HETEROGENEOUS CATALYTIC PROCESS FOR ALCOHOL FUELS FROM SYNGAS

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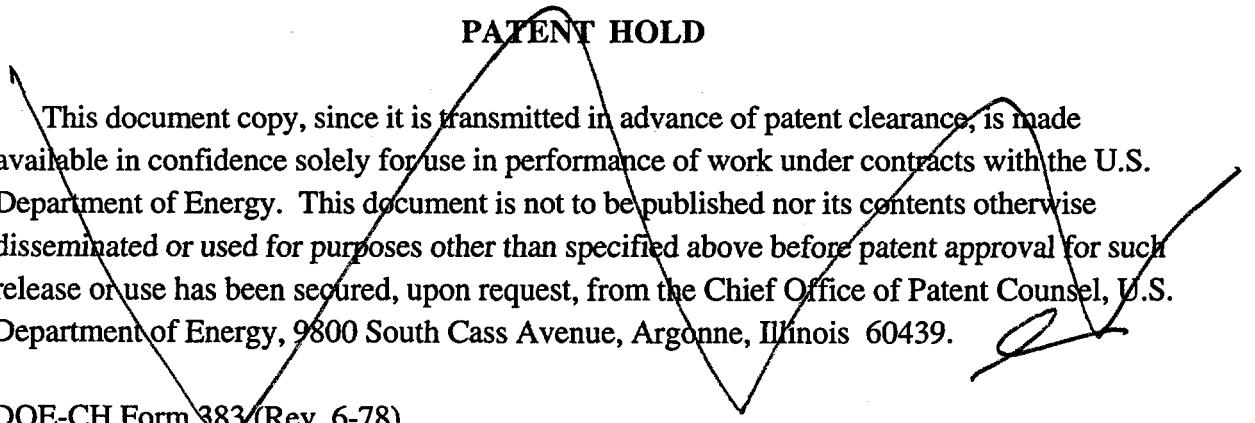
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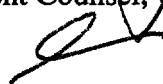
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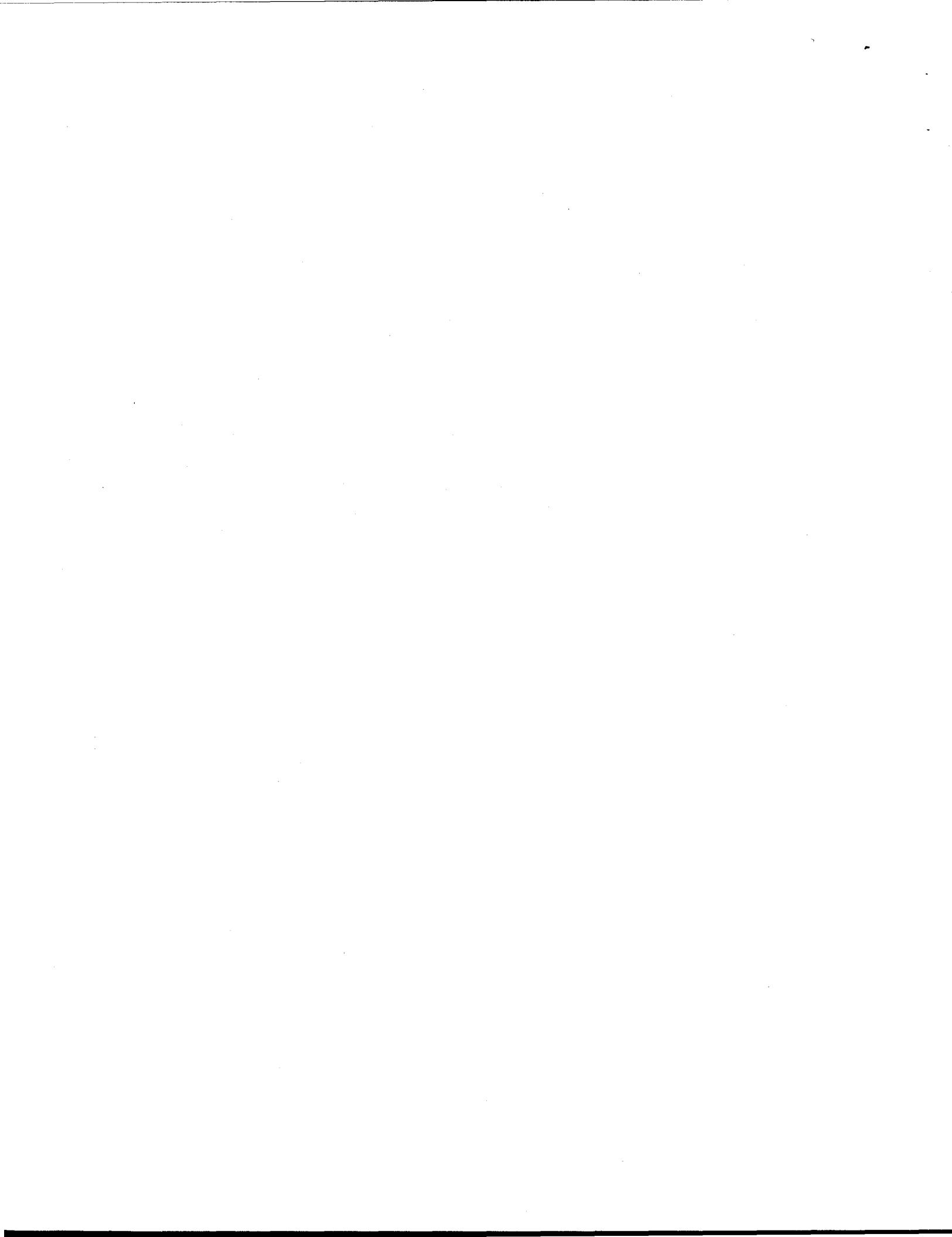
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1. Executive Summary

The principal objectives of this project are to discover and evaluate novel heterogeneous catalysts for conversion of syngas to oxygenates having use as fuel enhancers, to explore novel reactor and process concepts applicable in this process, and to develop the best total process for converting syngas to liquid fuels.

We have prepared an improved version of 10-DAN-54, a Zn/Cr/Mn spinel oxide promoted with Pd and K. This material (16-DMM-68) has acceptable elemental analysis for the expected composition and possesses the desired high surface area of >80 m^2/g. The catalyst has extra added potassium vs. our standard catalyst, 10-DAN-54, as previous work had indicated that more potassium is required for optimal performance.

In tests under standard conditions (400°C, 1000 psi, GHSV = 12000, syngas ratio = 1), this catalyst shows a selectivity to total alcohols of 84% and produces > 100 g/kg/hr of isobutanol with a MeOH/i-BuOH mole ratio = 4.7.

We have tested 16-DMM-68 at temperatures above 400°C and pressures up to 1500 psi (GHSV = 12000, syngas ratio = 1). At 440°C and 1500 psi, this catalyst shows a selectivity to total alcohols of 64% and produces 179 g/kg/hr of isobutanol with a MeOH/i-BuOH mole ratio = 2.2. This is our best overall performance to date.

The catalyst operates at syngas conversions up to 28% with good selectivity to total alcohols due to the extra added alkali. This performance can be compared with 10-DAN-54, which could only operate up to 20% conversion before hydrocarbon formation became a serious inefficiency.

2. Project Objectives

• To discover, study, and evaluate novel heterogeneous catalytic systems for the production of oxygenated fuel enhancers from synthesis gas. In particular, novel heterogeneous catalysts will be studied and optimized for the production of: (a) C_1-C_5 alcohols using conventional methanol synthesis conditions, and (b) methanol and isobutanol mixtures which may be used for the downstream synthesis of MTBE or related oxygenates.

• To explore, analytically and on the bench scale, novel reactor and process concepts for use in converting syngas to liquid fuel products.

• To develop on the bench scale the best combination of chemistry, catalyst, reactor, and total process configuration to achieve the minimum product cost for the conversion of syngas to liquid products.

3. Project Organization

This project has been divided into two tasks.

Task 1 is concerned with catalyst identification, preparation, performance evaluation, and characterization. This work is being largely conducted by catalyst chemists and analytical specialists. Chemical studies to support the engineering effort in Task 2 are included in this task, but fundamental aspects of the catalytic chemistry are emphasized in this effort.

Task 2 includes process conceptualization and economics, and bench-scale process evaluation of systems developed in Task 1. This is largely an engineering activity.

These tasks are being carried out concurrently throughout the project.

4. Technical Progress

4.1. Task 1 – Catalyst Studies

4.1.1. Introduction

It is well known that the addition of alkali promoters to ZnCrO, MnCrO, and ZnMnCrO systems will modify the selectivity of high temperature methanol catalysts towards C_{2+} alcohols. Interest in higher alcohol synthesis (HAS) from syngas has stemmed from the desire to use the alcohol mixtures as high-octane blending stock for gasoline. Currently refining modifications and the use of oxygenated petrochemicals such as methyl-tert-butyl-ether (MTBE) have become favored alternatives. The production of a mixture of methanol and isobutanol is of interest due to its possible use as a feedstock in the production of other oxygenates such as ethers related to MTBE. One could also envision dehydrating the isobutanol to isobutene, followed by reaction with methanol to form MTBE. We have been investigating a series of promoted Zn/Cr/Mn spinel oxide materials as promising catalysts for this process.

This quarter we have concentrated our efforts on making an improved version of 10-DAN-54, our previous "best" catalyst for higher alcohol synthesis. This new catalyst, 16-DMM-68, has extra added potassium which should increase its selectivity to total alcohols and allow operation at higher conversions. 16-DMM-68 was characterized and then tested under standard conditions (400°C, 1000 psi, GHSV = 12000, syngas ratio (H_2/CO) = 1) in order to compare its performance with 10-DAN-54. 16-DMM-68 was then tested at higher temperatures and pressures to confirm the expected improved performance.

4.1.2. Catalyst Preparation (16-DMM-68)

We have prepared a Zn/Cr/Mn spinel oxide promoted with Pd and K. The procedure involved the preparation the base spinel oxide, followed by incipient wetness impregnation of the spinel with solutions of potassium and palladium as the nitrates. This material (16-DMM-68) has acceptable elemental analysis for the expected composition and possesses the desired high surface area of >80 m^2/g. This material (16-DMM-68) has extra added potassium vs. our standard catalyst, 10-DAN-54, as previous work had indicated that more potassium is required for optimal performance.

4.1.3. 16-DMM-68 Comparison with 10-DAN-54

The results of tests with 16-DMM-68 are summarized below and are compared to 10-DAN-54 under identical conditions (400°C, 1000 psi, GHSV = 12000, H_2/CO = 1):

	16-DMM-68	10-DAN-54
Ref. No.	PR-020	PR-620
Sel. Total Alcohols (%)	84	68
Total Alcohol Rate (g/kg-hr)	233	200
Methanol Rate (g/kg-hr)	119	75
Ethanol Rate (g/kg-hr)	0	0
Isopropanol rate (g/kg-hr)	0	0
n-Propanol rate (g/kg-hr)	12	11
Isobutanol Rate (g/kg-hr)	102	94
MeOH/i-BuOH mole ratio	4.7	3.2
Hydrocarbon rate (g/kg-hr)	26	60

16-DMM-68 is slightly more active and significantly more selective for alcohols than 10-DAN-54, probably due to the extra alkali added. 16-DMM-68 also produces more methanol and, as a consequence, the methanol to isobutanol mole ratio rises from 3.2 (in the case of 10-DAN-54) to 4.7 for 16-DMM-68.

4.1.4. Testing at Higher Temperatures and Pressures

We have tested 16-DMM-68 at elevated temperatures (>400°C) and pressures (>1000 psi). GHSV was held constant at 12000 and the syngas ratio was also held constant at 1:1. The results are summarized below:

	T = 400°C P = 1000 psi	T = 400°C P = 1500 psi	T = 440°C P=1180 psi	T = 440°C P = 1500 psi
Ref. No.	PR-020	PR-113	PR-170	PR-125
Sel. Total Alcohols (%)	84	86	54	64
Total Alcohol Rate (g/kg-hr)	233	407	159	304
Methanol Rate (g/kg-hr)	119	248	35	99
Ethanol Rate (g/kg-hr)	0	7	0	0
Isopropanol rate (g/kg-hr)	0	0	0	0
n-Propanol rate (g/kg-hr)	12	21	15	27
Isobutanol Rate (g/kg-hr)	102	130	109	179
MeOH/i-BuOH mole ratio	4.7	7.6	1.3	2.2
Hydrocarbon rate (g/kg-hr)	26	37	94	112
Conversion (%)	14	24	23	28

The data show that the catalyst is most effective for higher alcohol synthesis (HAS) at elevated temperatures and pressures. Note that the *combination* of high temperature and high pressure is required for optimal for HAS. This is because the sum of the individual effects

promotes HAS over both hydrocarbon formation (favored at higher temperatures) and methanol formation (favored at higher pressures).

This catalyst (with extra added alkali as compared with 10-DAN-54) can also operate effectively at syngas conversions up to 28%. (See PR-125 in the table of Section 4.1.4.) 10-DAN-54 was limited to conversions of < 20%, otherwise hydrocarbon formation became a serious inefficiency.

Tests with other catalyst formulations are planned, as well as detailed catalyst and support characterization.

4.1.5. Experimental

4.1.5.1. Catalyst Preparation

The ZnCrMn oxides were prepared by coprecipitating the metal nitrate salts in aqueous medium at a constant pH. An aqueous solution containing the metal nitrate salts and a basic solution were dripped slowly into ~200 mL of the basic solution using two peristaltic pumps. Care is taken to assure that the resulting solution is well stirred during the addition and the pH of the solution is monitored continuously. The flow of the basic solution is adjusted to keep the solution at a constant pH. The resulting mixture is then heated for a given time and then solid precipitate is filtered and washed with at least three liters of water, mixing well during the washing. The solid is dried at 110-120°C overnight and calcined for the desired time at the appropriate temperature. The catalysts were impregnated using the incipient wetness method.

4.1.5.2. Catalyst Testing

The reactor tubes were made from 1/4 inch stainless steel tubing that had been treated overnight with a 50/50 solution of hydrochloric acid and water. The tubes were rinsed with water for 5 minutes followed by an acetone rinse. Newer reaction tubes have been made from 1/4 inch copper tube inserted into 3/8 inch stainless steel tubes. The copper tubing was rinsed well with acetone before use. Reactors were dried under vacuum. One gram of catalyst was mixed with 3 cm^3 of glass beads until the mixture was uniform. The reactors were then loaded while tapping on the sides of reactor tube. Due to the V-like nature of the reactor tubes, each side of the V was loaded with one-half of the catalyst mixture at a time. Glass wool was then put into place on both sides of the reactor. The catalysts were reduced with 5% hydrogen in nitrogen for four hours at the desired temperature.

The reduced catalysts were then loaded into the sand bath and the system was pressurized with nitrogen. Once the reactor reached the correct temperature, the nitrogen was turned off and the syngas feedstream was turned on and adjusted to the correct pressure.

4.1.6.   Task 1 Conclusions

We have prepared an improved version of 10-DAN-54, a Zn/Cr/Mn spinel oxide promoted with Pd and K. This material (16-DMM-68) has acceptable elemental analysis for the expected composition and possesses the desired high surface area of >80 m^2/g.

In tests under standard conditions (400°C, 1000 psi, GHSV = 12000, syngas ratio = 1), this catalyst shows a selectivity to total alcohols of 84% and produces > 100 g/kg/hr of isobutanol with a MeOH/i-BuOH mole ratio = 4.7.

Tests of 16-DMM-68 at temperatures above 400°C and pressures up to 1500 psi (GHSV = 12000, syngas ratio = 1) have confirmed the expected improved performance: at 440°C and 1500 psi, this catalyst shows a selectivity to total alcohols of 64% and produces 179 g/kg/hr of isobutanol with a MeOH/i-BuOH mole ratio = 2.2. This is our best overall performance to date.

The catalyst operates at syngas conversions up to 28% with good selectivity to total alcohols due to the extra added alkali. This performance can be compared with 10-DAN-54, which could only operate up to 20% conversion before hydrocarbon formation became a serious inefficiency.

In future work we will examine other catalyst formulations to seek improved performance, and we will characterize the catalyst by surface science techniques to look for structure/property relationships.

4.2. Task 2 – Engineering Studies
4.2.1. Reaction Engineering
4.2.1.1. Introduction

Task 2 work under this contract involves reaction engineering studies to examine the best catalysts identified in Task 1. New catalysts will be developed and screened in powder form in Task 1. We will develop scaleup and process strategies to make use of the best catalysts found in Task 1 and will develop kinetic models to describe their performance.

Our reaction system consists of both a microreactor and a Berty autoclave for larger-scale studies. We have made progress in improving the analytical capabilities required to support work in these systems.

4.2.1.2. Analytical

We purchased and installed a Hewlett-Packard ChemStationR for gas chromatograph data handling (UCC-funded). The new equipment has tremendously improved our capabilities to store, manipulate, and interpret our GC data. We also purchased and installed a Supelco High Capacity Gas Purifier for our GC carrier gas feed line (UCC-funded). The purifier is intended to remove moisture and oxygen from the carrier gas. We have had a nagging problem with an irregular contamination peak which would co-elute with hydrogen. Because we used helium as a carrier gas, hydrogen would appear as a negative peak which was not difficult to visually differentiate from the contaminant. Unfortunately, the integrators couldn't discern the difference as readily, and we had to make calculations off-line to measure hydrogen concentrations with reasonable accuracy.

With the new ChemStationR, we hoped to be able to use the added integration options to make more accurate measurements of the hydrogen peak, but found that the contaminant peak continued to impede our progress. In our efforts to eliminate the contaminant peak, we have reduced its size such that it is barely discernible from the baseline. We also found that the carrier gas head pressure affects the contaminant peak location. By manipulating the carrier gas head pressure, we were able to separate the hydrogen peak from the contaminant peak. This gives us more confidence in our measurement of hydrogen. Unfortunately, other peaks began to co-elute and we have had to change our temperature program to separate those peaks. With so many compounds which need to be identified, this process has been very tedious.

4.2.2. Task 2 Conclusions

A significant upgrade in our analytical system has been installed, which has greatly improved our capabilities to store, manipulate, and interpret our GC data.