at this stage will also support the engineering efforts of Task 3.

In the final 9 months of Task 2, chemical investigations will largely serve to provide guidance to the engineering evaluations, and will include fundamental studies and process-related activities.

Task 3 work during the first year involves engineering support for the chemical investigations, and seeks to quantify the economic impact of any developments to guide the research

in the optimum direction. Economic evaluations of a base case process for conversion of syngas to fuel alcohols have also begun.

Work in Task 3 during the second year will involve bench-scale experiments with selected catalytic systems, the development of kinetic and empirical models, and continuing economic and process conceptualization studies.

During the last 9 months of Task 3, the work will focus on catalyst stability studies, validations of models, and the synthesis of the best combination of catalyst and reactor systems.

III. ORGANIZATION

The development of an optimum process for alcohol fuels from syngas is the goal of a research and development program conducted by the Engineering, Manufacturing and Technology Services Division of Union Carbide Corporation.

The work is performed at Union Carbide Corporation's South Charleston Technical Center, South Charleston, West Virginia 25303.

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IV. SUMMARY OF PROGRESS

A. Task 2: Catalyst Research

Studies of catalyst lifetime with the methanol homologation system in small-scale batch reactions have been completed. Our most recent results confirm our previous suspicions that the halt in gas uptake during reaction is due to the buildup of volatile materials in the reactor. Methane, ethers, and acetaldehyde all contribute to a lowering of the syngas partial pressure during the course of the homologation. These studies show that within the timescale of our experiments (ca. 10 h), no catalyst decomposition is detected. Longer lifetime studies will need to be made in continuous type reactors rather than the batch reactors in which we now operate.

The two catalyst components isolated from the reactor at the end of the homologation experiments have now been conclusively identified. In addition, we have shown that these components can be charged to the reactor instead of the normal catalyst charge and used to homologate methanol with no loss in activity or selectivity. These observations strongly suggest that these complexes are active intermediates in the homologation reaction.

Our investigations into the mechanism of this reaction have also been very informative. We have shown that a complex we have isolated may be directly responsible for the novel homologation activity of this catalyst. We have also shown that we may be operating above the solubility limit of this complex under the reaction conditions. If true, then we should be able to reduce the amount of catalyst charge while maintaining rate. Our kinetic data further show that we can lower the concentration of another catalyst component by at least an order of magnitude with no loss in rate. Maintaining rate at lower catalyst/additive concentration significantly reduces operating cost and simplifies product separation.

We have continued work on the direct conversion of syngas to alcohols by ruthenium catalysts. The activity of the ruthenium catalyst system was shown to decrease as a function of the operating pressure; approximately a second-order dependence was seen. The selectivity to higher alcohols is also a function of pressure, decreasing with pressure.

The ratio of H_2/CO is also important to the selectivity to higher alcohols. A CO-rich syngas (2:1 CO/H_2) is better for the formation of higher alcohols despite a decrease in the total activity of the catalyst system as compared to experiments using a 1:1 syngas. Both the total activity and the selectivity to higher alcohols decrease when hydrogen-rich syngas (2:1 H_2/CO) was used.

Solvent is another important factor for the activity and selectivity of the system. We found that 1,3-dimethylethyleneurea is a very good solvent for the production of higher alcohols with this system. We have also found that LiI as the iodide source further increases the production of higher alcohols over that observed with KI.

We have initiated work on the heterogeneous conversion of syngas to alcohols by alkali-loaded molybdenum sulfide and cobalt-molybdenum sulfide catalysts. We are now working our way through a list of ideas which we hope will lead to a better understanding of the controlling factors in the production of alcohols versus hydrocarbons with these catalysts.

We are in the process of determining whether it is possible to change the edge site to basal plane site distribution in catalyst precursors, and whether this can change the catalyst performance.

We are also investigating the variability of particle size, surface area, and pore structure of various samples of a particular MoS_2 preparation. We are currently trying to determine whether we can get reliable information from porosimetry measurements.

We are interested in determining if the use of non-aqueous impregnating solutions can have an effect on

catalyst performance. Two identical K-MoS₂ catalysts were prepared, except that one was impregnated with an aqueous solution of potassium acetate and the other with an anhydrous ethanol solution of potassium acetate. The catalytic results with these materials do not appear to be significantly different.

B. Task 3: Bench Scale Concept Evaluation

The major efforts for this quarter have been in the definition of the base case economics and in support of the experimental program on heterogeneous catalysts.

The problems revealed in previous experimental work with the heterogeneous MoS₂ catalysts for conversion of syngas to alcohols included rates lower than commercially desirable, catalyst deactivation, and increasing methane formation as the conversion increased and the proportion of higher alcohols increased. Engineering support for this program has been focused on developing an understanding of catalyst preparation and whether modifications to the preparation procedure might improve performance.

One factor which may affect catalyst deactivation is the loss of sulfur. Addition of the appropriate concentration of H₂S to the feed may thus be essential for long term operation. We will attempt to develop a method to predict the sulfur feed rate needed to maintain a steady-state catalyst sulfur content.

It is possible that the alkali metal distribution on the catalyst obtained by impregnation might be very nonuniform. The large reduction in surface area observed after impregnation could be due simply to blocking of many of the pores during drying and salt decomposition. The possibility is being investigated that the impregnating solution does not wet the MoS₂ surface. Different procedures intended to improve wetting will be tested. Alternative means to dry the

material may also need to be explored to maintain uniform alkali metal distribution.

A base case process for economic studies of making fuel alcohols from syngas has been developed. It uses existing technologies which have been demonstrated to be feasible or have already been commercialized. The process consists of the following steps: coal or natural gas (reforming or partial oxidation) to syngas; syngas to methanol by ICI technology; methanol to light olefins by proprietary UCC technology using molecular sieves; olefins to alcohols by hydroformylation (with a homogeneous rhodium catalyst) followed by hydrogenation. Process economics for the two natural gas-based routes have been developed. With insights gained from this, an optimized and integrated multi-step process has been conceptualized which allows estimation of the lowest cost at which fuel alcohols can be produced.

A 60% methanol and 40% higher alcohol mix was assumed to be a suitable fuel alcohol blend for gasoline. At a natural gas price of \$2/MMBTU, the cost of producing this, by either partial oxidation or reforming, is \$1.12/gal.

An integrated process with autothermal reforming at 750 psia and methanol synthesis at 700 psia allows incorporation of the best features of reforming and partial oxidation as well as elimination of syngas compression. The production cost of fuel alcohols by this process is estimated to be \$0.90/gal. This is, therefore, the lowest cost at which fuel alcohols can be produced by an integrated, multi-step process.

An "ideal" process has also been conceptualized which establishes a target production cost that new technology should strive for to be competitive. This process incorporates autothermal reforming for producing syngas followed by conversion to fuel alcohols using emerging technologies. The target production cost is estimated to be \$0.65/gal.

V. CHANGES

There were no contract changes during this quarter.

VI. FUTURE WORK

Work during the next quarter will continue on Tasks 2 and 3, as described in the schedule of Section II.

Task 2 work will continue on homogeneous catalysts for the direct conversion of syngas to alcohols, and also on methanol homologation to ethanol. Work on heterogeneous catalysts for alcohol production will also continue.

Work on Task 3 will involve economic and engineering evaluations, as well as continuing engineering support for the chemical investigations.