# Kinetic Study of Ethanol Dehydration

A Major Qualifying Project Report

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By

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Approved:

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# Acknowledgements

I would like to thank Professor Timko for his substantial amount of support, Alex Maag for his resourceful guidance, Jeremy Filteau and Andersen Derosier for their pre-existing research, and Deanna Poirier for her foundational work that preceded theirs. This project has undoubtedly made me a much better scientist and engineer and I appreciate all that you have done to assist me in my study.

# Abstract

Last year, Andersen Derosier and Jeremy Filteau did research on ethylene production from ethanol dehydration using ZSM-5. They noticed a trend in water loading with their experimentation and came to a conclusion that water inhibited ZSM-5 active sites. This experiment studied the kinetics of ethanol dehydration at lower conversion to determine whether their hypothesis was true and to see any other factors that may have caused that trend. The results from this experiment show that their hypothesis was true, and the reaction was limited due to diffusion limitations from the catalyst.

# Background

This project is a continuation of a study done by Andersen DeRosier and Jeremy Filteau studying the effects of liquid phase catalyzed dehydration of ethanol to form ethylene. Their studies used ZSM-5 to produce liquid and gas products of ethylene analyzed using gas chromatography. Their results determined that ethanol conversion to ethylene is not significantly affected by the addition of water, but the vapor phase produced a significantly higher conversion than the liquid phase. Adding water had a nominal effect on the vapor phase and a positive correlation on the liquid phase. To explain this, they suggested a mechanism in which water inhibited the zeolite active sites. This experiment will analyze the reaction of ethanol to DEE rather than ethylene at lower conversions at differing temperatures, pressures, and catalyst amounts to determine the kinetics of the reaction and why Jeremy and Andersen got these trends in their data.

# Introduction

## Ethylene applications

Ethylene helps produce about 75% of all petrochemicals worldwide [1]. Approximately 146 million metric tons of ethylene were produced in 2016, making it one of the most widely synthesized raw materials in the world. It is the monomer of polyethylene, one of the world's most widely-used plastics and of which 81.8 million metric tons were produced in 2015 [2]. Almost all ethylene produced today is created through pyrolysis. The following figure shows ethylene and polyethylene structures:
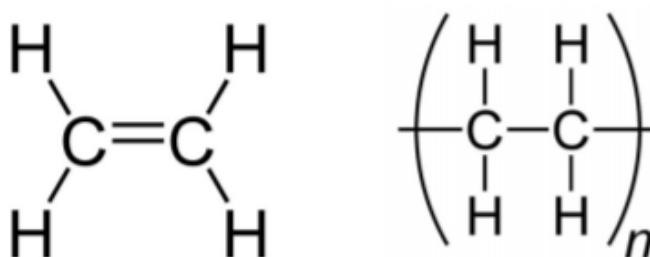


Figure 1: Structure of ethylene (left) and polyethylene (right)

The pyrolysis of ethylene is the use of steam and catalytic cracking to obtain compounds such as ethane, propane, naphtha and gas oils from crude oils and natural gases. The United States produces about 25 million tons of ethylene per year, which is processed mostly in the United States as well as across Europe [2]. It is used to make items including industrial alcohol, antifreeze, plastics, and synthetic rubber [3].

## Zeolites

Catalysts are used to decrease the activation energy of a reaction, allowing it to proceed at a faster rate. For this reaction, zeolites are used as a catalyst. Zeolites are microporous

minerals used to break down hydrocarbon molecules into smaller types of gasoline and petroleum products [4]. ZSM-5 is catalyst used in the dehydration reaction of ethanol. The process of a surface-catalyzed reaction is as shown below.
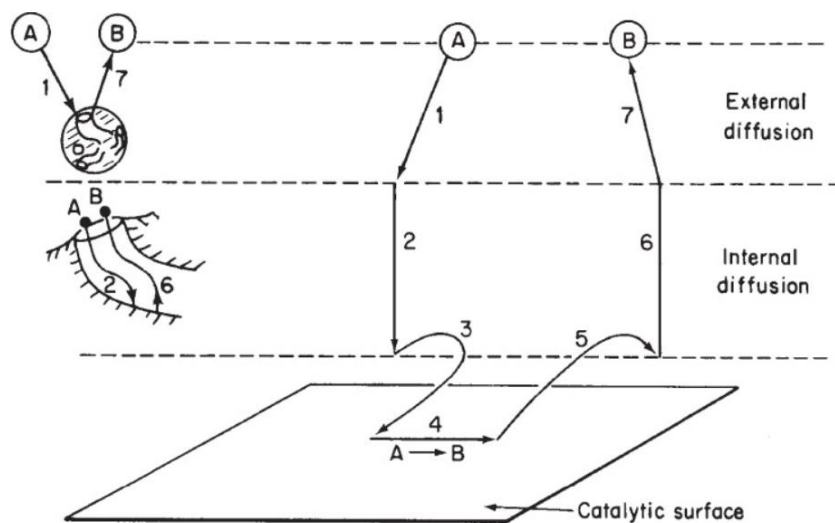


Figure 2: Major steps in a surface-catalyzed reaction

Ethanol has two major reactions it can undergo with a zeolite catalyst. One will form ethylene, and one will form diethyl ether (DEE). Due to the low conversion of ethanol, the majority of our product will be DEE at lower temperatures. The two dehydration reactions forming ethylene and DEE are shown below:

$$C_2H_5OH \xrightarrow{catalyst} C_2H_4 + H_2O$$

$$2C_2H_5OH \xrightarrow{catalyst} C_4H_{10}O + H_2O$$
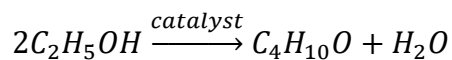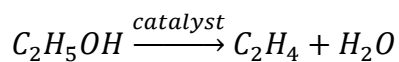
Equation 1: Dehydration of ethanol into ethylene and DEE, respectively

## Kinetics

Reaction kinetics determine the speed of a reaction, and therefore the amount of product created in the reaction. Kinetics rely on multiple factors, including reactant concentrations,

activation energy, and temperature. Most single-reactant reaction mechanisms will take on the form of the following:

$$r = -k[X]^\alpha$$

Equation 2: Proposed reaction mechanism for dehydration of methanol

This equation shows the direct relationship between the concentration of a reactant (X) and the rate of reaction. The rate constant (k) is a rate constant which is a factor of temperature and activation energy as shown in the following equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

Equation 3: Arrhenius equation

For a reaction like ethanol dehydration, temperature will be high and activation energy will be low for this equation, due to the high temperature the reaction will be taking place at along with the catalyst. This report will be comparing the effects of liquid phase ethanol reacting to form DEE and ethylene. Comparing the two of them, they should have very significant differences in rate due to the phase change affecting the frequency factor (A).

## Green Ethylene

The purpose of studying ethanol dehydration is its ability to form ethylene in an environment-friendly manner. A basic diagram of the green ethylene process can be seen below.



Figure 3: Process flow diagram of green ethylene production

Agricultural feedstock can be converted into ethanol through fermentation processes, and then to ethylene by catalytic dehydration before being converted into its everyday products. This gives an alternative mean of producing ethylene that doesn't involve steam cracking and makes it a drop-in substitute for processing plants [5].

The cost of green ethylene is prohibited by its economical constraints. Green ethylene costs between $1200-2000 per ton depending on the ethanol source, while production from steam cracking in the petrochemical industry costs about $600-1300 [6]. Most of these differences come in the cost of feedstock and production. Bio-ethanol is subject to feedstock qualities of many different qualities and prices which undergoes a highly endothermic reaction during fermentation, requiring temperatures exceeding 300°C to ensure acceptable selectivities are met and avoid losses to byproducts of the reaction [7]. This makes the energy requirements a main target to make the process economically viable and can be affected by different catalysts, types of reactors used, reaction phase, and feed composition.

# **Experimental**

## Safety

Standard safety precautions were used throughout all of experimentation. Personal protective equipment was used at all times in the lab, including eyewear and gloves. The reactor was properly insulated and checked every day before experimentation, reaching pressures of up to 1500psi and temperatures of 400°C.

## Preparation

Before experimentation, the reactor was partially disassembled and cleaned with deionized water and thoroughly dried with a multiple small paper towel pieces pushed through the reactor. Following, the reactor plug was placed back into the reactor and catalyst was measured and added in respective amounts for each trial. The reactor would then be reassembled and closed in the proper orientation, the heating rod would be positioned in the reactor, and the inlet and the outlet of the reactor reconnected. The thermocouple would then be connected to the end of the reactor, and all sections of the piping checked for loose pieces. The reactor will then be ready to operate for that day of trials.

## Procedure

The ethanol dehydration reaction was carried out in a plug flow reactor carried out in the schematic shown in figure X:
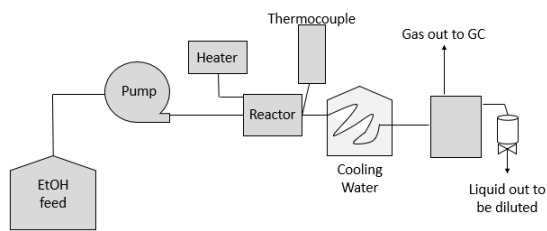
Figure 4: Schematic of experimental layout

The ethanol feed was stored in a covered glass container, which was then pumped to the

reactor. The reactor was heated by a heating rod which could be placed inside the reactor.

Temperatures from inside the reactor were read back to the heater and to a thermocouple at the

end of the reactor. Temperatures from the heater were adjusted until the thermocouple reached

the desired temperature. In the reactor, porous catalyst was placed. Following exiting the reactor,

the products would pass through cooling water before being separated into their gaseous and

liquid products. Pictures of the experimental layout can be seen in the following figures.



Figure 5: Ethanol feed, pump, heater, and reactor insulation (from right to left)
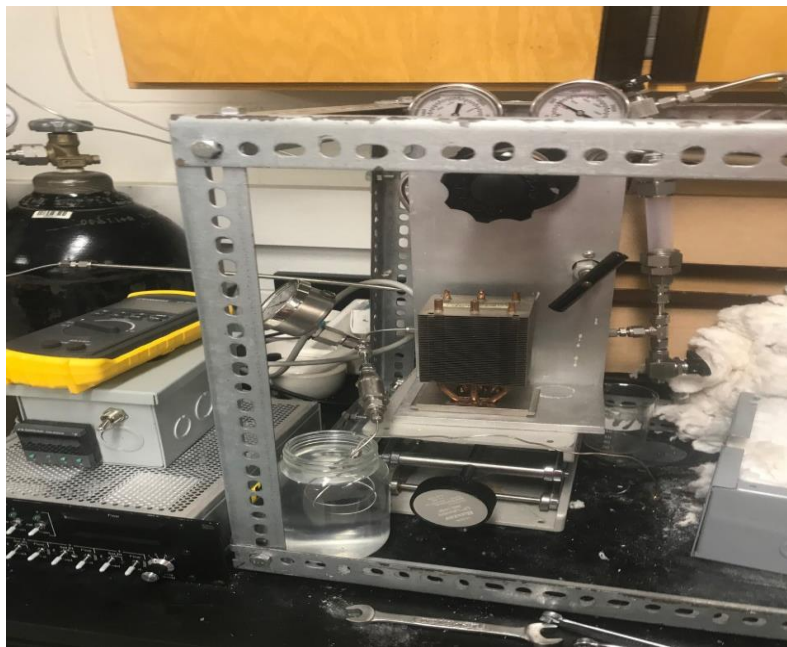
Figure 6: Thermocouple, cooling water coil, and liquid sample collector (from left to right)
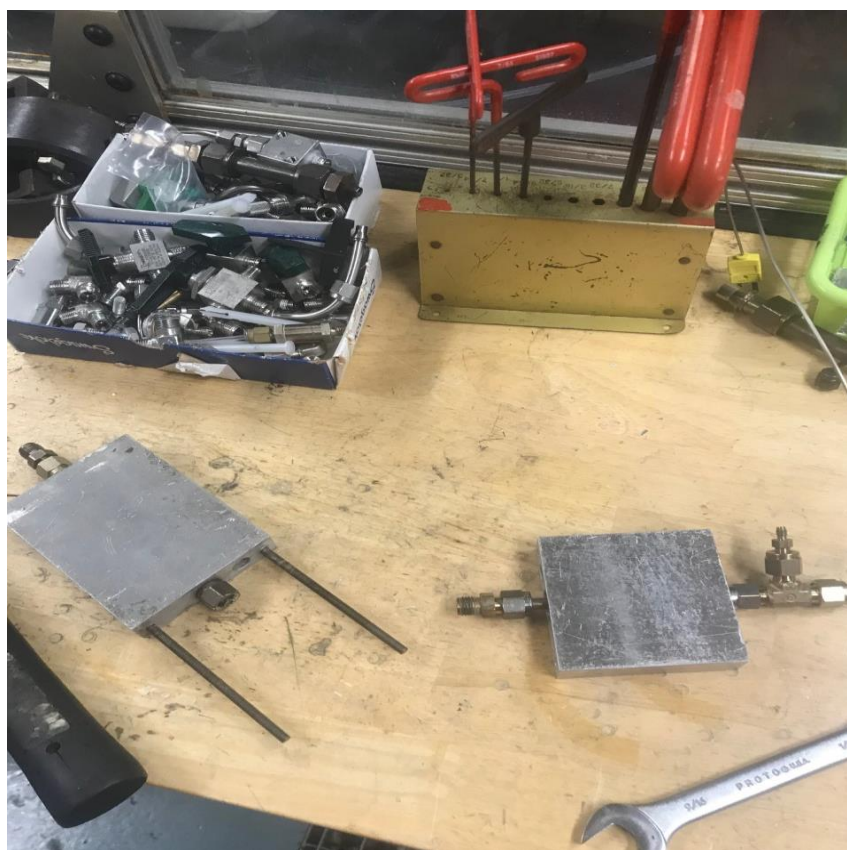


Figure 7: Partially disassembled plug flow reactor

## Data Collection

For each set of trials, a set of 3 data points was collected for each specified set of conditions. The pump would send 1-2 ml/min of ethanol through the reactor depending on the trial and produce liquid products in according amounts. This product was then diluted and then analyzed using a gas chromatographer. The dilution amount and amount of product added to the water during the dilution was also documented. The gas chromatographer program was designed through trial and error until conditions were met that would separate ethanol and DEE and the area under these curves would represent the amount of ethanol and DEE in the solution. The amount of ethanol and DEE produced was calculated by the area under these curves by creating a calibration curve for the areas under the peaks using known amounts of ethanol and DEE determining weight percentage. Taking the area under the curve calculated by the gas chromatographer and the calibration curve, I was able to determine the amount of ethanol and DEE in the product.

Following determining the amount of ethanol and DEE by weight percentage, these percentages, the product amount, and water dilution were then placed into an excel sheet created by Alex Maag. This excel sheet could take the information placed from these four numbers and calculate the weight percent of ethanol and DEE in the initial product solution as well as any intermediates that were calculated, such as grams of ethanol, grams of water produced, grams of DEE, and weight percent of dilution. After the excel sheet calculated these, the weight percent of ethanol and DEE in the initial product solution could be used in a material balance in the same excel sheet. This would calculate ml, grams, and moles of each product and reactant. For this part of the experiment, it was assumed that no ethylene was converted under these conditions as the temperatures were much lower than that which would produce ethylene. Conversion would

be based on the weight percent of ethanol and DEE, and extents would be zeroed one with weight percent of ethanol to determine ethanol conversion, expected DEE yield, and water yield, while zeroing to DEE would give the actual DEE yield. Taking the average ethanol conversion of each set of 3 data points at each given set of conditions over many comparable sets of conditions, turn over frequencies (TOFs) were able to be calculated for each of these conditions. Turn over frequency is a measurement of the activity of the catalyst based on conversion. Calculating the natural log of the TOF and plotting it against any condition would give an Arrhenius plot, a graph which plots the effects of the condition against the rate of the chemical reaction. These Arrhenius plots can then determine the effects of each condition on the reaction and what inhibits it.

# Results

The results of my experimentation can be categorized into four main kinetic studies: a phase / water loading study, pressure study, catalytic study, and space velocity study. Each of these covers a different possibility of what could have inhibited Jeremy's and Andersen's ethanol conversion to ethylene.

## Phase / water loading study

The phase / water loading study I did was completed by varying temperatures, inlet compositions, and inlet phases while holding a constant flow rate of 1ml/min and using .1g of ACS for each trial.



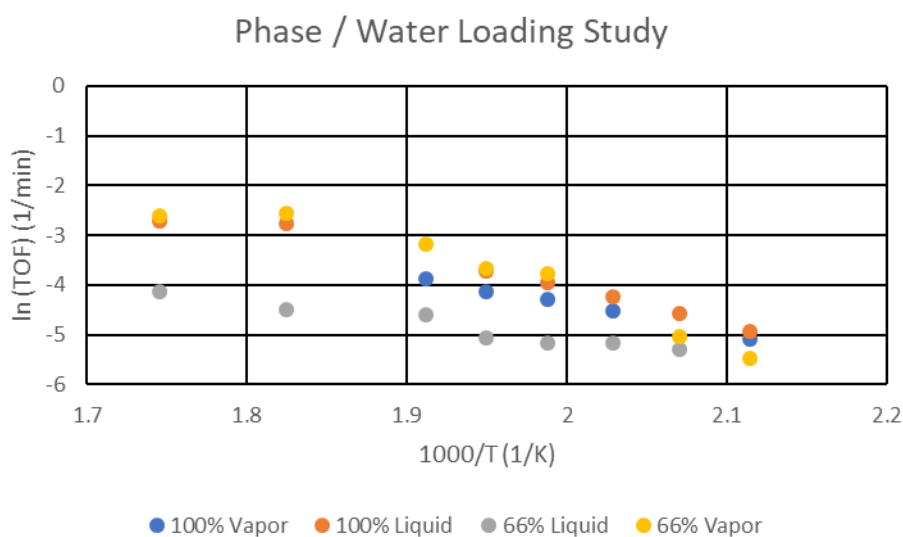Figure 8: Phase and water loading study results

This graph was created to mimic the phase study given by Jeremy and Andersen with ACS in comparison to their ZSM-5. This graph shows the same trends as their results did with regards to phase and water loading. Vapor showed overall greater activity which increased with water loading while liquid showed overall less activity which decreased with water loading.

Knowing that ACS shows the same trends as ZSM-5 makes it viable to use for this comparative study.

## Pressure Study

The pressure results were gathered by varying pressure in a liquid phase 66% ethanol feed with a constant flow rate of 1ml/min, constant temperature, and .1g of ACS. The pressure study produced the following results:
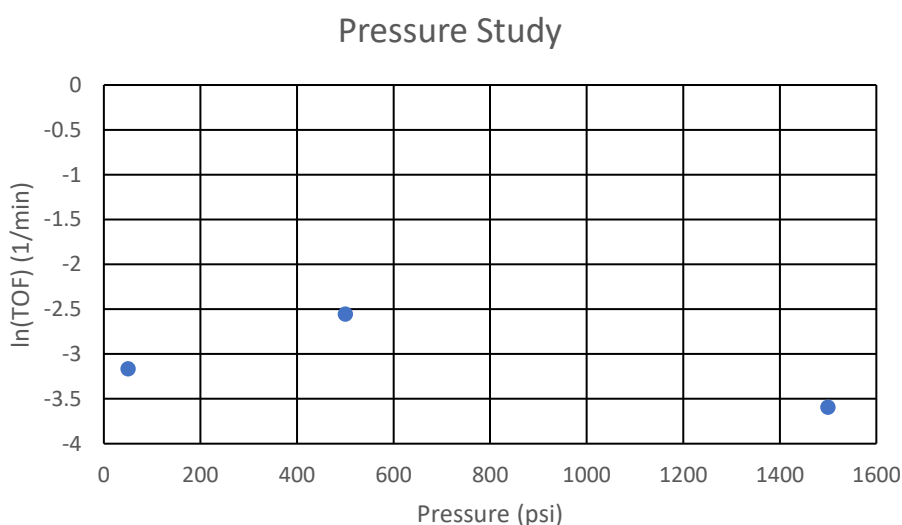


Figure 9: Pressure study results

The pressure study results show that there was a possibility that Jeremy and Andersen may have had the pressure of their reactor affecting their conversion. The graph shows that at increasingly high temperatures, conversion becomes inhibited. These results would agree with theirs as their conversion to ethylene occurred at pressures up to 3600 psi. This would also agree with Le Chateleir's principle as a large increase in pressure with a gaseous product and no gaseous reactants would inhibit conversion in a liquid phase reaction.

# Catalytic Study

The catalytic study was done comparing ACS and ZSM-5 in the vapor phase with 100% ethanol. Comparing these two produced the following results:
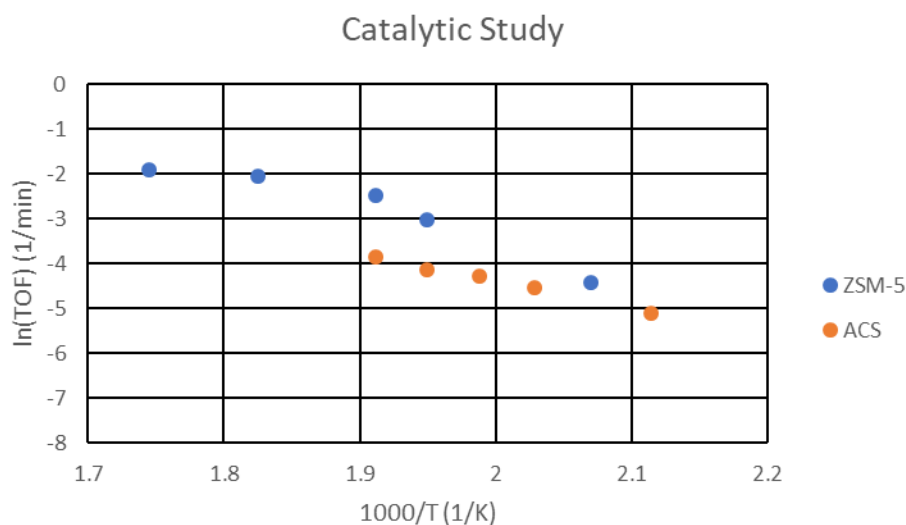


Figure 10: Catalytic study results

The purpose of a catalytic study was to show possible diffusion limitations. ZSM-5 is about ¼ the size of ACS. This graph showing ZSM-5 is more active than ACS at the same temperature. This would suggest that a larger catalyst would cause and prove diffusion limitations within the reaction mechanism. This means that Jeremy's and Andersen's conclusion that water may be inhibiting ethanol dimerization at active sites is true, as it would cause a diffusion limitation.

# Space Velocity Study

The space velocity study was done using ACS and ZSM-5 with 100% ethanol in a vapor phase reaction. In this study, a flow rate of 1ml/min with .1g of catalyst (low space velocity) was

compared to a flow rate of 1.5ml/min with .025g of catalyst (high space velocity). The space

velocity results are as shown in the following graph.



Figure 11: Space velocity study results

The space velocity results show that space velocity is more impactful in larger catalysts.

ACS shows much more activity at a higher space velocity than a lower space velocity. However,
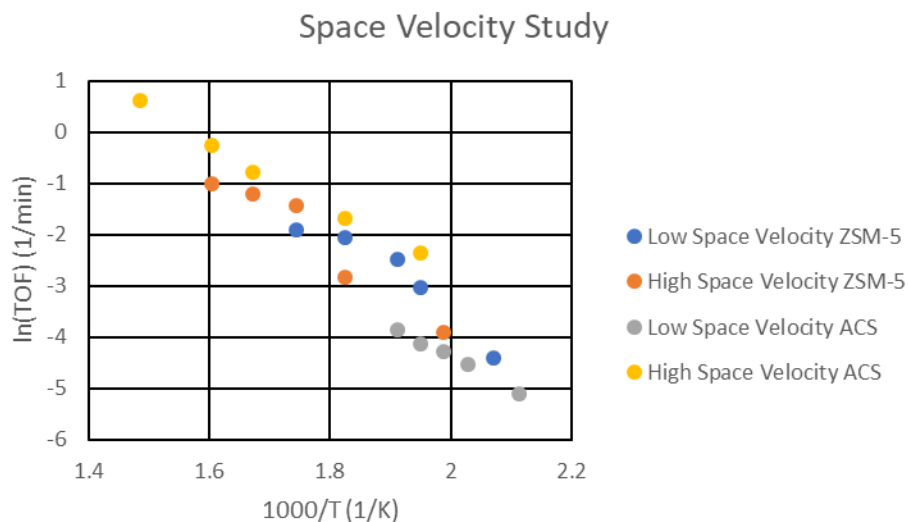
ZSM-5 shows very little difference in activity as an effect of space velocity due to its smaller

size. This means space velocity can be eliminated as a major factor in limitations of ethanol

dehydration.

# Conclusions and Recommendations

The purpose of this experiment was to validate the hypothesis made that water inhibition would limit ethanol dehydration. Each study shown has shown something can contribute to what did or didn't affect dehydration limitations. The results from this experimentation showed that ACS was a viable substitute as a catalyst for ZSM-5 at varying phases and water loads. The pressure study showed that pressure may have been an influence in Jeremy's and Andersen's results. The space velocity study showed that the space velocity had not enough effect on the reaction to cause a significant difference in activity. The primary takeaway from my findings is the results of the catalytic study in comparison to Jeremy's and Andersen's hypothesis. The catalytic study was able to prove their hypothesis that water inhibition was limiting dimerization of ethanol at zeolite active sites. They also suggested that more finely coked catalyst would improve conversion in the liquid phase, which would also be true here. Recommendations to be made would be to run a similar catalytic study at a much higher conversion with ethylene to verify that this diffusion limitation has applications to real-world ethylene production.

# References

1. P. L. Coutinho, A. T. Morita, L. F. Cassinelli, A. Morschbacker, and R. W. Do Carmo, "Braskem's Ethanol to Polyethylene Process Development," in Catalytic process development for renewable materials, Weinheim, Germany: Wiley-VCH, 2013.

2. J. Lazonby, "Poly(ethene) (Polyethylene)." [Online]. Available: http://essentialchemicalindustry.org/polymers/polyethene.html. [Accessed 4-Oct-2017].

3. Francis A. Carey. Ethylene | structure, sources, production, uses, & facts. 2019 [Online]. Available: https://www.britannica.com/science/ethylene [Accessed 18-Mar-2019].

4. C. Woodford, "What are zeolites? | how do zeolite catalysts work?" [Online]. Available: http://www.explainthatstuff.com/zeolites.html [Accessed 7-Feb-2019].

5. D. Fan, D.-J. Dai, and H.-S. Wu, "Ethylene Formation by Catalytic Dehydration of Ethanol with Industrial Considerations," *Materials; Basel,* vol. 6, no. 1, pp. 101-115, 2013.

6. International Renewable Energy Agency, "Production of Bio-Ethylene," International Energy Agency, Jan 2013.

7. M. Zhang and Y. Yu, "Dehydration of Ethanol to Ethylene." *Ind. Eng. Chem. Res.*, vol. 52, no. 28, pp. 9505-9514, Jul. 2013.

# Appendices

## Appendix A: Gas Chromatography Example
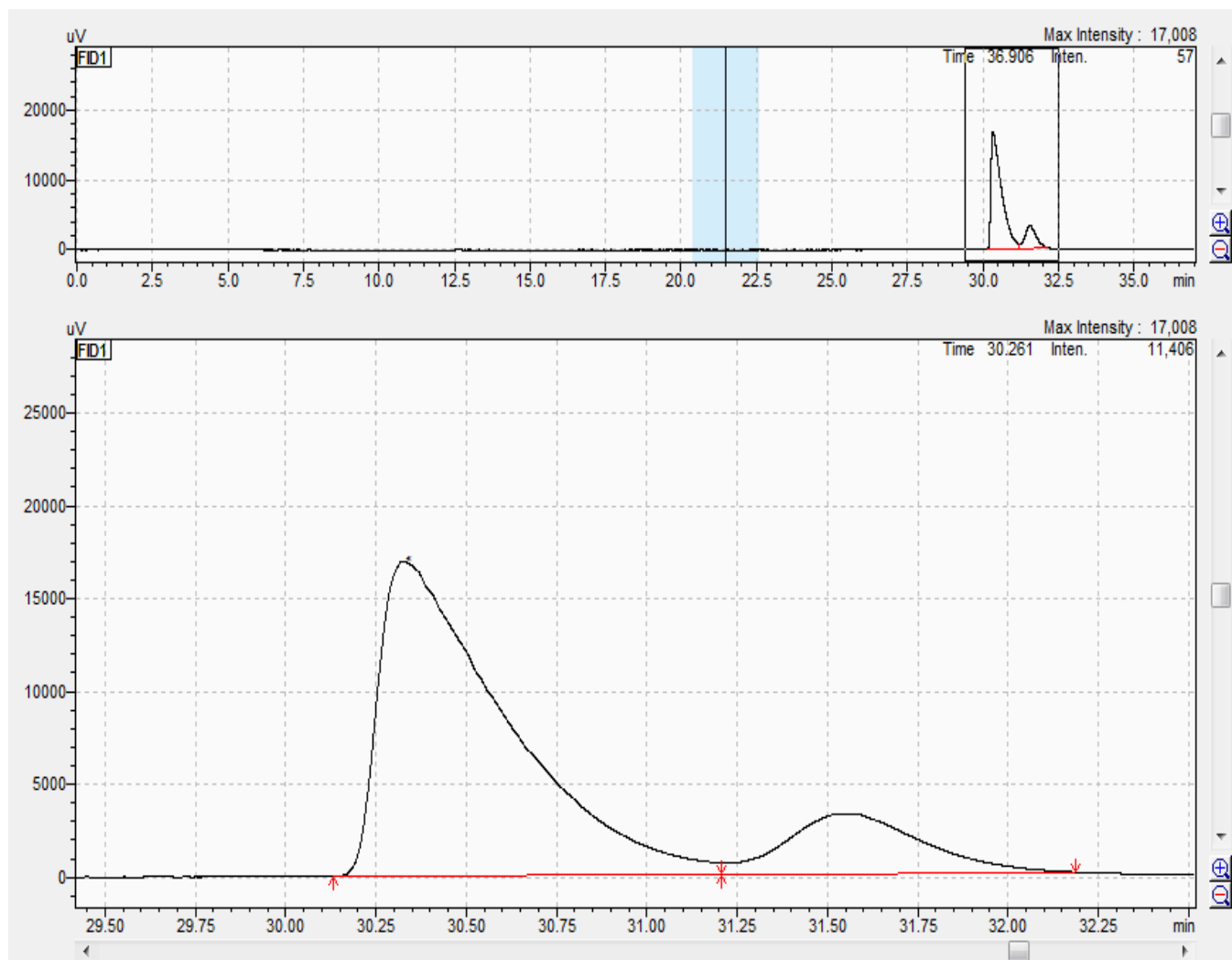
# Appendix B: Gas Chromatography Methods

Temperature: 70.0 ℃

Equilibration Time: 3.0 min

Column Information(Rt-U-Bond)

Column ID: 19752

Installation Date: 11/15/2017

Column Max Temp: 190.0 ℃

Length: 30.0 m

Inner Diameter: 0.32 mm ID

Film Thickness: 10.00 µm

Comment: Alcohol Column

Set



Column Oven Temperature Program: Total Program Time: 37.00 min

|   | Rate | Temperature | Hold Time |   |
|---|------|-------------|-----------|---|
|   | –    | 70.0        | 2.00      |   |
| 1 | 2.00 | 140.0       | 0.00      |   |
| 2 | 0.00 | 0.0         | 0.00      |   |

Temperature: 110.0 ℃

Injection Mode: Split

Sampling Time: 1.00 min

Carrier Gas: He

Flow Control Mode: Pressure

Pressure: 30.9 kPa

Total Flow: 74.1 mL/min

Column Flow: 0.57 mL/min

Linear Velocity: 13.4 cm/s

Purge Flow: 5.0 mL/min

Split Ratio: 120.0

⊻ Program



Inj. Program: Pressure Total Program Time: 0.00 min

|   | Rate | Pressure | Hold Time |
|---|------|----------|-----------|
|   | –    | 30.9     | 0.00      |
| 1 | 0.00 | 0.0      | 0.00      |
| 2 | 0.00 | 0.0      | 0.00      |

# Appendix C: Excel Sheet Data Analysis Example

| | Molar balance | | | | | | Calculated FR | Extent | 0 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Feed | | | Product | | | | C2H4 Yield | 0 | | | | | |
| | ml/min | g/min | mol/min | mol/min | g/min | ml/min | ml/min | Zero | -42.2535 | | | | | |
| Ethanol | 1 | 0.789 | 0.01713 | 0.0083 | 0.3822 | 0.4844 | | Extent2 | 0.00441518 | | | | | |
| Water | 0 | 0 | 0 | 0.0044 | 0.0795 | 0.0795 | | Zero2 | 0.0000 | EtOH wt% | DEE wt% | DEE Yield | Water Yield | EtOH conversion |
| Diethyl Ether | - | - | - | 0.0044 | 0.3273 | 0.4635 | | DEE Yield | 0.257795252 | 0.484413834 | 0.414773219 | 0.4147695 | 0.100812045 | 0.515590504 |
| Ethylene | - | - | - | 0.0000 | 0.0000 | 0.00 | | | | | | | | |

| | Wet Test Meter (ml/min) | | Vial | g H20 | g Solute | wt% Dilution | wt% Ethanol | g EtOH | g H20 Prod | wt% Ethanol Rem | wt% DEE | g DEE | wt% DEE Prod |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| E12_50 psi | 42.3 | 0.82313 | Ethanol Test | 33.862 | 0.82313 | 0.02373 | 0.017331779 | 0.6012 | 0.2220 | 0.730 | 0.00E+00 | 0.0000 | 0.0000 |
| 66% EtOH | | 0.2638 | E12_50_1 | 33.103 | 0.2638 | 0.00791 | 0.003618796 | 0.1207 | 0.1259 | 0.458 | 5.13E-04 | 0.0171 | 0.0648 |
| .1g ACS | | 0.3182 | E12_50_2 | 33.326 | 0.3182 | 0.00946 | 0.004431225 | 0.1491 | 0.1504 | 0.469 | 5.56E-04 | 0.0187 | 0.0587 |
| Liq | | 0.2265 | E12_50_3 | 33.706 | 0.2265 | 0.00668 | 0.003054064 | 0.1036 | 0.1080 | 0.458 | 4.37E-04 | 0.0148 | 0.0655 |

| EtOH Conversion | DEE Yield, liq | Ethylene Yield, liq | Water Yield, liq | Expected DEE Yield | Avg EtOH Yield | 1000/T or P | TOF | ln(TOF) |
|---|---|---|---|---|---|---|---|---|
| 0.251967082 | 6.48E-02 | | 0.049804121 | 0.202696 | 0.246189064 | 50 | 0.042164 | -3.16619 |
| 0.234321364 | 5.87E-02 | | 0.046354188 | 0.188501 | | | | |
| 0.252278747 | 6.52E-02 | | 0.049865347 | 0.202947 | | | | |