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**Novel Approaches To The Production of Higher Alcohols
From Synthesis Gas**

**Quarterly Report
April 1 - May 31, 1997**

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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report

April 1, 1997 though May 31, 1997

CONTRACT OBJECTIVES

- Task 1. Program Management.
- Task 2. Liquid-Phase, Higher Alcohol Process with Recycle of Lower Alcohols.
- Task 3. Novel Catalysts for Synthesis of Higher Alcohols (complete).
- Task 4. Synthesis of Higher Alcohols via Acid-Base Catalysis (complete).
- Task 5. Technology Evaluation (complete).

SUMMARY OF ACTIVITY

Analysis of the data from a run that was carried out in the continuous stirred autoclave during February, 1997 was completed. A cesium-promoted "zinc chromite" catalyst was used, with decahydronaphthalene as the slurry liquid. Reaction conditions were: 375°C, 2000 psig total pressure, 0.5 H₂/CO ratio and 5000 sL/Kg (cat.)-hr space velocity. On a CO₂-free basis, olefins were the predominant product. The isobutanol/methanol ratio was about 0.13 and the i-butene/n-butene ratio was about 0.10. The net conversions of H₂ and CO were both about 10%.

A paper entitled "Liquid-Catalyst Interactions in a Slurry Reactor for Alcohol Synthesis Using "Zinc Chromite" Catalyst" was presented at the 213th National American Chemical Society Meeting.

A manuscript on the thermal stability of potential slurry liquids was revised and resubmitted to *Industrial and Engineering Chemistry Research*.

This contract is now complete. The draft Final Report is being prepared.

TECHNICAL DETAILS

A. Higher Alcohols Run-Data Analysis

A run was carried out in the continuous stirred autoclave reactor during February, 1997. Decahydronaphthalene (Decalin®, DHN) was the slurry liquid and the catalyst was Engelhard Zn-0312T 1/8 "zinc chromite" promoted with 3 weight percent cesium. This catalyst was evaluated at a single set of conditions: temperature - 375°C; total pressure - 2000 psig; space velocity - 5000 sL/Kg. (cat)-hr, and; H₂/CO feed ratio - 0.5. A 20 wt.% slurry of catalyst in DHN was used, i.e., 16.5 gr. catalyst in 95 mL of DHN. This run was discussed in the Quarterly Report for January 1, 1997 through March 31, 1997.

All of the analytical data has now been received and analyzed. In general, the revamped analytical system appeared to provide the expected level of detail, subject to the uncertainties described in the previous Quarterly Report.

Three material balances were obtained over a two-day period at the above conditions, involving two liquid samples. In general, the component material balances did not close as well as they had in methanol synthesis runs with unpromoted "zinc chromite" catalyst. The closures for the three balance periods were:

<u>Species</u>	<u>Closure(%)</u>
C	96, 110, 111
O	99, 112, 115
H	89, 101, 104

In runs with unpromoted "zinc chromite", all three component balances generally closed to 100 ± 5%. Closures in excess of 100% indicate that

output is greater than input. It may be that the inlet CO flowrate was underestimated during the last two balance periods, perhaps due to error in the mass flowmeter readings and/or calibrations.

The data for the three balance periods was reasonably consistent, as shown in Table 1. The high CO₂ selectivity was expected since the H₂/CO ratio was low and "zinc chromite" is an excellent water-gas-shift catalyst. An isobutanol/methanol ratio of about 0.10 is consistent with published results at 405°C. Achieving this ratio at 375°C, with the first Cs-promoted catalyst evaluated, is somewhat encouraging.

The surprising result is the high selectivity to olefins. High olefin selectivity has not been reported previously with promoted "zinc chromite" catalysts. Olefin production probably is a favorable result since olefins have a high commercial value and since alcohols such as isobutanol have to be dehydrated to the corresponding olefin in order to produce methyl tertiary butyl ether (MTBE). It is not clear whether the high olefin selectivity resulted from the properties of the particular catalyst that was used, or whether it was associated with the use of a slurry reactor, perhaps from an interaction between the slurry liquid and the catalyst surface. This would be a promising direction for the future research, with high commercial potential.

B. Paper Presented at American Chemical Society (ACS) Meeting

A paper entitled "Liquid-Catalyst Interactions in a Slurry Reactor for Alcohol Synthesis Using "Zinc Chromite" Catalysts" was presented at the 213th National ACS Meeting on April 17, 1997. A condensed version of the paper appeared in ACS Division of Fuel Chemistry Preprints, 42, No. 2, 710(1997). A copy of this preprint is appended.

C. Thermal Stability of Potential Slurry Liquids

A manuscript covering all of the research that has been carried out to date to evaluate the thermal stability of various liquids that might be used as slurry media for "zinc chromite" catalyst was submitted to *Industrial and*

Engineering Chemistry Research for possible publication in February, 1997. Comments from four reviewers were received in April, 1997. The manuscript was revised based on these comments and was resubmitted to *Industrial and Engineering Chemistry Research* this month. A copy of the revised manuscript is appended.

D. Completion Activities

This contract is now complete; this will be the last Quarterly Report. Preparation of a manuscript on liquid/catalyst interactions for publication in a scientific journal is underway. Work has begun on the draft Final Report.

Table 1
Performance of Cs-Promoted "Zinc Chromite" Catalyst

<u>Parameter</u>	<u>Range</u>
H ₂ Conversion(%)	8.0-11.6
CO Conversion(%)	7.7-10.3
Carbon Selectivity (%)	
Paraffins	0.078-0.11
Methane	0.053-0.082
Olefins ¹	0.18-0.24
Alcohols	0.048-0.088
Methanol	0.027-0.037
i-Butanol	0.0063-0.020
CO ₂	0.61-0.65
i-Butanol/Methanol(moles/mole)	0.058-0.13

¹-Ethylene was assumed to be 90% of the combined ethane + ethylene peak based on the propene/propane and butene/butane ratios.