MQP MT2 AALP

Ethanol Dehydration

Major Qualifying Project Proposal completed in partial fulfillment
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Abstract

Plastics have become one of the most used materials in the manufacturing industry. Ethylene is the main component of most commonly made plastics. One of the most common ways of making ethylene is by a process called ethanol dehydration which is the process of producing ethylene from ethanol. The purpose of this project was to study and compare the ethylene yield of ethanol dehydration in both the liquid and vapor phases. This was done by studying the activity and crystallinity of a catalyst and the heat transferred in the reactor all while varying the flow rate and ethanol composition of the feed. It was found that liquid phase ethanol dehydration does yield ethylene, however not as much as vapor phase. This could be improved if the catalyst did not degrade as easily in hot liquid. Liquid phase ethanol dehydration can compare economically to vapor phase because it has a lower reaction temperature, resulting in less energy used, thus it is cheaper to manufacture. Not as much ethylene is produced but it is cheaper to manufacture. If more ethylene could be created, liquid phase ethanol dehydration could become a viable candidate for the manufacture of ethylene.

Acknowledgements

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Secondly, we would like to acknowledge Alex Maag for all the time he took to help us. He taught us everything we needed to know about this project involving the laboratory equipment. He was there every time we had a run or used the GC to make sure everything was going smoothly. Not only was he there to help run the reactor but he was also there to help analyze our data and was willing to answer any questions we needed. We really could not have done this project without him.

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Chapter 1: Introduction

Plastics have become one of the most used materials in the manufacturing industry. The low cost, ease of manufacture, and versatility of this material makes it a great choice to use for almost anything. As time goes on plastics are starting to replace a lot of other materials such a wood or steel. Plastics are very durable and degrade slowly which makes them not very renewable which can be harmful to the environment when it is time to get rid of them. There is strong encouragement currently to produce polymers that have lower impacts on the environment. It is therefore important to make these polymers more renewable, one way to do that is to change the process in which polymers are made.

Ethylene is the main component in most commonly made plastics. The process begins with a renewable biological material, or biomass. Glucose is extracted from this mass and fermented to end up with ethanol and water. The most commonly used process to make ethylene from ethanol is primarily by steam-cracking of hydrocarbons.[1] There is, however, an alternative option to make ethylene called ethanol dehydration. Ethanol dehydration has been discovered to use less fossil fuel in the process and lower greenhouse gas production. With increasing fuel prices and concerns for the environment, this could become a more cost effective option to steam-cracking of hydrocarbons.

In the ethanol dehydration process, studies have indicated that an addition of a catalyst will increase ethylene yield and lower the reaction temperature. Thus, using less energy and making the reaction more cost-efficient and pertinent in industry. [2] Many researchers have investigated different catalysts to use in this process; some of the most common are zeolites. Zeolites are used widely in the oil refining and petrochemical industries due to their wide-ranging features. [3]

Ethanol dehydration has been mostly commonly done in the vapor phase as that is where the zeolite is most stable. However, liquid phase reactions of ethanol dehydration are run at high temperatures and lower pressures and promote an economically practical reaction speed. Zeolites are an attractive choice to be catalysts in these reactions; a downside however, is that they have tendencies to lose their crystallinity when in the presence of liquid water in temperatures above 150°C. It is also observed that coking forms at the Bronsted acid sites where the zeolites are most reactive; therefore the zeolites become deactivated and lose the ability to catalyze. [4]

This study is aimed to study and compare the dehydration of ethanol to ethylene in both vapor and liquid phase using the zeolite catalyst, ZSM-5. The process was carried out at different feed flowrates and compositions both in vapor and liquid phases and their corresponding conversions were compared. Runs were also started in different phases to see if starting in the liquid or vapor phase had an effect on the outcome. Moreover, the crystallinity and reactivity of the zeolite was studied by comparing the untreated catalyst to the catalyst after a run using X-ray diffraction (XRD). The changes in heat transfer rates at different flowrates in both vapor and liquid phases were also studied.

Chapter 2: Background

2.1 Biomass

Biomass is biological material derived from living, or recently living organisms. From biomass, come biofuels and biochemicals which are important products. Some of the most common examples of biomass feedstock are grains and starch crop such as corn and sugarcane, food waste, animal byproducts, switch grass, and wood. Biomass can be used as a substitute for fossil fuels in the manufacturing of energy and other products. Living biomass takes in carbon as it grows and uses it for energy when it is released. This results in a release of carbon into the atmosphere rather than a greenhouse gas that harms the environment. [6] Biomass is an extremely important part in the plastic development process because it can get the same result as the use of fossil fuels but with much less harm to the environment. However, there is a downside; the use of biomass with the current technology is not economically competitive enough with the use of fossil fuels. It has been discovered that bio-oil is not suitable for thermal fractionation after it has been condensed from pyrolysis vapors. This might be avoided with reactions in the liquid phase at moderate temperatures instead. [7]

Although biomass can come from a variety of different feedstocks, it is still composed of the same original components; hemicellulose, cellulose and lignin. These components of biomass are carbon-based can generally have a composition of 20-40 wt. % hemicellulose, 40-60 wt. % cellulose, and 10-25 wt. % lignin in each feedstock. [8] The process of biomass to ethanol conversion can be seen in the figure below:

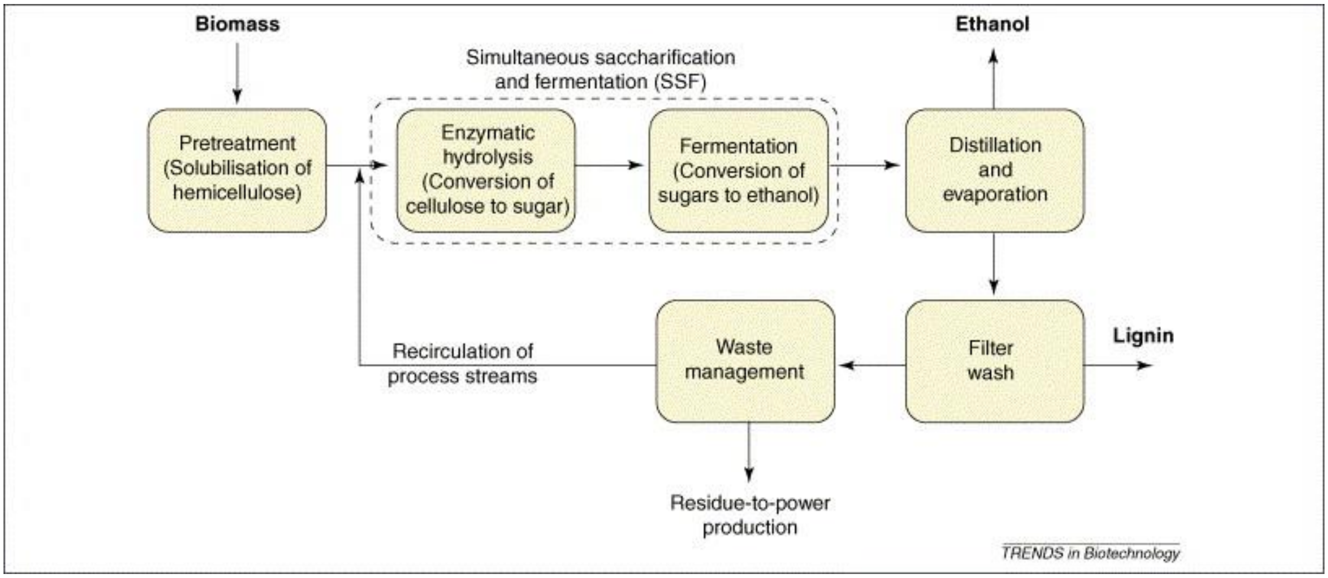

Figure 1: Biomass to ethanol Conversion [9]

2.2 Catalysts

A catalyst is a chemical substance, which is capable of increasing the rate of a chemical reaction known as catalysis. The catalysis can be realized as a cyclic process where reactants are bound to the catalysts, which lead to the formation of intermediate catalysts-reactant complex. This further leads to the formation of product where catalysts are regenerated to its initial state as shown in figure 2 below. [10] In the presence of a catalyst, the reaction requires less free energy to reach its transitional state. Therefore, the catalyzed reaction has a lower activation energy (Ea) than the corresponding uncatalyzed reaction, resulting in an increase of reaction rate or selectivity and enables the reaction to occur at lower temperatures as seen in figure 3. Catalysts work by increasing the number of successful collisions, which is required to reach the transition state.

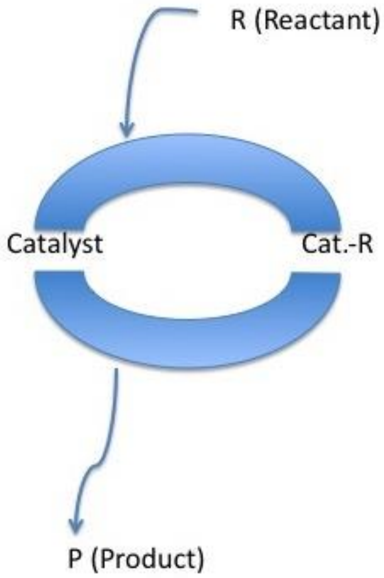

Figure 2: The cyclic process of catalysis

Catalysts are generally categorized in different types depending on their phases with substrate. Heterogeneous catalysts are solid that act on liquid or gaseous subtracts. Heterogeneous catalysts have active sites where the reaction occurs. The activity of heterogeneous catalysts depends upon the strength of chemisorption and the reactant must be absorbed strongly on the catalyst to become active. Homogeneous catalysts act in the same phase as the reactants. They are generally dissolved in a solvent with substrates. Catalysts are widely used in chemical industries in production of important chemicals. Moreover, it is used in automobiles as catalytic converting for converting toxic pollutants in exhaust gas to less toxic pollutants [11]. A number of catalysts such as alumina, silica, and various metal oxides are use in dehydration of ethanol to ethylene [11].

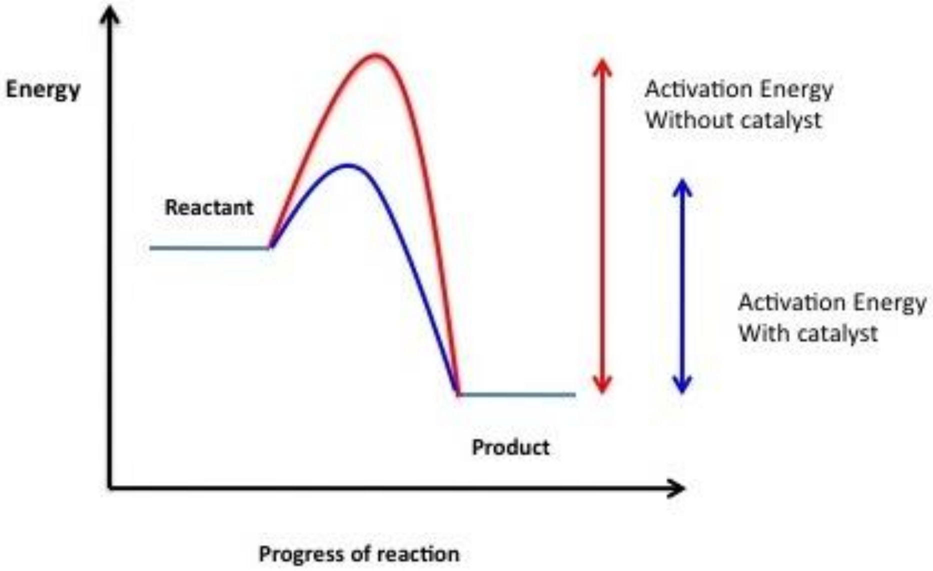

Figure 3: Activation energy profile with and without a catalyst

2.3 Zeolites

Zeolites are attractive catalyst for in the refining industries because of their physical and chemical properties. Zeolites have well defined pore structure, high activity per acid/active site and can be produced at reasonable price (1). Zeolites are microporous aluminosilicates with three-dimensional network of silicates in which some silicon atoms are replaced by aluminium atom giving Al-O-Si framework [12]. The structural formula of zeolite is given by M- where n is the valence of cation M, x+y the total number of tetrahedral per unit cell and y/x the atomic Si/Ai ratio. It can selectively sort molecules based on a size exclusion process due to its porous nature. Thus, the reaction taking place in zeolites depends upon the size, shape and porosity of the zeolites. Zeolites are found naturally as well as synthesized by industries on large scale. Zeolites have a wide range of commercial uses. They are used in wastewater treatment for removal of ammonia in sludge and removal of heavy metals [13]. For industries application, they are used as absorbents for oil and spills and gas separation [13]. Moreover, they are extensively used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerization. ZSM-5 zeolite is also used in dehydration of alcohol into gasoline in petroleum industries.

2.4 Ethanol Dehydration

Ethylene is one of the most used raw materials in petrochemical companies. It is one of the largest chemical products being produced in the world (*table 1*).

Company	**Location**	**Ton/year**
Steam-Cracking plants		
Formsa Petrochemical Corporation	Mailiao, Taiwan	2,935,000
Nova Chemicals Corporation	Joffre, Canada	2,811,792
Arabian Petrochemical Company	Jubail, Saudi Arabia	2,250,000
ExxonMobile Chemical Company	Baytown, TX, USA	2,197,000
ChevronPhilips Chemical Company	Sweeny, TX, USA	1,865,000
Dow Chemical Company	Ternuezen, Netherlands	1,800,000
Ineous Olefins & Polymers	Chocolate Bayou, TX, USA	1,752,000
Equistar Chemical LP	Channelview, TX, USA	1,750,000

Table 1: Top ethylene production companies and their locations [22]

About 75% of petrochemical products such as acetaldehyde, acetic acid, ethylene oxide, etc. are actively produced from ethylene. [23] At the present, the most widely used process to produce ethylene is cracking of hydrocarbon where fossil fuels are used as raw materials. However, ethylene is also produced from ethanol extracted from renewable sources like corn and sugarcane. Different petrochemical industries have developed their own ethanol dehydration technologies. Acid catalysts are used in catalytic dehydration of ethanol to ethylene. The reaction is highly endothermic and it requires temperature ranging from 180 C-500 C. [24] The formation of diethyl ether or acetaldehyde are favored outside the temperature (180-500 C) required for the production of ethylene.[24] A number of research have studied different modified catalysts to increase the ethylene yield and lower reaction temperature. According to catalyst studied by Zhang, SAPO-11-4 gave 98% ethylene selectivity at 250 C. [22] Modified catalyst such as HZSM-5 and MCM-41 were able to achieve over 99% selectivity. [22]

2.4.1 Mechanism

In the catalytic dehydration of ethanol, acid catalysts are used to form ethylene. An acid catalyst first protonates the hydroxyl group of the ethanol, which losses water molecule to form carbocation. This process is followed by removal of a hydrogen ion to form a double bonded hydrocarbon, ethylene.

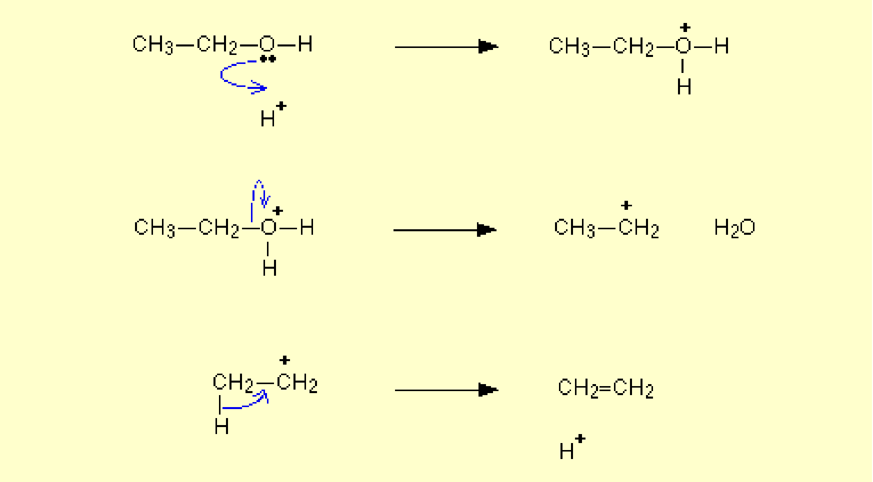

Figure 4: Mechanism of acid catalysts of ethanol dehydration [25]

2.5 ZSM-5 in Ethanol Dehydration

ZSM-5, Zeolite Socony Mobil #5, is a catalyst first made by Argauer and Landolt in 1972 [16]. It is frequently used in petroleum industries in conversion of methanol feed to a hydrocarbon fraction containing aliphatic as well as aromatic compounds (<=C10) in the gasoline boiling range [16]. According to Phillips and Datta research on production of ethylene from ethanol, they studied the performance of H-ZSM-5 under mild acidic homogeneous solution [4]. Ethylene is assumed to be produced via direct formation of ethylene as well as consecutive reaction of forming diethyl ether. At low temperature (<503 K), diethyl ether is produced in larger quantities. Ethylene is produced in significant quantities at higher temperature (> 573 K). These studies have reported that use of other catalysts give rise to concerns such as deactivation due to coke formation, thermal degradation and effected of water on reaction rates [4]. Thus for this study, H-ZSM-5 zeolite was chosen as the catalysts for this reaction. Here, H-ZSM-5 catalysts with Si/Ai of 25:1 and 37.5:1 were studied. The study found that H-ZSM is an active and selective catalyst for the direction conversion of ethanol at temperature less than 473 K. A very sharp deactivation curve was observed under mild conditions where activity of catalyst started to decline more gradually due to the formation of reversibly adsorbed coke species [4]. Moreover, the formation of carbonaceous species was observed when Bronsted acid sites of untreated catalyst give rise to oligomerization of ethylene. This results in reduction of H-ZSM-5 activity. However, water in the ethanol was found to enhance the steady state catalytic activity of H-ZSM-5 and selectivity for the formation of ethylene [4]. Water affects the acidity of the catalytic sites; result in moderate acidity of the catalytic sites, which decreases the deactivation due to coking.

2.6 ZSM-5 Stability in Hot Liquid

The framework of the zeolites plays an important role for the stability of zeolite in hot liquid. Unlike other zeolites, ZSM-5 is more stable at 150 and 200 C despite change in its Si/Ai ratio. The structural change of Si-O-Al and Si-O-Si induced by water is not observed in ZSM-5. [21] In addition, ZSM-5 can maintain its crystallinity and micropore volume after sever dealumination [17] due to few structur0al defects produced during its synthesis. [18] The framework of aluminum atoms are removed from zeolite lattice in the presence of steam. The removed aluminum atoms lead to formation of extra framework aluminum (EFAl) species. [21] These extra framework aluminum species are observed to form a separate alumina phase outside the zeolite crystal. [19, 20] The presence of this species was found to have improved hydrothermal stability, increased Lewis acidity, and enhanced catalytic activity for reaction that requires Bronsted acid sites.[19, 20] According to Ryan M. Ravenelle, etc research, they investigated the stability of zeolites Y and ZSM-5 with different Si/Ai ratio in liquid water at 150 and 200 C. The experiment was carried out by elucidating zeolites changes under atomic absorption spectroscopy, X-ray diffraction, scanning electron microscopy, argon physiosorption, Al and Si MAS NMR spectroscopy, etc. They found out that there was no appreciable change in the signature peaks both in untreated and treated ZSM-5 at 150 and 200 (Figure 5).

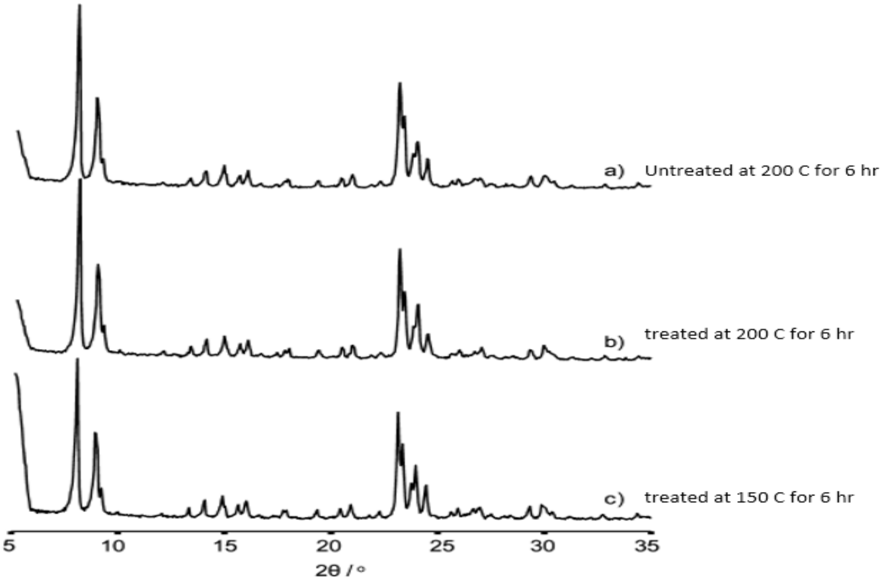

Figure 5: X-ray diffractograms of ZSM-5 at 150 and 200 C [21]

This indicates that the crystallinity of the ZSM-5 remained undestroyed throughout the entire treatment. [21] Moreover under Argon Physisorption, ZSM-5 samples do not show significant changes in their micropore volume. However, increase in mesopore volume was observed for ZSM5-40 (Table 2).

Zeoylyst ID	Zeolite Type	Si/Ai	Na content/ wt%	Sample Code	pH
CBV 712	Y (FAU)	5^{a}	0.04	Y5	4.4
La exchange of CBV 712	Y (FAU)	5^{a}	0.04	LaY5	5.1
CBV 720	Y (FAU)	14^{a}	0.02	Y14	5.1
CBV 780	Y (FAU)	41^{a}	0.04	Y41	3.4
CBV 3024E	ZSM-5 (MFI)	15^{b}	0.04	ZSM-5-15	5.2
CBV 5524G	ZSM-5 (MFI)	25^{b}	0.04	ZSM-5-25	3.6
CBV 8014	ZSM-(MFI)	40^{b}	0.04	ZSM-5-40	5.1

Table 2: Material Specifications and Codes [21]

Zeolite	Vmicropore untreated ($\frac{cm^3}{g}$)	Vmesopore untreated ($\frac{cm^3}{g}$)	Vmicropore 6 h, 200 °C ($\frac{cm^3}{g}$)	Vmesopore 6 h, 200 °C ($\frac{cm^3}{g}$)	Vmicropore 6 h, 150 °C ($\frac{cm^3}{g}$)	Vmesopore 6 h, 150 °C ($\frac{cm^3}{g}$)
Y41	0.32	0.13	0	0.18	0.04	0.23
Y14	0.31	0.16	0.19	0.26	0.27	0.19
Y5	0.34	0.13	0.22	0.15	0.29	0.13
LaY5	0.32	0.1	0.27	0.09	0.29	0.1
ZSM-5-40	0.24	0.03	0.22	0.07	0.23	0.06
ZSM-5-25	0.21	0.03	0.19	0.04	0.22	0.04
ZSM-5-15	0.21	0.04	0.21	0.04	0.21	0.05

Table 3: Micropore and Mesopore volume measured by Ar. Physisorption for zeolite samples before and after 6 h of treatment at 150 and 200 C [21]

Chapter 3: Methodology

Ethanol Dehydration has shown to be promising in the liquid phase. However, not much is known about how to make it more effective at this time. This chapter will describe the experimental methods used to develop a greater understanding of ethanol dehydration in the liquid phase and comparing it to the vapor phase. The project focuses on the ethylene yield and the activity of the zeolite catalyst in the liquid and vapor phases. Different feed flowrates as well as different feed compositions were used to study the differences. Runs were started in the vapor phase as well as the liquid phase to study the effects it had on the effectiveness of the catalyst. The zeolites were calcined and packed into the reactor. The oven was turned on and at the maximum temperature the reaction would start. The products were studied in a gas chromatograph.

3.1 Process Description

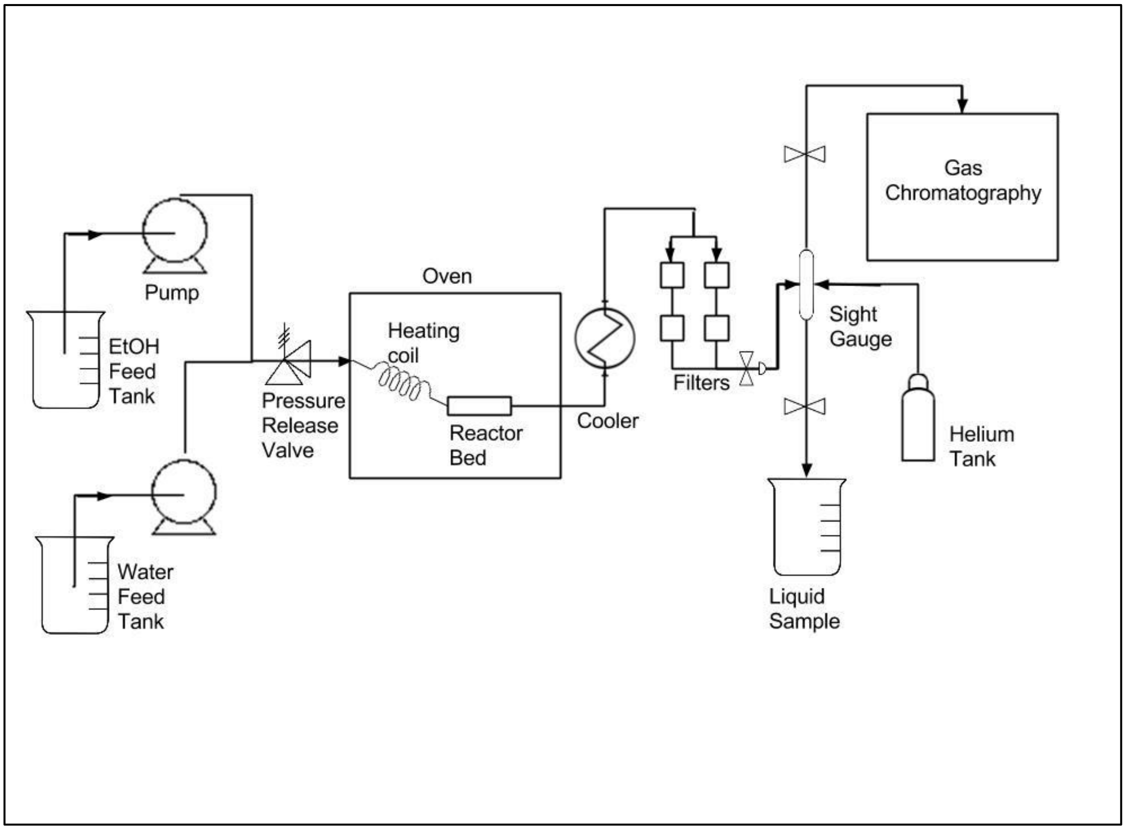

Figure 6: Process Flow Diagram

Figure 6 above shows the ethanol dehydration process to create ethylene from ethanol. This process produces ethylene, diethyl ether and trace amounts of various other elements. A feed is made up of a varying composition of a mixture of water and ethanol. One pump pumps water from the water feed tank, while the other pump pumps ethanol from the ethanol from the ethanol feed tank. These streams are combined into one line that goes through the pressure release valve that releases if the pressure in the line goes above 3000 psi. The fluid mixture is sent into the oven and hits the heating coil so the fluid heats before reaching the reactor bed. Once the fluid enters the reactor bed and the reaction begins. The reactor is packed with sand and the calcined catalyst, ZSM-5, with quartz wool on either end to keep the bed from shifting and getting into the rest of the piping.

After the reactor, the product is sent through a chiller to cool it from very high temperatures. After the chiller, the fluid is sent through a set of filters to filter out any remaining particles that the quartz wool did not catch. The larger filter, 15 µm, is first for the larger particles in the stream and the smaller filter, 1 µm, is second to filter out the final particles in the in stream. The now clean stream is sent to the sight gauge which shows the amount of liquid building up from the stream sent to the gas chromatograph (GC). From the sight gauge the stream can either leave the system or go to the GC by the switch of a valve. When the valve is open, the stream exits the system as a liquid sample. This is the liquid analyzed to calculate the conversion of ethanol. If the valve is open, the fluid is pushed by helium to the GC where a sample is taken every ten minutes. A helium tank is set to a constant flowrate which pushes ethylene to the GC. These samples are analyzed in the GC for the ethylene content.

3.2 Calcination of ZSM-5

Before starting and setting up the run, 10 grams of the zeolite, ZSM-5, were placed in crucibles and put in the oven overnight at 400 C for calcination. This is done to remove impurities in the zeolite. The calcination was done such a way that powdered form of ZSM-5 was treated at 150 C for an hour and half in order to prevent loss of crystallinity by instant heat flux. After treating it at 150 C, the temperature was raised to 400 C and kept overnight. The purpose of calcination was to bring thermal decomposition and removal of volatile impurities in the ZSM-5 such as water.

3.3 Packing the Reactor Bed

The reactor bed contains 0.17g of calcined ZSM-5 and 2g of sand. The ZSM-5 was measured from the calcined ZSM-5 and 2g of sand was mixed with it. The sample was mixed well in an evaporating dish. Quartz wool was used to fill the reactor on either end to prevent loss of the sample. One side of the reactor was packed with quartz wool then the mixture was poured into reactor, shown in figure 7, using a funnel.

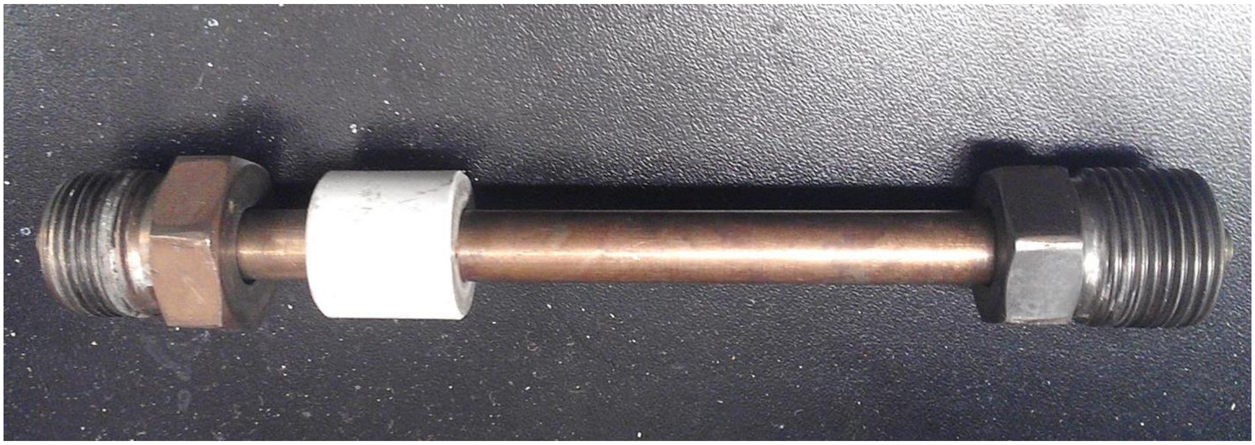

Figure 7: Reactor

At the other end more quartz wool and small filter were added; this would be the outlet of the reactor. The pack reactor was then placed in the oven. Both ends were tightened into the inlet and outlet of the oven with wrenches into position as shown in figure 8 below.

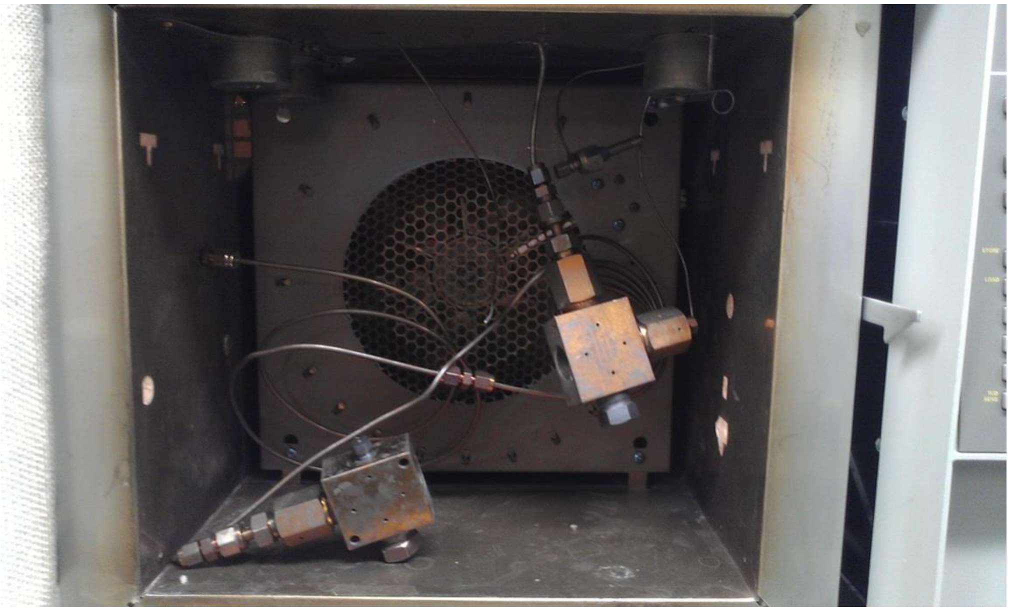

Figure 8: Inside the oven where the reactor is put in place

3.4 Running the Reactor

After placing the packed reactor in the oven and tightening either end in place, the oven (shown in Figure 9) was turned on and the temperature was set to 400 C. Once the temperature of the oven reaches its set point of 400 C, the water pump was turned on to measure the pressure drop across the bed.

Figure 9: Oven

For liquid phase reactions, at this point the system would be pressurized to about 2400 psi by turning on the nitrogen tank. Once at the correct pressure the ethanol pump would be turned on to the desired flow rate to give the chosen composition.

If the reaction was to take place in the gas phase, the ethanol pump would be turned on after the pressure drop of the system was measured. The system would not be pressurized.

3.4.1 Temperature recording

Thermal couples placed at the inlet, outlet and the wall of the reactor recorded the temperatures of each location respectively. These thermocouples are connected to a computer that takes the temperatures and makes a graph of temperature over time using the program TracerDAQ.

3.4.2 Mass Balance

A mass balance was placed at the liquid outlet of the system. It was turned on when the feed began flowing and took measurements every fifteen seconds. Most of the time the valve was closed going to this outlet but there were two instances when it would be opened. The first was to take a liquid sample and second was to empty the system. Liquid samples were taken approximately every thirty minutes. At this time the valve would be opened and the built-up liquid would drain onto the mass balance. The balance measured the weight different of liquid over that time and a flowrate could be calculated. Once the built-up liquid was drained the regular flow began and a sample was taken. The system was drained whenever the liquid level on the sight gauge got too high and the system was at risk of flooding. Any liquid coming out of the system was measured on the balance to compare the flowrate going in to the flowrate coming out.

3.5 Gas Chromatography

To be able to determine the amount of ethylene produced in the gas stream and the amount of ethanol left in the liquid sample, gas chromatography was used as well as respective calibration curves for ethylene and ethanol. The GC used is shown below in figure 10.

Figure 10: Gas Chromatograph

To make the calibration curves, known concentrations of ethanol and ethylene were injected and analyzed in the GC. A linear correlation between the response of the area on the GC and the concentrations of the solutions were found. Graphs of this correlation were created and used to relate the peak response shown on the GC to their respective concentrations for the rest of the experiments.

For the gas sample, the GC was set for continuous data collection for the entirety of the experiment, where the GC took data from the gas stream every ten minutes. These samples were analyzed by the GC and the peak areas were compared to the ethylene calibration curve. This was the amount of ethylene found in the sample which was used to calculate ethylene yield.

The liquid samples were done in a similar fashion, however instead of continuous data collection, each sample was run individually. The GC injected one sample and analyzed it; the area of the peak was then compared to the ethanol calibration curve. This process was repeated for all liquid samples. This was the amount of ethanol found in the liquid sample which was the residual ethanol that had not reacted. This amount could be compared to the amount of ethanol that entered the system to calculate the conversion of ethanol in the overall reaction.

3.5.1 Liquid Sample Dilution

Liquid samples were taken from the system approximately every thirty minutes. These samples were collected in GC micro-vials as shown in the picture below:

Figure 11: GC Micro-vials

These samples then needed to be injected into the GC for analyzing but first they needed to be diluted to about 1 wt% sample. To do this, about 0.1 g of the sample was measured out and diluted with about 10 g of 1-butanol. This mixture was injected to the GC to be analyzed for ethanol content. The corresponding peak area from the GC was compared to the calibration curve described below for the amount of ethanol.

3.5.2 Calibration Curve

A calibration curve was created to compare the liquid sample peak areas to the curve and calculate the volume of ethanol in the sample. The calibration curve for ethanol is shown below in figure 12.

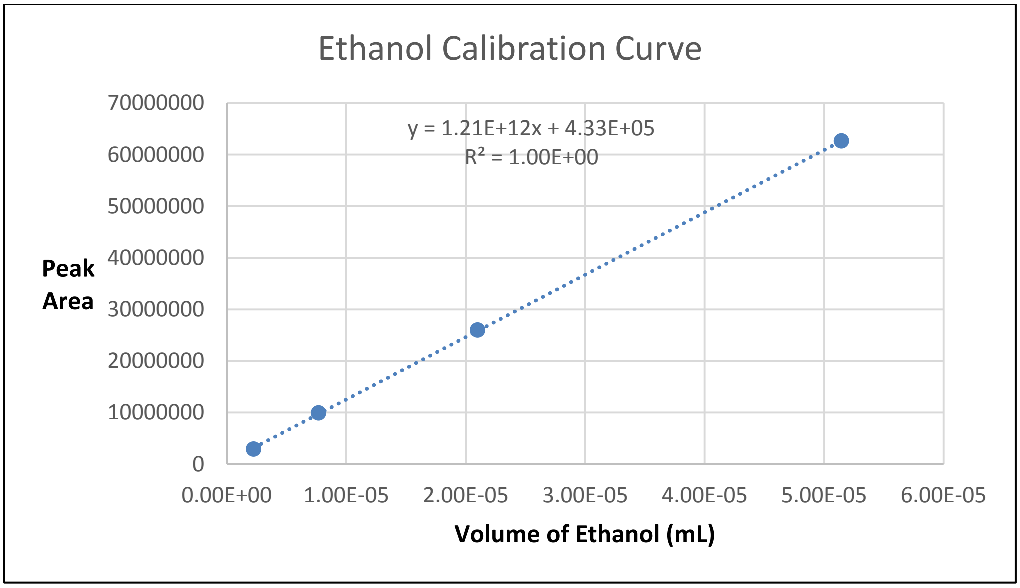

Figure 12: Ethanol Calibration Curve

This curve was created the same way as the diluted samples explained above. This only difference is that samples were made of pure ethanol and butanol. A measured weight of ethanol was diluted with approximately 14 g of butanol to get 0.2 wt%, 0.7 wt%, 2 wt%, and 5 wt%. These points gave the trend line shown above. The peak areas of the samples were plugged into the equation of this line to find the corresponding volume of ethanol.

3.6 X-Ray Diffraction

After a run has been completed, the contents of the reactor bed are pushed out of the reactor and placed in a dish. The dish then sits until all of the liquid has evaporated. The remaining contents are then put into the x-ray diffraction machine or XRD. The XRD is used to observe the crystallinity of the catalyst. It measures the contact angle of the structure of the catalyst; the higher the contact angle, the greater the crystallinity in the structure. A control experiment is done with a pure catalyst before anything has been done to it. This way the catalyst can be compared before and after the run to see if the crystallinity has been compromised by the reaction.

3.7 Heat Transfer

The energy balance over the reactor was made in order to calculate heat supplied to the reactor.

$$Q^{\cdot} = \varepsilon \Delta \mathrm{Hrx} + \Sigma\, n^{\cdot} Hout - \Sigma\, n^{\cdot} Hin$$

The heat capacity of each component in the vapor phase is calculated using the heat capacity table in Introduction to Chemical Engineering Thermodynamics by Smith VanNess and Abbott. [25] Enthalpies of each component were determined using the equation:

$$\Delta H = \Delta H_f^o + \int_{Tin}^{Tou} CpdT$$

The inlet and outlet enthalpy of mixture in liquid phase were determined using Aspen Plus. (Figure 13) In Aspen Plus, a stoichiometric reactor was used and pressure was set 2300 psig (operating pressure) and the temperature was set accordingly to the inlet temperature of the reactor.

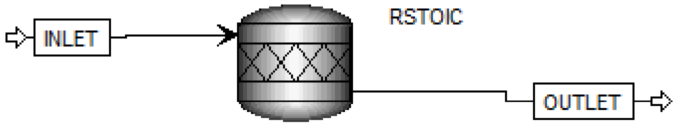

Figure 13: Aspen Model

Extent of the reaction (ε) was calculated using the equation:

$$\varepsilon = \left|\frac{\dot{n}_{c2H5}out - \dot{n}_{c2H50}in}{\vartheta_{c2H50}}\right|$$

The heat of reaction was calculated using standard enthalpy of formation of product and reactants:

$$H_r^0 = \Sigma\left(\vartheta_i H_f^0\right)product - \Sigma\left(\vartheta_i H_f^0\right)reactant$$

Chapter 4: Results and Analysis

The objective of this study was to study and compare the ethylene yield from ethanol dehydration in both vapor and liquid phases. This was done by studying the crystallinity and reactivity of the zeolite catalyst, the heat transfer of the reaction, the conversion of ethanol and the starting phase. The data was analyzed to determine which phase would be best to run ethanol dehydration in.

4.1 Ethanol Conversion

Ethanol conversion was one of the first things calculated. This was done by analyzing the liquid samples in the GC. The GC gave peaks for each separate component:

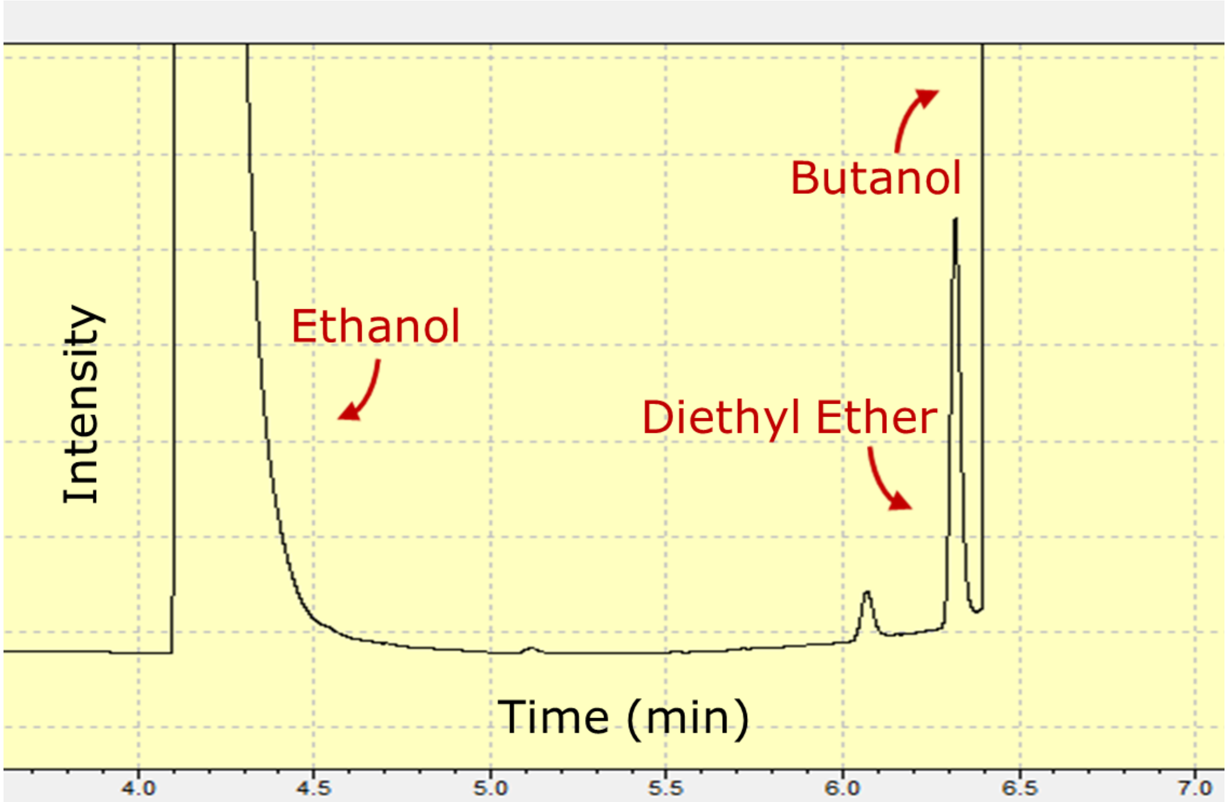

Figure 14: GC Liquid Data

The figure above shows three different components: the reactant, ethanol, the diluent, butanol and the by-product, diethyl ether. The area of the ethanol peak was used with the calibration curve to calculate the conversion. Knowing the amount of ethanol that went into the system and the amount coming out, the percent difference was the conversion percent.

Ethanol conversion was compared to varying feed flowrates at a constant composition of 50 vol% EtOH to find the optimal flowrate for this reaction. The flowrates were varied from 2ml/min to 10 ml/min and the following was our result.

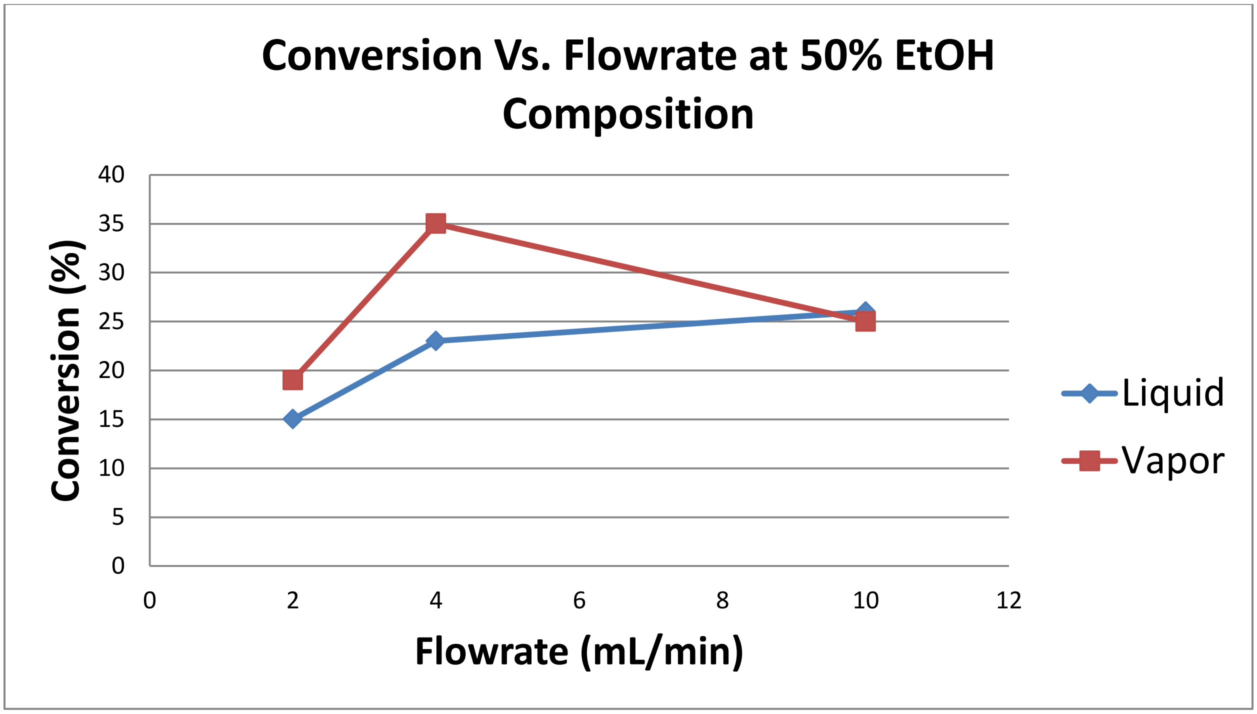

Figure 15: Conversion Vs. Flowrate at 50% EtOH Composition

As you can see in figure 15, the vapor phase has a significantly higher conversion then the liquid phase. This was expected due to background research. The interesting part is that the conversion increases with increasing flowrate until a certain point then it decreases. This is due to the varying residence times of the system. When the flowrate is slow, like 2ml/min the residence time is large. This causes the reaction to not happen very quickly causing the conversion not to be very high. If the flowrate is too high, like 10ml/min the residence time is too short and it does not give enough time for the reaction to go to completion.

In this graph the optimal flowrate is 4ml/min, but more runs would need to be done at more flowrates between 4ml/min and 10 ml/min to accurately say what flowrate would give the greatest ethanol conversion at 50 vol% Ethanol. The lines connecting the data points are not data they are only there to guide the eye. It is unknown what would happen between 4ml/min and 10ml/min but it is predicted that the optimal flowrate is somewhere between 4ml/min and 10 ml/min.

4.2 Crystallinity and Reactivity of the Catalyst

Crystallinity and reactivity of a catalyst plays a big part in the yield of ethylene which is the overall goal of the project. The zeolite catalysts were tested for crystallinity in an XRD. The crystallinity of a catalyst correlates directly to its reactivity. In the diffractogram below, figure 16, two different catalysts are shown, unreacted ZSM-5 and ZSM-5 after the ethanol dehydration reaction.

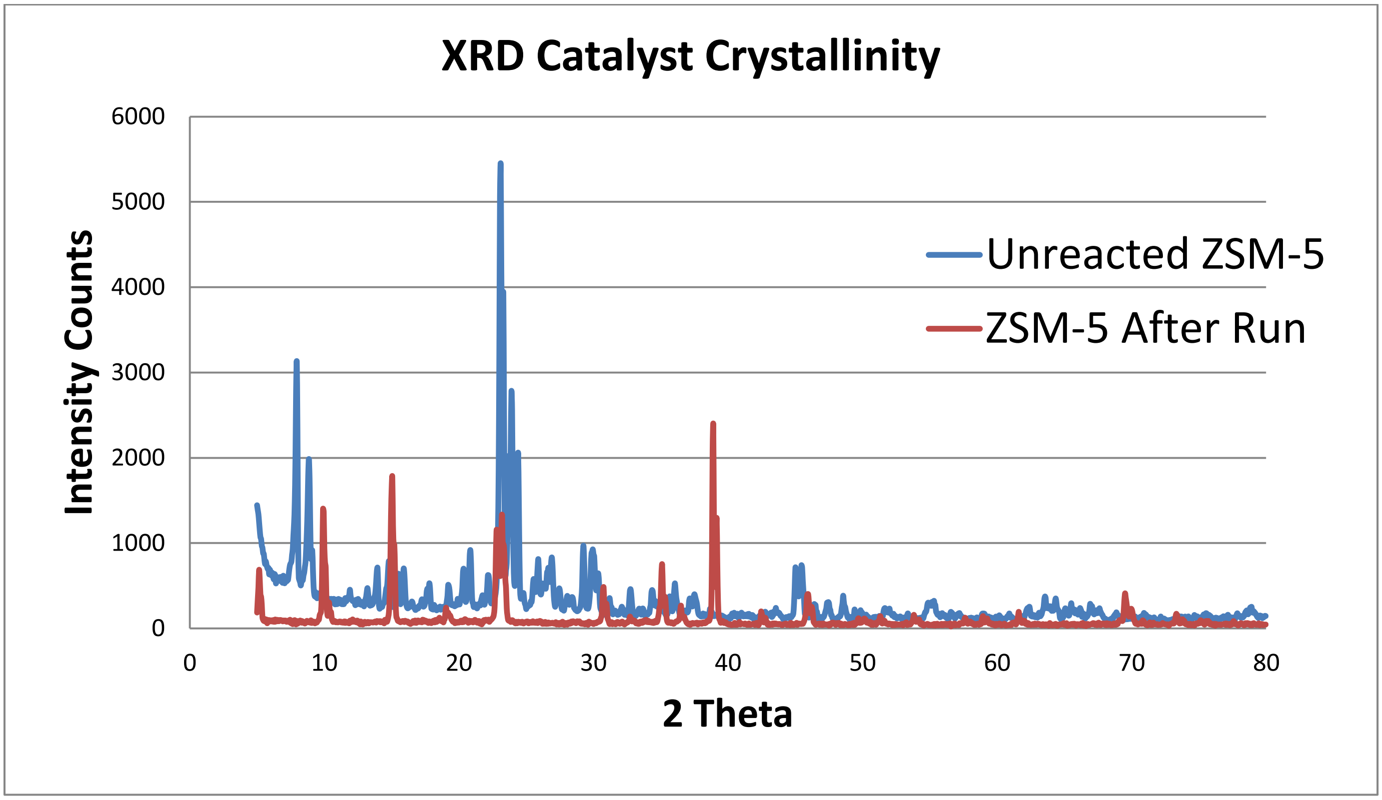

Figure 16: XRD Catalyst Crystallinity

In a diffractogram, the higher the intensity counts, the greater the crystallinity, thus a greater reactivity. As you can see the blue line above has a greater intensity counts overall. This is the unreacted ZSM-5. It was expected that the unreacted catalyst would have a greater crystallinity as it has not gone through the reaction yet.

The line in red is the zeolite that had been through one of our most successful runs. This run had many different conditions both in liquid and vapor phase. From this run it is indistinguishable whether or not the vapor or liquid phase made this catalyst lose its crystallinity. A zeolite will lose crystallinity in both liquid phase and vapor phase reactions but it is predicted that liquid phase reactions will make the catalyst degrade more easily due to the fact that it is already unstable in hot liquids.

4.3 Heat Transferred to the Reactor

Water Feed (mL/min)	Ethanol Feed (mL/min)	Phase	Ethanol Conversion %	Heat Q (J/s)
2.5	2.5	Liquid	12.15	-12.76
1.5	1.5	Vapor	7.28	-5.64

Table 4: Heat Transfer rates of ethanol dehydration

As we can see in table 4 the heat transfer rates Q (J/s) were negative which was we expected because the dehydration of ethanol reaction is an endothermic reaction. It requires temperature range of 150 °C to 400 °C to produce ethylene. Heat transfer rate (Q) was higher in liquid phase compared to vapor phase. The heat transfer rate difference was within factor of 2.3. This was because the flowrates of both water and ethanol were higher in liquid phase than in vapor. The conversion was also higher in run 1 which could result in higher transfer of heat because the liquid have better conduction and contact with zeolite inside the reactor.

Moreover, conversion has significant contribution to the extent of reaction. In later runs, similar trends were noticed. However, the heat transferred rates were significantly higher compared to this data. This is because flowrates of both ethanol and water were lower (1 ml/min each) in later runs than feed flowrates of these runs. The lower flowrates of feed will provide more contact time with zeolite and eventually give more conversion. The higher the conversion, more the heat is transferred.

Sample	Water Feed (ml/min)	Ethanol Feed (ml/min)	Phase	Ethanol Conversion %	Heat Q (J/s)	Operating Pressure (Psig)
#1	2	2	V	22.1	-75.7	670
#2	2	2	V	21.4	-73.5	670
#3	2	2	V	25.1	-85.09	670
#4	2	2	L	23.3	-94	2300
#5	2	2	L	30.7	-120.96	2300
#6	2	2	L	47.9	-178.23	2300
#7	2	2	L	27.5	-109.74	2300
#10	2	2	L	22.6	-92.2	2300
#11	2	2	L	25	-90.83	2300
#13	2.5	2.5	L	25.1	-113.04	2300
#14	2.5	2.5	L	27.8	-111.13	2300
#15	2.5	2.5	L	26.4	-112.11	2300
#17	2.5	2.5	V	21.4	-91.29	670
#18	2.5	2.5	V	28.4	-127.3	670

Table 5: Heat Transfer rates of the most successful run

The most successful run, (shown in table 5) was carried on flowrates of 2 ml/min and 2.5 ml/min feed of ethanol and water. Heat transfer rates (Q) were significantly higher in liquid phase than vapor for both flowrates of 2 and 2.5 ml/min. For 2 ml/min of ethanol and water feed, the highest heat transfer rates were -178.23 (J/s) and -85.09 (J/s) in liquid and vapor phase. The conversions were also highest for these heat transfer rates. For the flowrate of 2.5 ml/min of both ethanol and water, the highest heat transfer rate was higher in vapor phase than liquid phase. Similarly, the corresponding conversion was also higher in vapor phase than liquid. From these results, it is clear that heat transfer rate was higher in liquid than vapor providing same feed flowrates. One factor that significantly affected the heat transfer rate was conversion. The higher the conversion in either vapor or liquid, higher the heat transfer rate.

One factor that was noticed to affect the heat transfer rate was pressure drop. Pressure drop affects the inlet and outlet enthalpies.

4.4 Ethylene Yield

In this project, several different runs were completed with varying conditions, some in the liquid phase, some in the vapor phase, and some with different feed flow rates and feed concentrations. One of the main points that were studied was the way the run was started. Some runs were started in the liquid phase and some were started in the vapor phase. Below in figure 17, two different run conditions are shown. The black squares are the run started in the liquid phase and the gray diamonds are the run started in the vapor phase.

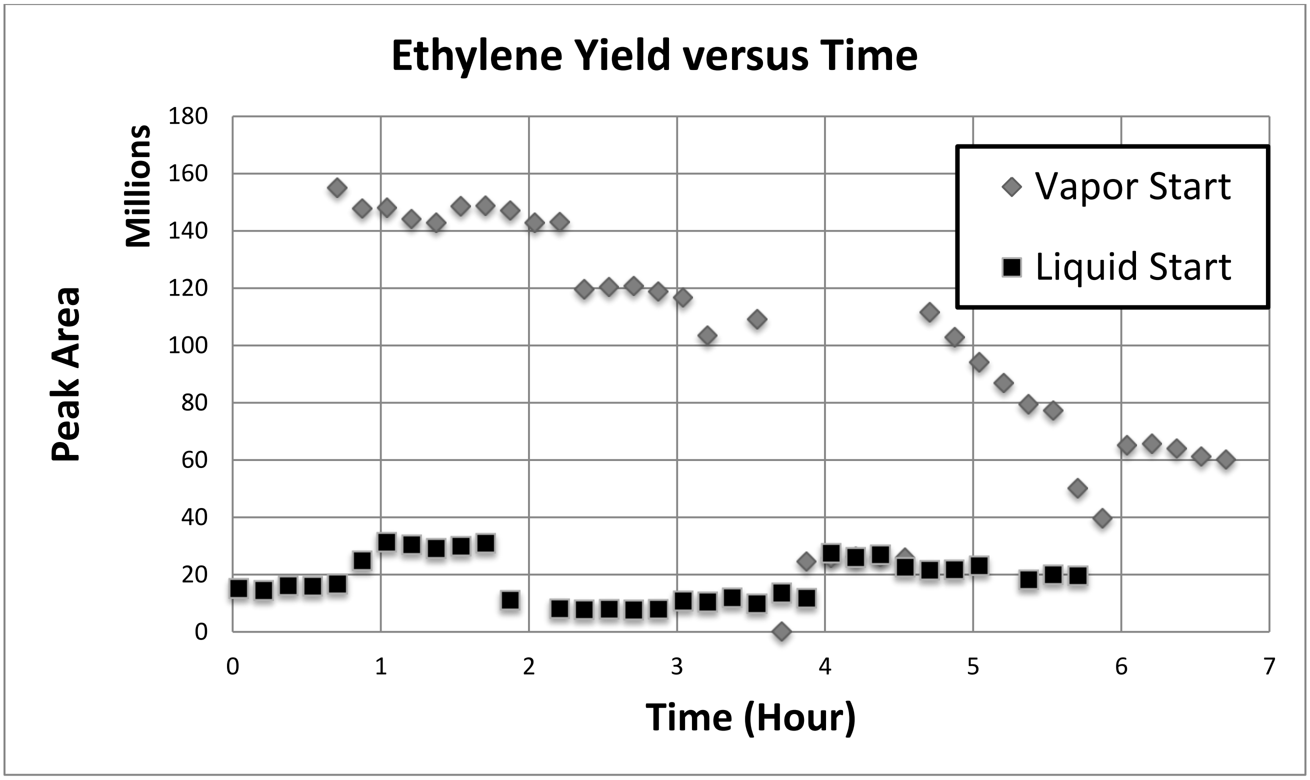

Figure 17: Ethylene Yield versus Time

As one can see, the vapor phase yield is significantly higher than the liquid phase yield. The run that starts in the vapor phase has a high ethylene yield to start, around 155 million. This gradually decreases over time as the catalyst slowly degrades. A large decrease is observed around 3.5 hours and this is when the run switched to the liquid phase causing the catalyst to degrade at a much higher rate, thus producing a decreased ethylene yield. Around hour 4.5, the system is switched back to the vapor phase and the yield increases again but at a lower point than before because the hot liquid in the liquid phase degraded the catalyst, affecting its ability to react.

The run that started in the liquid phase has a very low ethylene yield. It starts very low and stays around 20 million for the entirety of the run. At hour three, the system is switched to the vapor phase. Switching to the vapor phase from the liquid phase does not show much of a different in ethylene yield. This is due to the hot liquid degrading the catalyst, as mentioned earlier. Since, this run started in the liquid phase, the catalyst is almost immediately degraded causing less ethylene yield from the start of the reaction.

Chapter 5: Conclusions and Recommendations

After a thorough analysis of the results, the following conclusions and recommendations were established. Liquid phase ethanol dehydration does create a notable amount of ethylene. However, vapor phase ethanol dehydration generates a much larger amount of ethylene than liquid phase. It is believed that this is due to the fact that the catalyst degrades so easily and loses its reactivity in hot liquids while the reaction is in the liquid phase. This process could be improved if the catalyst did not degrade as easily. This could be done by modifying the way the catalyst is made to make it less likely to degrade. It is also possible to use a different catalyst in the process but recent studies have shown that ZSM-5 is very good for reactivity.

The reaction is best run at an optimal flow rate between 4 mL/min and 10 mL/min. This is to make sure the residence time is long enough for the reaction to go to completion but not too long where the reaction is not fast enough to produce a substantial amount of ethylene. A feed composition of 50% seemed to be the most ideal to yield the most ethylene. During the reaction, more heat is transferred in the liquid phase than in the vapor phase. This is because liquid phase reactions often gave a higher conversion and higher conversions have a higher heat transfer rate.

When making ethylene commercially, currently vapor phase is preferred to liquid phase solely for the fact that it produces more ethylene. If liquid phase ethanol dehydration could produce as much or more ethylene then it would be much more likely to be used in industry simply because it would be cheaper to manufacture while producing the same, if not more ethylene than vapor phase ethanol dehydration. In the liquid phase, this reaction is run at a much lower temperature than the liquid phase which results in the use of much less energy. Heating the feed for the vapor phase requires a lot of energy since the reaction temperature needed is so high for the reaction to go to completion while remaining in the vapor phase. Since the liquid phase reaction uses less energy it is automatically cheaper, thus making it an ideal candidate for ethanol dehydration.

For future studies, it is recommended that the catalyst is studied further in this reaction in the liquid phase. As stated above, it is believed that the liquid phase could produce more ethylene if the catalyst did not degrade as easily in the presence of hot liquid. In the future, zeolites could be studied to make them more stable so they don't degrade and lose their reactivity as easily in the liquid phase. This could be done by using a different catalyst that can withstand hot liquids more easily. The difficulty there would be finding the proper catalyst that would still produce enough ethylene like ZSM-5 does. Another thing to study is different coatings for the catalyst. These coatings could make the zeolite more hydrophobic and make it less likely for the catalyst to degrade as quickly and easily in hot liquid. A more intensive study could be to change the way the catalysts are made. Modifying the overall structure of the zeolite could change the way it reacts to liquid at high temperatures.

If a study is done using is similar reactor set up, it is recommended to create a way to pack the reactor. The way it is done now causes a great deal of human error because there is no exact way to do it, thus causing it to be different every time. The way the reactor is packed is very important because it affects the pressure drop across the bed, which affects how the feed run through it causing the reaction to be altered.

Appendices

Appendix A – Conversion

Ethanol Weight		BuOH	EtOH vol%	Volume of EtOH	Weight of EtOH	
5 wt%	0.75	14.250	0.051263	5.13E-05	4.04E-05	
3 wt%	0.45	14.550	0.030774	3.08E-05	2.43E-05	
2 wt%	0.3	14.700	0.020521	2.05E-05	1.62E-05	
1 wt%	0.15	14.850	0.010263	1.03E-05	8.10E-06	
0.7 wt%	0.105	14.895	0.007185	7.19E-06	5.67E-06	
0.5 wt%	0.075	14.925	0.005132	5.13E-06	4.05E-06	
0.2 wt%	0.03	14.970	0.002053	2.05E-06	1.62E-06	
0.1 wt%	0.01	14.985	0.001027	1.03E-06	8.10E-07	Peak Area
0.002212	0.0332	14.975	0.002271	2.27E-06	1.79E-06	2935367.8
0.007492	0.1124	14.89	0.007686	7.69E-06	6.06E-06	9926106.40
0.020487	0.3074	14.6975	0.021020451	2.10E-05	1.66E-05	25986284.1
0.050203	0.7532	14.25	0.051470041	5.15E-05	4.06E-05	6.26E+07

Table 6: Calibration Curve Datae

Sample	mass buoh	mass sample	total mass check	initial moles etoh	initial moles water	total sample moles
1	14.6882	0.1535	0.153499113	0.001564503	0.005067	0.006632
2	13.6985	0.1658	0.165799497	0.001686325	0.005462	0.007148
3	12.8835	0.1265	0.126499966	0.001300615	0.004213	0.005513
4	15.4155	0.1563	0.156299964	0.001598405	0.005177	0.006776
5	14.8983	0.1036	0.103622157	0.001082808	0.003507	0.00459
6	14.2575	0.1162	0.116219728	0.001278609	0.004141	0.00542
7	13.0164	0.1348	0.134799962	0.001395272	0.004519	0.005915
10	13.6772	0.1191	0.119099981	0.001215746	0.003938	0.005154
11	14.9138	0.1066	0.106599972	0.001095471	0.003548	0.004644
13	12.8604	0.1554	0.155399959	0.001597404	0.005174	0.006771
14	14.8928	0.1645	0.164499954	0.001704557	0.005521	0.007226
15	12.7843	0.1508	0.150799959	0.00155608	0.00504	0.006596
17	11.943	0.1342	0.134199572	0.001365109	0.004422	0.005787
18	12.719	0.1523	0.152299957	0.001580601	0.00512	0.0067

Table 7: Conversion Calculation Run 8 Part 1

Sample	mole etOH	mole water	volume etoh	volume water	volume buOH	vol ethoh inj	mol etoh
1	0.001219	0.005413	0.091213	0.091213	18.13358	4.97997E-06	8.54E-08
2	0.001326	0.005822	0.098316	0.098316	16.91173	5.74664E-06	9.86E-08
3	0.000974	0.00454	0.075828	0.075828	15.90556	4.72236E-06	8.1E-08
4	0.001226	0.005549	0.09319	0.09319	19.03148	4.84912E-06	8.32E-08
5	0.00075	0.00384	0.063129	0.063129	18.39296	3.40886E-06	5.85E-08
6	0.000666	0.004754	0.074545	0.074545	17.60185	4.1995E-06	7.2E-08
7	0.001012	0.004902	0.081347	0.081347	16.06963	5.0114E-06	8.6E-08
10	0.000941	0.004213	0.07088	0.07088	16.88543	4.16275E-06	7.14E-08
11	0.000822	0.003822	0.063868	0.063868	18.4121	3.4449E-06	5.91E-08
13	0.001197	0.005574	0.093131	0.093131	15.87704	5.79777E-06	9.94E-08
14	0.00123	0.005996	0.099378	0.099378	18.38617	5.34726E-06	9.17E-08
15	0.001145	0.005451	0.090722	0.090722	15.78309	5.68272E-06	9.75E-08
17	0.001073	0.004714	0.079588	0.079588	14.74444	5.34019E-06	9.16E-08
18	0.001132	0.005568	0.092152	0.092152	15.70247	5.80053E-06	9.95E-08

Table 8: Conversion Calculation Run 8 Part 2

peak area		volume etoh	mole etoh		conversion
5127070		3.88E-06	6.65E-08		0.220999
5900968		4.52E-06	7.75E-08		0.21363
4710389		3.54E-06	6.06E-08		0.251427
4934854		3.72E-06	6.38E-08		0.232738
3311897		2.38E-06	4.08E-08		0.302039
3095986		2.2E-06	3.77E-08		0.475934
4831491		3.64E-06	6.24E-08		0.27463
4329942		3.22E-06	5.52E-08		0.226326
3560441		2.58E-06	4.43E-08		0.249713
5689764		4.34E-06	7.45E-08		0.250671
5101790		3.86E-06	6.62E-08		0.278415
5493944		4.18E-06	7.17E-08		0.26398
5511186		4.2E-06	7.2E-08		0.214101
5459877		4.15E-06	7.13E-08		0.283781

Table 9: Conversion Calculation Run 8 Part 3

Appendix B – Heat Transfer

Water feed (ml/min)	Ethanol feed (ml/min)	Conversion %	Heat Q (J/s)
2.5	2.5	12.15	-12.76

Table 10: Heat transfer rate of ethanol dehydration in liquid phase (Run 1)

Water feed (ml/min)	Ethanol feed (ml/min)	Conversion %	Heat Q (J/s)
1.5	1.5	7.28	-5.64

Table 11: Heat transfer rate of ethanol dehydration in vapor phase (Run 2)

Sample	Water feed (ml/min)	Ethanol Feed (ml/min)	Phase	Conversion %	Heat Q	Pressure (psig)
#1	1	1	L	16.9	-40	2300
#2	1	1	L	23.9	-65.8	2300
#3	1	1	L	20.6	-58	2300
#4	1	1	L	24.2	-66.54	2300
#5	1	1	L	13.1	-40	2300
#6	1	1	V	14.1	-29.32	500
#7	1	1	V	16.2	-34.98	500

Table 12: Heat transfer rates of collected samples (Run 6)

Heat Transferred in Tube (RUN 1 Liquid Phase)				
Components	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.043	0.0377755	12.15	
Ethylene	0	0.0052245		
Water	0.139	0.000634777		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture(kJ/mol)
	578	-227.199568	548	-246.738848
	Σ ήHin (KJ/min)	-9.769581424	Σ ήHout (kJ/min)	-10.76639455
ΔHrx standard				
Substances	Products (kJ/mol)	Reactants (KJ/mol)		
Ethanol	0	-277.6		
Water	-285.8	0		
ethylene	52.4	0		
Total	-233.4	-277.6		
delta Hrx (kJ/mol)	44.2			
ξ (mol/min)	0.0052245			
ξΔHrx (KJ/min)	0.2309229			
Q(KJ/min)	-0.765890224			
Q(J/s)	-12.76483707			

Table 13: Calculation of heat transfer rates of collected samples in liquid phase

Heat Transferred in Tube (RUN 2 Vapor Phase)				
Components	n in (mol/min)	nout (mol/min)	Conversion %	
Ethanol	0.026	0.023608	7.28	
Ethylene	0	0.002392		
Water	0.0833	0.002392		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture(kJ/mol)
	588	-228.4618808	523	-225.01552
	Σ ήHin (KJ/min)	-5.940008901	Σ ήHout (kJ/min)	-6.388640644
Δ Hrx standard				
Substances	Products (KJ/mol)	Reactants (KJ/mol)		
Ethanol	0	-235.3		
Water	-241.82	0		
ethylene	52.4	0		
Total	-189.42	-235.3		
delta Hrx (kJ/mol)	45.88			
ξ (mol/min)	0.002392			
ξΔHrx (KJ/min)	0.10974496			
Q(KJ/min)	-0.338886783			
Q(J/s)	-5.648113051			

Table 14: Calculation of heat transfer rates of collected samples in vapor phase

Heat Transferred in Tube (RUN 5 Liquid Phase)				
Components	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0343	0.0313845	8.5	
Ethylene	0	0.0029155		
Water	0	0.0029155		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture(kJ/mol)
	578	-223.9942056	548	-206.3498592
	Σ ήHin (kJ/min)	-7.683001252	Σ ήHout (kJ/min)	-7.679413185
Ethanol	0.0343	0.0318304	conversion %	
Ethylene	0	0.0024696	7.2	
Water	0	0.0024696		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-223.9942056	548	-209.0652752
	Σ ήHin (KJ/min)	-7.683001252	Σ ήHout (KJ/min)	-7.687246543
Ethanol	0.0343	0.0311444	9.2	
Ethylene	0	0.0031556		
Water	0	0.0031556		
	inlet temp, k	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-223.9942056	548	-204.9147472
	Σ ήHin (KJ/min)	-7.683001252	Σ ήHout (kJ/min)	-7.675204805
Δ Hrx standard				
Substances	Products (KJ/mol)	Reactants (KJ/mol)		
Ethanol				-277.6
Water	-285.8	0		
ethylene	18.5	0		
Total	-267.3	-277.6		
delta Hrx (kJ/mol)	10.3			
ξ (mol/min)	0.0031556			
ξΔHrx (KJ/min)	0.03250268			
Q(KJ/min)	0.040299127			
Q(J/s)	0.671652114			
Sample	Conversion (%)	Phase	ξ (mol/min)	Q(J/s)
2	8.5	liquid	0.0029155	1.75
3	7.2	Liquid	0.0024696	0.3531
5	9.2	Liquid	0.003155	0.671
6	7.9	Vapor	0.002709	2.7

Table 15: Calculations of heat transfer rates of collected samples in liquid phase (Run 5)

Heat Transferred in Tube (RUN 5 Vapor Phase)				
Components	n in (mol/min)	nout (mol/min)		
Ethanol	0.0343	0.0315903	conversion %	
Ethylene	0	0.0027097	7.9	
Water	0	0.0027097		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-213.367264	548	-196.7764488
	Σ ήHin (KJ/min)	-7.318497155	Σ ήHout (KJ/min)	-7.282637337
Δ Hrx standard				
Substances	Products (KJ/mol)	Reactants (KJ/mol)		
Ethanol	0	-235.3		
Water	-241.82	0		
ethylene	52.4	0		
Total	-189.42	-235.3		
delta Hrx (kJ/mol)	45.88			
ξ (mol/min)	0.0027097			
ξΔHrx (KJ/min)	0.124321036			
Q(KJ/min)	0.160180854			
Q(J/s)	2.669680901			
Sample	Conversion (%)	Phase	ξ (mol/min)	Q(J/s)
2	8.5	Liquid	0.0029155	1.75
3	7.2	Liquid	0.0024696	0.3531
5	9.2	Liquid	0.0031556	0.671
6	7.9	Vapor	0.0027097	2.7

Table 16: Calculations of heat transfer rates of collected samples in vapor phase (Run 5)

Heat Transferred in Tube (RUN 6 Liquid Phase)

Components	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0172	0.0142932	16.9	
Ethylene	0	0.0029068		
Water	0.0556	0.0093964		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture(kJ/mol)
	578	-258.8950416	538	-262.1058432
	Σ ήHin (KJ/min)	-4.452994716	Σ ήHout (kJ/min)	-6.971071848
Ethanol	0.0172	0.0130892	conversion %	
Ethylene	0	0.0041108	23.9	
Water	0.0556	0.0132884		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-223.22	548	-261.5175728
	Σ ήHin (KJ/min)	-3.839384	Σ ήHout (KJ/min)	-7.973252367
Ethanol	0.0172	0.0136568	conversion %	
Ethylene	0	0.0035432	20.6	
Water	0.0556	0.0114536		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-223.22	548	-261.7945536
	Σ ήHin (KJ/min)	-3.839384	Σ ήHout (KJ/min)	-7.501356421
Ethanol	0.0172	0.0130376	conversion %	
Ethylene	0	0.0041624	24.2	
Water	0.0556	0.0134552		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-223.22	548	-261.4920504
	Σ ήHin (KJ/min)	-3.839384	Σ ήHout (KJ/min)	-8.016091103
Ethanol	0.0172	0.0149468	conversion %	
Ethylene	0	0.0022532	13.1	
Water	0.0556	0.0072836		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-223.22	548	-262.4259192
	Σ ήHin (KJ/min)	-3.839384	Σ ήHout (KJ/min)	-6.425131235

Δ Hrx standard				
Substances	Products (KJ/mol)	Reactants (KJ/mol)		
Ethanol	0	-277.6		
Water	-285.8	0		
ethylene	52.4	0		
Total	-233.4	-277.6		
delta Hrx (kJ/mol)	44.2			
ξ (mol/min)	0.0041624			
ξΔHrx (KJ/min)	0.18397808			
Q(KJ/min)	-2.401769155			
Q(J/s)	-40.02948592			
Sample	Conversion (%)	Phase	ξ (mol/min)	Q(J/s)
1	16.9	liquid	0.0029068	-40
2	23.9	liquid	0.0041108	-65.8
3	20.6	liquid	0.0035432	-58
4	24.2	liquid	0.0041624	-66.54
5	13.1	liquid	0.0041624	-40

Table 17: Calculations of heat transfer rates of collected samples in liquid phase (Run 6)

Heat Transferred in Tube (RUN 6 Vapor Phase)				
Components	n in (mol/min)	nout (mol/min)	Conversion %	
Ethanol	0.0172	0.0147232	14.4	
Ethylene	0	0.0024768		
Water	0.0556	0.0080064		
	inlet temp (K)	Hin of mixture (KJ/mol)	outlet temp (K)	Hout of mixture(kJ/mol)
	578	-232.4375176	548	-232.9031968
	Σ ήHin (KJ/min)	-3.997925303	Σ ήHout (kJ/min)	-5.87065114
	n in (mol/min)	nout (mol/min)	Conversion %	
Ethanol	0.0172	0.0144136	conversion %	
Ethylene	0	0.0027864	16.2	
Water	0.0556	0.0090072		
	inlet temp (K)	Hin of mixture (KJ/mol)	outlet temp (K)	Hout of mixture (KJ/mol)
	578	-232.4375176	548	-232.7525728
	Σ ήHin (KJ/min)	-3.997925303	Σ ήHout (KJ/min)	-6.099793226
ΔHrx standard				
Substances	Products (KJ/mol)	Reactants (KJ/mol)		
Ethanol	0	-235.3		
Water	-241.82	0		
ethylene	52.4	0		
Total	-189.42	-235.3		
delta Hrx (kJ/mol)	45.88			
ξ (mol/min)	0.0027864			
ξΔHrx (KJ/min)	0.127840032			
Q(KJ/min)	-2.099081523			
Q(J/s)	-34.98469205			
Sample	Conversion (%)	Phase	ξ (mol/min)	Q(J/s)
6	14.4	Vapor	0.0024764	-29.32
7	16.2	Vapor	0.0027864	-34.98

Table 18: Calculations of heat transfer rates of collected samples in vapor phase (Run 6)

Heat Transferred in Tube (RUN 8 liquid Phase)				
Components	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0343	0.0263081	23.3	
Ethylene	0	0.0079919		
Water	0.1111	0.0258863		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, k	Hout of mixture(kJ/mol)
	578	-245.3447392	548	-240.1327304
	Σ ήHin (KJ/min)	-8.415324555	Σ ήHout (kJ/min)	-14.45270055
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0343	0.0237699	30.7	
Ethylene	0	0.0105301		
Water	0.1111	0.0341077		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, k	Hout of mixture (KJ/mol)
	578	-245.3447392	548	-235.9223712
	Σ ήHin (KJ/min)	-8.415324555	Σ ήHout (KJ/min)	-16.13890679
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0343	0.0178703		
Ethylene	0	0.0164297	47.9	
Water	0.1111	0.0532169		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, k	Hout of mixture (KJ/mol)
	578	-245.3447392	548	-226.6481168
	Σ ήHin (KJ/min)	-8.415324555	Σ ήHout (KJ/min)	-19.83554057
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0343	0.0248675		
Ethylene	0	0.0094325	27.5	
Water	0.1111	0.0305525		
	inlet temp, k	Hin of mixture (KJ/mol)	outlet temp, k	Hout of mixture (KJ/mol)
	578	-245.3447392	548	-237.7260936
	Σ ήHin (KJ/min)	-8.415324555	Σ ήHout (KJ/min)	-15.41713149
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0343	0.0265482		
Ethylene	0	0.0077518	22.6	
Water	0.1111	0.0251086		

	inlet temp, k	Hin of mixture (KJ/mol)	outlet temp, k	Hout of mixture (KJ/mol)
	578	-245.3447392	548	-240.5385784
	Σ ήHin (KJ/min)	-8.415324555	Σ ήHout (KJ/min)	-14.29006019
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0343	0.0265482		
Ethylene	0	0.0077518	25	
Water	0.1111	0.0251086		
	inlet temp, k	Hin of mixture (KJ/mol)	outlet temp, k	Hout of mixture (KJ/mol)
	578	-245.3447392	548	-239.153256
	Σ ήHin (KJ/min)	-8.415324555	Σ ήHout (KJ/min)	-14.20776012
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.04288	0.03318912		
Ethylene	0	0.00969088	25.1	
Water	0.1388	0.0313688		
	inlet temp, k	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-245.8217152	548	-239.0825464
	Σ ήHin (KJ/min)	-10.54083515	Σ ήHout (KJ/min)	-17.75159217
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.04288	0.03318912		
Ethylene	0	0.00969088	27.8	
Water	0.1388	0.0313688		
	inlet temp, k	Hin of mixture (KJ/mol)	outlet temp, k	Hout of mixture (KJ/mol)
	578	-245.8217152	548	-237.5419976
	Σ ήHin (KJ/min)	-10.54083515	Σ ήHout (KJ/min)	-17.63720827
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.04288	0.03318912		
Ethylene	0	0.00969088	26.4	
Water	0.1388	0.0313688		
	inlet temp, k	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-245.8217152	548	-238.3386312
	Σ ήHin (KJ/min)	-10.54083515	Σ ήHout (KJ/min)	-17.69635736

Table 19: Calculations of inlet and outlet flowrates and their respective enthalpies in liquid phase (Run 8)

Δ Hrx standard				
Substances	Products (KJ/mol)	Reactants (KJ/mol)		
Ethanol	0	-277.6		
Water	-285.8	0		
ethylene	52.4	0		
Total	-233.4	-277.6		
delta Hrx (kJ/mol)	44.2			
ξ (mol/min)	0.0164297			
$\xi\Delta$Hrx (KJ/min)	0.72619274			
Q(KJ/min)	-10.69402328			
Q(J/s)	-178.2337213			
Sample	Conversion (%)	Phase	ξ (mol/min)	Q(J/s)
4	23.3	Liquid	0.00799	-94.7
5	30.7	Liquid	0.0105	-120.96
6	47.9	Liquid	0.0164	-178.23
7	27.5	Liquid	0.0094	109.74
8	22.6	Liquid	0.007751	-92.2
11	25	Liquid	0.0077518	-90.83
13	25.1	Liquid	0.00969	-113.04
14	27.8	Liquid	0.0096908	-111.13
15	26.4	Liquid	0.00969088	-112.11

Table 20: Calculations of heat transfer rates of collected samples in liquid phase (Run 8)

Heat Transferred in Tube (RUN 8 vapor Phase)				
Components	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0343	0.0267197	22.1	
Ethylene	0	0.0075803		
Water	0.1111	0.0245531		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture(kJ/mol)
	578	-228.4915872	548	-216.2328856
	Σ ήHin (KJ/min)	-7.837261441	Σ ήHout (kJ/min)	-12.72597564
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0343	0.0269598		
Ethylene	0	0.0073402	21.4	
Water	0.1111	0.0237754		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, k	Hout of mixture (KJ/mol)
	578	-228.4915872	548	-216.6450096
	Σ ήHin (KJ/min)	-7.837261441	Σ ήHout (KJ/min)	-12.58174559
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.0343	0.0256907		
Ethylene	0	0.0086093	25.1	
Water	0.1111	0.0278861		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-228.4915872	548	-214.4810448
	Σ ήHin (KJ/min)	-7.837261441	Σ ήHout (KJ/min)	-13.3377397
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.04288	0.03370368		
Ethylene	0	0.00917632	21.4	
Water	0.1388	0.0297032		
	inlet temp, k	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-228.9518272	548	-216.524092
	Σ ήHin (KJ/min)	-9.81745435	Σ ήHout (KJ/min)	-15.71601147
	n in (mol/min)	nout (mol/min)	conversion %	
Ethanol	0.04288	0.03070208		
Ethylene	0	0.01217792	28.4	
Water	0.1388	0.0394192		
	inlet temp, K	Hin of mixture (KJ/mol)	outlet temp, K	Hout of mixture (KJ/mol)
	578	-216.524092	548	-212.4338136
	Σ ήHin (KJ/min)	-9.284553065	Σ ήHout (KJ/min)	-17.48313291

Table 21: Calculations of inlet and outlet flowrates and their respective enthalpies in vapor phase (Run 8)

Δ Hrx standard				
Substances	Products (kJ/mol)	Reactants (kJ/mol)		
Ethanol	0	-235.3		
Water	-241.82	0		
ethylene	52.4	0		
Total	-189.42	-235.3		
delta Hrx (kJ/mol)	45.88			
ξ (mol/min)	0.01217792			
ξΔHrx (KJ/min)	0.55872297			
Q(KJ/min)	-7.639856878			
Q(J/s)	-127.330948			
Sample	**Conversion (%)**	**Phase**	**ξ (mol/min)**	**Q(J/s)**
1	22.1	vapor	0.0075803	-75.7
2	21.4	vapor	0.0073402	-73.5
3	25.1	vapor	0.0086093	-85.09
17	21.4	vapor	0.00917	-91.29
18	28.4	vapor	0.01217	-127.3

Table 22: Calculation of heat transfer rates of collected samples in vapor phase (Run 8)

References

[1] L. Kniel, O. Winter, K. Stork, Ethylene: Keystone to the Petrochemical Industry, Marcel Dekker New York, 1980.

[2] D. Fan, D.-J. Dai, H.-S. Wu, Ethylene Formation by Catalytic Dehydration of Ethanol with Industrial Considerations, Materials, 6 (2012) 101-115.

[3] Impact of Zeolites on the Petroleum and Petrochemical Industry, (2014).

[4] C.B.P. and, R. Datta, Production of Ethylene from Hydrous Ethanol on H-ZSM-5 under Mild Conditions, (1997).

[5] P.A. Zapata, J. Faria, M.P. Ruiz, R.E. Jentoft, D.E. Resasco, Hydrophobic Zeolites for Biofuel Upgrading Reactions at the Liquid–Liquid Interface in Water/Oil Emulsions, Journal of the American Chemical Society, 134 (2012) 8570-8578.

[6] I. Piccirilli Dorsey, Bioenergy (Biofuels and Biomass) | EESI, (2014).

[7] P.A. Zapata, Y. Huang, M.A. Gonzalez-Borja, D.E. Resasco, Silylated hydrophobic zeolites with enhanced tolerance to hot liquid water, Journal of Catalysis, 308 (2013) 82-97.

[8] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose, cellulose and lignin pyrolysis, Fuel, 86 (2007) 1781-1788.

[9] B. Hahn-Hägerdal, M. Galbe, M.-F. Gorwa-Grauslund, G. Lidén, G. Zacchi, Bio-ethanol–the fuel of tomorrow from the residues of today, Trends in biotechnology, 24 (2006) 549-556.

[10]Catalytic Dehydration of Alcohol. (n.d.). Retrieved October 20, 2014, from http://www.chem.uw.edu.pl/people/AMyslinski/nowy/zarzadzanie/26ME.pdf

[11]Andrade Coutinho, P., Monita, A., & Cassinelli, L. (2013). Braskem's Ethanol to Polyethylene Process Development. *Catalytic Process Development for Renewable Material,* 149-165.

[12]Teber, S., Elnekave, M., & Tatlier, M.. (2010). Preparation of zeolite a coatings on copper plates by using the substrate heating method. *Brazilian Journal of Chemical Engineering*, *27*(4), 619-626. Retrieved October 25, 2014, from http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-66322010000400014&lng=en&tlng=en. 10.1590/S0104-66322010000400014.

[13]Zeolite. (n.d.). Retrieved October 16, 2014, from http://www.epa.gov/rpdweb00/docs/cleanup/nanotechnology/chapter-2-zeolites.pdf

[14]Erdem-Şenatalar, A., Tatlier, M. and Ürgen, M., Preparation of Zeolite Coatings by Direct Heating of the Substrates. Microporous and Mesoporous Materials, 32, 331 (1999).

[15]Zapata, P., Huang, Y., Gonzalez-Borja, M., & Resasco, D. (2013). *Silyalted Hydrophobic Zeolite with Enhanced Tolerance to Hot Liquid*. Journal of Catalyst.

[16]Lisensky, G., & Blitz, I. (n.d.). Zeolite ZSM5. Retrieved October 17, 2014, from http://education.mrsec.wisc.edu/nanolab/zeolite/

[17]Triantafillidis, C.S.; Vlessidis, A. G.; Nalbandian, L.; Evmiridis, N. P. Effect of the Degree and Type of the Dealumination Method on the Structural, Compositional and Acidic Characteristics of H-ZSM-5 Zeolites. *Microporous Mesoporous Mater.* 2001, *47, 369-388.*

[18]Kooyman, P. J.; van der Waal, P,; van Bekkum, H. Acid Dealumination of ZSM-5. Zeolites 1997, *18, 50-53.*

[19]Beyerlein, R. A.; Choi-Feng, C.; Hall, J. B.; Huggins, B. J.; Ray, G. J. Effect of Steaming on the Defect Structure and Acid Catalysis of Protonated Zeolites. *Top. Catal.* 1997, *4,* 27-42.

[20]Carvajal, R.; Chu, P.-J.; Lunsford, J. H. The Role of Polyvalent Cations in Developing Stron Acidity: A study of Lanthanum-Exchanged Zeolites. *J. Catal.* 1990, *125*, 123-131.

[21]Ryan M. R.; Florian, S.; Andrew,D.; Nadiya,D.; Jeroen, A. B.; Johannes, A. L.; Christopher, W. J.; Carsten, S.; Stability of Zeolite in Hot Liquid Water. *Journal of Physical Chemistry* C2010*114*(46), 19582-19595.

[22] Fan, D.; Dai, D.; Wu, H. Ethylene Formation by Catalytic Dehydration of Ethanol with Industrial Considerations. *Materials.* 2013,*6,*101-115

[23] Zhang, M.; Yu, Y. Dehydration of Ethanol to Ethylene. *Ind.Eng.Chem,* 2013, *52(28)*, 9505-9514

[24] Zhang, D.; Wang, R.; Yang, X. Effect of P content on the catalytic performance of P-modified HZSM-5 catalysts in dehydration of ethanol to ethylene. *Catal. Lett.* **2008**, *124*, 384–391.

[25] Smith, J. M., Hendrick C. Van. Ness, and Michael M. Abbott. *Introduction to Chemical Engineering Thermodynamics*. 7th ed. New York [etc.: McGraw-Hill, 2001. Print.