

**Promoted Zinc Chromite Catalysts for Higher Alcohol Synthesis**  
**Semi-Annual Report**

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**Patent Information:**

No patentable subject matter is disclosed in this request.

## **Abstract**

Work during the report period was concentrated on developing analytical techniques. Thin-layer chromatography (TLC) was used in an attempt to define the best mobile phase to separate the components of "spent" tetrahydroquinoline by liquid chromatography in a silica gel column.

Conditions have been defined for separating the light gases produced by the reaction of carbon monoxide (CO) and hydrogen (H<sub>2</sub>) over promoted "zinc chromite" catalysts. This will be done with a temperature-programmed Carboxen-1000 column, using a thermal conductivity detector for analysis. A Petrocol DM 150 capillary column will be purchased to separate the heavier products, which will be analyzed using a flame ionization detector.

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## Executive Summary

The overall objective of this research project is to evaluate promoted "zinc chromite" catalysts for the production of higher ( $C_2^+$ ) alcohols in a slurry reactor, using synthesis gas as the feedstock. Work during the report period was concentrated on developing analytical methods. The need for improved and expanded analytical techniques for both reactor effluent and used ("spent") slurry liquid was identified in previous research.

Thin-layer chromatography (TLC) was used in an attempt to define the best mobile phase to separate the compounds of "spent" tetrahydroquinoline (THQ) by liquid chromatography (LC). Preparations to use LC to separate "spent" THQ produced in earlier experiments are in progress.

Conditions have been defined for separating the light gases produced by the reaction of synthesis gas over cesium-promoted "zinc chromite" on a temperature-programmed Carboxen-1000 column, using a thermal conductivity detector (TCD). A Petrocol DH 150 capillary column will be purchased to analyze the heavier products, using a flame ionization detector.

## A. Introduction

Branched higher alcohols, such as isobutanol (2-methyl-1-propanol) or isoamyl alcohol (2-methyl-1-butanol) could provide the raw material needed to produce established octane enhancers such as methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME). These branched alcohols also could be of interest *per se* as oxygenated additives for motor gasoline.

With the exception of ethanol, current processes for producing higher alcohols are based primarily on imported petroleum. The objective of this research is to explore the synthesis of branched higher alcohols using synthesis gas as the starting raw material. Synthesis gas is a mixture containing hydrogen ( $H_2$ ) and carbon monoxide (CO), which can be produced from a variety of domestically-available materials, e.g., coal, natural gas, and waste biomass.

Most previous attempts to produce branched higher alcohols from synthesis gas have been based on modified methanol synthesis catalysts, either the "low-pressure," Cu/ZnO catalyst or the "high-pressure", ZnCrO ("zinc chromite") catalyst. Either of these catalysts can be promoted with Group I elements such as potassium (K), rubidium, and cesium (Cs) to shift the product distribution away from methanol towards higher alcohols.

Promoted "zinc chromite" catalysts will be the focus of this research. All previous studies of this family of catalysts have been carried out in fixed-bed reactors. However, due to the highly exothermic character of higher alcohol synthesis (HAS), it is difficult to control the temperature of a fixed-bed reactor, especially on a pilot-plant or commercial scale. A slurry reactor, by contrast, has excellent heat removal capability and many other advantages that may make this type of reactor ideal for HAS.

The synthesis of methanol in a slurry reactor, using an unpromoted "zinc chromite" catalyst was studied in depth by two previous Ph.D. students (1,2). In addition, some preliminary experiments were carried out with a Cs-promoted "zinc chromite" catalyst by a previous M. Eng. student.

In previous research, three slurry liquids were identified that appear to have the necessary thermal and chemical stability at 375°C, in the presence of the unpromoted "zinc chromite" catalyst (3). These liquids were: decahydronaphthalene (DHN, Decalin®); tetrahydronaphthalene (THN, tetralin), and; tetrahydroquinoline (THQ). The rate of methanol synthesis was substantially higher in THQ than in the other two liquids (4). However, THQ was alkylated extensively during the reaction, raising questions about whether it participated in the catalytic cycle, and whether its composition would eventually stabilize. An analysis of a sample of THQ taken from the reactor after about 100 hours of operation is shown in Appendix I.

The prior experiments with Cs-promoted "zinc chromite" were qualitative in nature. However, they showed that the product contained significant concentrations

of C<sub>2</sub><sup>+</sup> alcohols, C<sub>2</sub><sup>+</sup> olefins and C<sub>2</sub><sup>+</sup> paraffins. The analytical system that was used in the previous study of unpromoted "zinc chromite" was not adequate to separate and quantify all of those compounds.

Based on these prior results, the objectives for this reporting period were:

1. To study the influence of the slurry liquid on the HAS reactions by analyzing the "spent" slurry liquid, and;
2. To develop a gas chromatograph (GC) system that is capable of analyzing the expected products on-line.

## **B. Results and Discussion**

### **1. Analysis of Slurry Liquid**

It has been shown (5) that the composition of the liquid in a slurry reactor can affect the rates of heterogeneously catalyzed reactions by:

1. Competitive adsorption on the active catalyst sites;
2. Significant intermolecular interactions between the liquid and the adsorbed reactants, products and intermediate species.

To understand the influence of different slurry liquids on the HAS reaction, it is important to define any reaction in which a slurry liquid molecule might participate, i.e., to define the final composition of the slurry liquid when a catalyst-evaluation experiment is concluded. This is done by analyzing the "spent" liquid to identify the compounds that are present.

Marquez (1) made an attempt to identify and quantify the composition of the "spent" slurry liquid by using gas chromatography/mass spectrometry (GC/MS). Appendix I shows the results of one such analysis of "spent" THQ. Obviously, GC-MS alone is not sufficient to identify all of the compounds in the liquid sample. Therefore, we decided to apply some additional analytical techniques.

One of those techniques was High Performance Liquid Chromatography (HPLC). After a tedious series of trial-and-error experiments with different columns and different eluent liquids, we were able to collect six fractions, each of which contained a major peak. However, the HPLC was very sensitive, possibly because of column deterioration and the experiment was not reproducible when an attempt was made to collect the same fractions for further analysis by GC/MS and NMR (nuclear magnetic resonance).

We then decided to attempt to isolate the components of "spent" THQ using column chromatography. To define the proper mobile phase for the column, we carried out some Thin-Layer Chromatography (TLC) experiments.

## **a. Thin-Layer Chromatography**

Thin Layer Chromatography (TLC) is based on differences in the affinity of a substance between two phases, a stationary and a mobile phase, the sorbent and the eluent. The substance is transported through the column by the mobile phase, adsorbs and resides for a certain time on the stationary phase, and is then desorbed and carried along again in the mobile phase. In this way, the movement of the substance is slowed down relative to the velocity of the mobile phase. The more preferentially the substance adsorbs on the stationary phase, the lower the net velocity. Thus, substances that are very similar structurally and chemically can be separated; even small differences can lead to a difference in the relative net velocities of the substances (6).

There are two main steps for column chromatography experiments. First, a TLC plate experiment is conducted, which can be used to determine a suitable eluent (mobile phase) for the sample's separation. Second, fractions are collected by using the CC (column chromatograph). Here, the column is made by using the same sorbent (silica) as the TLC plate. Column chromatography can produce much larger samples than HPLC, so this approach should make it easier for us to collect fractions for subsequent analysis.

The choice of mobile phase (eluent) exerts a decisive influence on the separation (6). The eluent dissolves the substances to be separated and transports them through the column. The more strongly the eluent is adsorbed, the greater will be its eluting strength (displacement strength). If a substance has a greater affinity for the mobile phase than for the sorbent, then it will be eluted closer to the front (earlier). The choice of suitable eluent can be guided by TLC plate experiments. Appendix II shows a selection of the principal solvents in the elutropic series for silica gel.

Experiments have been carried out using silica gel TLC plates to determine a suitable eluent. Standard samples, such as: 1) a mixture of 2-methyl-quinoline, 7-methyl-quinoline, and 8-methyl-quinoline; 2) a mixture of THQ and 2-methyl-THQ, and; 3) "spent" THQ from previous experiments, have been tested. From these experiments, we have shown that a mixture of methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) and ethyl acetate gives a reasonable separation of this type of compound.

## **b. Column Chromatography**

Appendix III shows the experimental system that has been assembled to collect fractions of various samples. Our work to date has been focused on separating a mixture of standard samples #1 and #2 above.



### **c. Future Work**

Additional silica gel TLC plate separation experiments will be carried out in the next report period. This is because the present experiments did not give a sufficient extent of separation for the "spent" THQ. The reason may be that there are too many similar compounds in this sample. To reduce the complexity of this mixture, we will use acid and base separately to wash the spent THQ. By this technique, we might get separate acid-like and base-like compounds. Simplified "spent" THQ mixtures should give us a much cleaner silica gel TLC plate and CC separation. We will also test additional eluents. The column chromatograph shown in Appendix III will be used to separate both standard samples and actual "spent" liquids. Once good fractions have been obtained, we will use GC-MS and NMR to identify the pure compounds in each fraction

## **2. Development of an On-Line Gas Chromatographic Technique**

It has been shown that the use of alkali metals, such as K and Cs, to promote ZnCrO, MnCrO and ZnMnCrO catalysts shifts the product distribution from methanol towards  $C_2^+$  alcohols (7). Branched alcohols are produced preferentially, among which isobutanol is the main component. Secondary alcohols, hydrocarbons, aldehydes, esters, small amounts of ketones, and traces of ethers are also formed. In our laboratory, previous experiments with a Cs-promoted ZnCrO catalyst, and with DHN as the slurry liquid, have shown that the product consists of  $C_1$ - $C_6$  alcohols and paraffins,  $C_2$ - $C_6$  olefins, carbon dioxide, and dimethyl ether.

Clearly, promoted ZnCrO catalysts produce a much more complicated product distribution than unpromoted catalysts. To obtain a good product analysis, a new analytical system is required, capable of identifying and quantifying the broad spectrum of components formed. High resolution is also required because many similar compounds and isomers exist.

### **a. Drawbacks of Previous Analytical Method**

With the previous analytical system, the unconsumed reactants and noncondensable products (e.g.,  $C_1$ - $C_6$  hydrocarbons, low molecular weight oxygenated compounds, and  $CO_2$ ) were analyzed on-line. The condensable products, (e.g.  $C_6^+$  hydrocarbons, alcohols, and  $H_2O$ ) were collected, separated into an organic and aqueous phase, and then analyzed off-line. This approach, while capable of providing good product identification, suffers from a number of disadvantages. The principal ones are (8):

(1) Quantification: Accurate volumetric measurements of each phase must be made. Components usually appear in more than one phase, and the amounts in different phases must be added to yield the full product spectrum;

(2) Handling: Products may vaporize and/or oxidize during storage and handling, prior to analysis;

(3) Conversion: Reactions must be run at high conversion in order to accumulate sufficient amounts of condensate in short periods of time (typically 5 to 10 h). Low conversion studies, ideal for determining kinetics, are impractical;

(4) Analysis turnaround: One complete analysis involves many hours of collection plus analysis time. This makes it difficult to follow the dynamics of catalyst deactivation or changes in reaction conditions.

## b. New On-Line Technique

Many of the difficulties cited above can be overcome by complete on-line analysis of all products. The GC in our laboratory is a Perkin Elmer Auto System gas chromatograph. This is a dual-column, temperature-programmable GC, equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors. The chromatograph is interfaced with a computer which is used for both data acquisition and reduction.

During the report period, we determined that the light gases, e.g., CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, could be separated using a 15 foot, 1/8 in o.d., 60/80 Carboxen-1000 stainless steel column. The products eluting from this column were detected by the TCD.

## c. Future Work

We plan to buy a new capillary column - Petrocol DH 150 (150m by 0.25mm ID, 1.0μ film) — to use in conjunction with the FID. This column has been recommended for its capability of separating C<sub>2</sub>-C<sub>6</sub> alcohols, olefins, and paraffins.

The following gas and liquid standards will be used to calibrate the new capillary column.

### Gas Standards

#### Standard #1

Dimethyl Ether	504ppm
Methanol	514ppm
Ethanol	525ppm
1-Propanol	500ppm
iso-Butanol	529ppm
Balance N <sub>2</sub>	

#### Standard #2

Propylene	507ppm
Propane	502ppm
Dimethyl Ether	500ppm
Isobutane	499ppm
Methanol	517ppm
Isobutylene	502ppm
1-Butene	502ppm
n-Butane	502ppm
Balance N <sub>2</sub>	

#### Standard #3

Ethylene	1000ppm
Propylene	1000ppm
1-Butene	1000ppm

#### Standard #4

Methane	1040ppm
Ethane	1000ppm
Propane	1000ppm

1-Pentene 1030ppm  
 1-Hexene 1050ppm  
 Balance N<sub>2</sub>

n-Butane 992ppm  
 n-Pentane 1010ppm  
 n-Hexane 954ppm  
 Balance He

**Standard #5**

2-Methyl-Propene 14.5ppm  
 Isopropyl Ethylene 14.9ppm  
 2-Methyl-1-Butene 14.6ppm  
 2-Methyl-1-Pentene 17.9ppm  
 4-Methyl-1-Pentene 15.2ppm  
 Balance N<sub>2</sub>

**Standard #6**

cis-2-Butene 15.4ppm  
 cis-2-Pentene 16.3ppm  
 cis-2-Hexane 16.2ppm  
 trans-2-Butene 15.4ppm  
 trans-2-Pentene 16.3ppm  
 trans-2-Hexene 15.9ppm  
 Balance N<sub>2</sub>

**Standard #7**

Methane 16.3ppm  
 Ethane 16.3ppm

Propane 16.3ppm  
 n-Butane 16.3ppm  
 n-Pentane 16.4ppm  
 n-Hexane 16.9ppm

Balance N<sub>2</sub>

**Standard #8**

Iso-Butane 14.6ppm  
 2,2-Dimethyl  
 Propane 15.0ppm

2-Methyl-Butane 14.5ppm  
 2-Methyl-Pentane 14.6ppm  
 3-Methyl-Pentane 14.7ppm  
 2,2-Dimethyl-  
 Butane 14.5ppm

Balance N<sub>2</sub>

**Standard #9**

Cyclohexane 13.6ppm  
 Cyclopentane 15.2ppm  
 Methyl-Cyclohexene 13.2ppm  
 Methyl-Cyclopentane 14.5ppm  
 Balance N<sub>2</sub>

**Standard #10**

CO 1.0%  
 CO<sub>2</sub> 1.0%  
 CH<sub>4</sub> 1.0%  
 C<sub>2</sub>H<sub>4</sub> 1.0%  
 C<sub>2</sub>H<sub>6</sub> 1.0%  
 C<sub>3</sub>H<sub>6</sub> 1.0%

**Liquid Standards**

Methanol  
 n-Butanol  
 2-Methyl-1-Butanol  
 2-Octanol

Ethanol  
 sec-Butanol  
 2-Pentanol  
 MTBE

1-Propanol  
 iso-Butanol  
 3-Pentanol

2-Propanol  
 t-Butanol  
 2-Methyl-1-Pentanol

## C. Conclusions

- 1) Column chromatography shows some promise as a technique for separating the compounds of "spent" tetrahydroquinoline slurry liquid. Such a separation should permit a more detailed analysis of the composition of the "spent" liquid than gas chromatography/mass spectrometry alone.
- 2) Operating conditions and a temperature program have been developed that permit the light gases, through ethane, to be analyzed on the existing Carboxen-1000 column using a thermal conductivity detector.
- 3) A Petrocol DH 150 capillary column should be ordered to analyze the heavier components.

## D. References

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## APPENDIX I

### Estimated Composition and Molecular Weight based on GC/MS for "Spent" THQ (96 hrs) [1]

(Sample taken from the liquid recycle line at 96 hrs of 12/95 test, Reactor temperature = 325°C)

Component	Retention time(min)	Probability (% accuracy)	Peak Area	Molecular Formula	MW (gr/mol)	mol %	wt %
MW 135 ?	9.92-9.97	?	40296	C9H13N ?	135	0.4	0.4
Trans or cis-DHQ	11.33	94	11193	C9H17N	139	0.1	0.1
Tetralin	11.69-11.78	96	994121	C10H12	132	9.5	8.5
MW 153 ?	11.91-11.95	41	254910	C10H19N	153	2.4	2.5
Quinoline, decahydro-1-methyl	12.08-12.11	84	44461	C10H19N	153	0.4	0.4
Naphthalene or Azulene	12.13-12.2	89	32081	C10H8	128	0.3	0.3
MW 163 ?	12.24-12.3	?	78630	C11H17N ?	163	0.7	0.8
MW 167 ?	12.73-12.8	?	75490	?	167	0.7	0.8
MW 167 ?	13.31	?	23586	?	167	0.2	0.3
MW 167 ?	14.68	?	257630	?	167	2.5	2.8
Isoquinoline, 1,2,3,4,-tetrahyd-3m	14.93-15.08	?	7669856	C10H13N	147	73.1	72.8
MW 147 ?	15.32	?	196693	C10H13N	147	1.9	1.9
C11H15N ?	15.47-15.50	?	334395	C11H15N	161	3.2	3.5
MW 161 ?	16.21	?	483448	?	161	4.6	5.0
Unknowns (BP>300°C)(*)	-	-	0	-	-	0.0	0.0
Total area			10496790			100	100

Average MW (gr/mol)

148

% THQ

0

% Molecular Weight reduction

none

(\*) contribution of unknown components with BP > 300°C assumed to be negligible.

## APPENDIX II

### Selection of the Principal Solvents in the Elutropic Series for Silica Gel[6]

Eluotropic series	Formula	Polarity index according to Synder*	Dielectric constant  DC (20 or 25°C)	Molar mass  [g/mol]	Boiling point  [°C]	Vapor pressure  [mbar] (20°C)	Max. work conc. (MAK values) 1983 [ml/m <sup>3</sup> ] or [ppm]
n-Heptane	C <sub>7</sub> H <sub>16</sub>	-	1.9	100.21	98.4	48	500
n-Hexane	C <sub>6</sub> H <sub>14</sub>	0.0	1.9	86.18	68.9	160	100
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	0.0	2.0	84.16	80.7	104	300
Isooctane	C <sub>8</sub> H <sub>18</sub>	0.4	1.9	114.23	99.2	51	500
1,1,2-Trichlorotrifluoroethane	Cl <sub>2</sub> FCFClF <sub>2</sub>	-	2.4	187.38	47.7	368	1000
Carbon tetrachloride	CCl <sub>4</sub>	1.7	2.2	153.82	76.5	120	10
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	2.3	2.4	92.14	110.6	29	200
Chloroform	CHCl <sub>3</sub>	4.4	4.8	119.38	61.7	210	10
Dichloroethane	ClCH <sub>2</sub> CH <sub>2</sub> Cl	3.7	10.6	98.97	83.4	87	20
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	3.4	9.1	84.93	40.0	453	100
1-Butanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	3.9	17.8	74.12	117.2	6.7	100
Acetonitrile	CH <sub>3</sub> CN	6.2	37.5	41.05	81.6	97	40
2-Propanol	CH <sub>3</sub> CH(OH)CH <sub>3</sub>	4.3	18.3	60.10	82.4	43	400
Ethyl acetate	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	4.3	6.0	88.10	77.1	97	400
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	5.4	20.7	58.08	56.2	233	1000
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	5.2	24.3	46.07	78.5	59	1000
1,4-Dioxane	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	4.8	2.2	88.11	101.0	41	50
Tetrahydrofuran	C <sub>4</sub> H <sub>8</sub> O	4.2	7.4	72.11	66.0	200	200
Methanol	CH <sub>3</sub> OH	6.6	32.6	32.04	65.0	128	200
Water	H <sub>2</sub> O	9.0	80.2	18.01	100.0	23	-

APPENDIX III

**Silica Gel LC Column**

