

Novel Approaches to the Production of Higher Alcohols From Synthesis Gas

**Quarterly Report
October 1 - December 31, 1996**

Work Performed Under Contract No.: DE-AC22-90PC90043

For
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FEB 16 1999

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NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report
October 1, 1996 to December 31, 1996

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

During the previous quarter, a run was carried out in the continuous stirred autoclave reactor with a cesium-promoted "zinc chromite" catalyst. Decahydronaphthalene was used as the slurry liquid. Reaction conditions were: 375°C temperature, 2000 psig total pressure, 0.5 H₂/CO feed ratio and 5000 sL/Kg. (cat)-hr space velocity. A much wider range of products was produced than in previous runs with the unpromoted catalyst including substantial quantities of olefins. Unfortunately, the various chromatographic peaks could not be identified with absolute certainty, and the elemental balances did not close to within acceptable tolerances.

Most of the present quarter was spent attempting to upgrade the existing analytical system so that a product stream containing C₁ through C₇ paraffins, olefins, and alcohols could be analyzed accurately. It does not appear as though the Poraplot Q column is capable of separating all of these potential products, even if the

GC/MS (gas chromatography/mass spectrometry) facility in the Chemistry Department at North Carolina State University is used for supplementary analysis. A different column plus a condensor for high-boiling products probably will be required.

TECHNICAL DETAILS

A. Analytical System Upgrading

1. Gas Chromatograph (GC)

Various alkane and alkene gas standards were tested in the laboratory using a 25m Poraplot Q column at 150°C. This is the same column and oven temperature that was used for analysis of the hydrocarbon and alcohol products in the run with Cs-promoted "zinc chromite" catalyst that was made last quarter. The results showed that three important product pairs: propane/propylene; 1-butene/2-methyl-1-propene, and; 1-pentene/3-methyl-1-butene were not separated satisfactorily.

The length of the Poraplot Q column was doubled, to 50 m, by adding an identical 25m column in series with the first. At 150°C oven temperature, the resolutions of propane/propylene and 1-pentene/3-methylene-butene were improved, but there was again no separation of 1-butene/2-methyl-1-propene.

Another series of experiments was then run with the 25m Poraplot Q column. The focus of these experiments was on temperature programming. Unfortunately, all of the temperature programs that were tested proved unsuccessful in separating 1-butene and 2-methyl-1-propene.

2. Off-Line Gas Chromatography/Mass Spectrometry(GC/MS) of Gas Standards

GC/MS analysis was performed off-line in the North Carolina State University Chemistry Department on the following purchased gas standards:

- Standard #2: 2-Methyl-1-Pentene; 2-Methylpropene; 2-Methyl-1-Butene; Isopropyl Ethylene; 4-Methyl-1-Pentene { each near 15ppm}
- Standard #4: Ethylene; Propylene; 1-Butene; 1-Pentene; 1-Hexene {each near 1000 ppm}
- Standard #6: Isobutane; 2-Methyl butane; 2, 2-Dimethyl propane; 2-Methyl pentane; 3-Methyl pentane; 2,2-Dimethyl butane {each near 15 ppm}
- Standard #9: Dimethyl Ether(DME); Methanol; Ethanol; Isobutanol {each near 500 ppm}

The compounds in Standards #2 and #6 were undetectable due to their low concentrations. All of the compounds in Standard #4 were detected, except for ethylene. This was expected since the molecular weight of ethylene is below the limit of detection for this instrument. The library function of the GC/MS correctly identified all Standard #4 compounds except for 1-butene, which was identified as 2-methyl-1-propene.

Standard #9 was analyzed both directly from the standard cylinder and after transfer to a stainless steel bomb. DME was not identified by the library search. However, it had consistent residence times and its molecular weight was correctly identified. For both the cylinder and the bomb, DME, ethanol and isobutanol were detected, although in different relative amounts. Due to lower pressure, the MS peak areas were smaller for the bomb. Adsorption appears to occur in the bomb. However, it is not pronounced enough to prevent the detection of alcohols with concentrations near or above 500 ppm. The bomb was capable of holding pressure for several hours.

These results show that GC/MS analysis of "spot" samples could be a useful supplement to on-line GC analysis. However, the utility of off-line GC/MS analysis would be limited to qualitative determination of the medium-to-heavier compounds that are present in the product stream at concentrations of several hundred ppm and higher.

3. System Redesign

In view of the failure of the existing on-line GC, even in conjunction with off-line GC/MS analysis, to separate and quantify several important product pairs, it appears likely that the analytical system will have to be redesigned before another run can be attempted with Cs-promoted "zinc chromite" catalyst. Therefore, as a first step, a comprehensive search for an improved GC column was initiated. All known GC column vendors were contacted and provided with specifications on the compounds present, and their expected concentrations, in the product stream. Second, the design of a system to condense the alcohols, and some of the higher-boiling hydrocarbons, out of the effluent stream was begun. The condensed liquid would be analyzed off-line, using either GC or GC/MS. Eliminating the alcohols from the vapor stream should facilitate on-line GC analysis of the light olefins and paraffins.

B. Preprint for April, 1997 American Chemical Society

A paper entitled "Liquid/Catalyst Interactions in a Slurry Reactor for Methanol Synthesis Using "Zinc Chromite" Catalyst" will be presented as part of the Clean Fuels Symposium sponsored by the Fuel Chemistry Division of the American

Chemical Society on the ACS Meeting in April, 1997. A preprint of this paper was prepared and submitted to the Session Chairpersons.