Liquid Phase Catalytic Dehydration of Hydrous Ethanol for Synthesis of Green Ethylene

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In Chemical Engineering
By

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Approved:

_________________________________
Professor Michael Timko, Advisor
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Abstract

Ethylene is one of the mostly widely synthesized raw materials in the world, with 146 million metric tons produced in 2016. It is a precursor to polyethylene, one of the world’s most important plastics, which in turn forms everyday items like food packaging, water bottles, and shopping bags. Our study used HZSM-5 (a zeolite catalyst) in the catalytic dehydration of ethanol to form ethylene, particularly focusing on applications to biological feedstock. While the reaction is commonly performed in the vapor phase, the liquid phase was examined, as well as the addition of water in the feedstock. Using a micro flow reactor, ethanol and water were flowed to a zeolite packed bed. Liquid and vapor products were collected for analysis of ethylene yields and ethanol conversions in both reaction phases through gas chromatography. Our results suggest that ethanol conversion is not significantly affected by the addition of water in either phase. However, vapor phase has consistently higher ethanol conversion than in the liquid phase. The addition of water had a nominal effect on vapor phase ethanol dehydration, but demonstrated a positive correlation with ethylene yield in liquid phase ethanol dehydration. Our data suggests water improved ethylene selectivity in the liquid phase. To explain this phenomenon, we suggest a mechanism in which water reduces ethanol dimerization at zeolite active sites. Furthermore, analysis of coked catalyst and oil suggest greater initial oligomerization in the liquid phase.
Introduction

1.1 Ethylene as a Global Product

Ethylene is one of the mostly widely synthesized raw materials in the world, with 146 million metric tons produced in 2016 [1]. In fact, 75% of all petrochemicals worldwide are produced from ethylene [2]. It is a precursor to polyethylene, one of the world’s most important plastics, which in turn forms everyday items like food packaging, water bottles, and shopping bags [1]. Polyethylene is the most commonly produced plastic with a production of 81.8 million metric tons in 2015 [1]. The chemical structures of ethylene and polyethylene are provided in Figure 1, below:

![Chemical structures of ethylene and polyethylene](image.png)

Figure 1: Chemical structures of ethylene (right) and polyethylene (left)

Ethylene is made up of two carbons, with two bonded hydrogens each, linked by a double bond. Polyethylene is the polymer derived from monomeric ethylene. Today, 99% of ethylene is created through steam cracking (pyrolysis) of hydrocarbons using petroleum products [3]. The two mainstream processes used, steam and catalytic cracking, elevate crude oil or natural gas to temperatures as high as 850 C to breakdown the large compounds into constituent parts. These methods are energy intensive, but are capable of producing large amounts of ethylene with the
largest facilities producing 1.5 million tons annually [4]. As shown below in Figure 2, a majority of large-scale ethylene production facilities utilize steam-cracking:

<table>
<thead>
<tr>
<th>Company</th>
<th>Location</th>
<th>Ton/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam-cracking plants</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>Formosa Petrochemical Corporation</td>
<td>Mailiao, Taiwan,</td>
<td>2,935,000</td>
</tr>
<tr>
<td>Nova Chemicals Corporation</td>
<td>Joffre, Alberta, Canada</td>
<td>2,811,792</td>
</tr>
<tr>
<td>Arabian Petrochemical Company</td>
<td>Jubail, Saudi Arabia</td>
<td>2,250,000</td>
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<tr>
<td>ExxonMobil Chemical Company</td>
<td>Baytown, TX, USA</td>
<td>2,197,000</td>
</tr>
<tr>
<td>ChevronPhillips Chemical Company</td>
<td>Sweeny, TX, USA</td>
<td>1,865,000</td>
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<tr>
<td>Dow Chemical Company</td>
<td>Terneuzen, Netherlands</td>
<td>1,800,000</td>
</tr>
<tr>
<td>Ineos Olefins &amp; Polymers</td>
<td>Chocolate Bayou, TX, USA</td>
<td>1,752,000</td>
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<tr>
<td>Equistar Chemicals LP</td>
<td>Channelview, TX, USA</td>
<td>1,750,000</td>
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<tr>
<td>Yanbu Petrochemical Company</td>
<td>Yanbu, Saudi Arabia</td>
<td>1,705,000</td>
</tr>
<tr>
<td>Equate Petrochemical Company</td>
<td>Shuaba, Kuwait</td>
<td>1,650,000</td>
</tr>
<tr>
<td>Ethanol to ethylene plants</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>Braskem</td>
<td>Triunfo, Brazil</td>
<td>200,000</td>
</tr>
<tr>
<td>Dow Chemical Company</td>
<td>Santa Vitoria, Brazil (under construction)</td>
<td>190,000</td>
</tr>
<tr>
<td>Solvay Indupa</td>
<td>Santo Andre, Brazil</td>
<td>60,000</td>
</tr>
</tbody>
</table>

Figure 2: Comparison of ethylene production facilities and their outputs. [5]

The combination of high utility cost and the use of fossil fuels to produce ethylene leaves an opportunity for environmentally-minded methods. As a means to limit greenhouse emissions and to reduce the dependency on fossil fuels, there is an interest in developing “green ethylene,” specifically through the catalyzed dehydration of ethanol from a renewable source.

1.2 Ethanol Dehydration and Green Ethylene

Ethanol dehydration is an alternative method for producing ethylene from ethanol. A proposed mechanism for the formation of ethylene from ethanol dehydration is shown below:
Figure 3: Proposed Ethanol Dehydration Mechanism [3]

The mechanism shows the acid catalyst protonating a hydroxyl group, causing it to leave as a water molecule. Then, the conjugate base deprotonates the methyl group and the hydrocarbon rearranges into ethylene. This chemistry shows promise due to its environmental benefits. A basic flow diagram of the overall “green ethylene” process is shown below in Figure 4:

Figure 4: Process Flow Diagram

Agricultural feedstock, or biomass, can be fermented to create ethanol, which can then be converted to ethylene through catalytic dehydration. The bio-based ethylene can then be transformed into chemical products through additional processing. Because ethylene created from biomass is chemically identical to ethylene produced from steam cracking, it is a drop-in substitute for current additional processing plants [4].

A Brazilian company, Braskem, developed an industrial scale ethanol-dehydration plant with a capacity of 200,000 tons per year in 2010. The “green polyethylene” from this plant and others like it have several environmental benefits over steam cracked ethylene. First, the ethanol feedstock used in the reaction is a renewable resource instead of fossil fuels. In Braskem’s case, the ethanol comes from Brazil’s abundant sugarcane resources. Second, growing the feedstock
serves as a method of carbon sequestration, assisting the process in being carbon neutral. Bio-
ethylene production is estimated to save 60% of the fossil fuel energy used by the traditional
petrochemical process and generate 40% less greenhouse gases [5]. Agreeing with this statement,
Mohsenzadeh et al. calculated that bioethylene production saves an average of an energy
equivalent of 28 MJ of natural gas per kilogram of ethanol. Additional Brazil-based plants are
owned by Dow Chemical Company and Solvay Indupa, making use of Brazil’s abundant supply
of sugar cane [3]. Despite these efforts, steam cracking plants dwarf ethanol to ethylene plants in
terms of ethylene production [3].

The cost of green ethylene is prohibitive and the process is economically strained. Green
ethylene costs between $1200-2000 per ton, depending on the source of ethanol, while the
petrochemical alternative costs approximately $600-1300 [5]. The primary differences in cost
between petrochemical ethylene and bio-ethylene come from differences in cost of feedstock and
production cost. Bio-ethanol is subject to variable feedstock qualities and fluctuating prices,
causing economic issues for the bio-ethylene process. Additionally, the reaction is highly
endothermic and requires temperatures exceeding 573 K to ensure acceptable selectivities are met,
and avoiding losses to major reaction byproducts [3]. As a result, the heat requirement for the
process is large. This reveals targeting the energy requirements of the process as a viable way to
make the process more economically viable and these energy requirements can be adjusted by
research into various process variables such as the catalyst, types of reactors used, phase of
reaction, and feed characteristics.

Currently in industry, the reaction is run in the vapor phase with a series of adiabatic fixed
beds packed with alumina-based catalysts [4]. A different catalyst types, zeolites, are an alternative
to alumina-based catalysts, but have not yet been employed widely in industry. Most zeolite
catalysis research with ethanol dehydration focuses on the reaction in the vapor phase. There has been little research conducted on ethanol dehydration in the liquid phase, which is theorized to have superior heat transfer and mass transfer characteristics [2]. Liquid phase ethanol dehydration can be performed at elevated pressures, as an increase in pressure does not affect reaction equilibrium. Studies of dimethyl ether synthesis from methanol, a related reaction, have shown that higher pressures increased the contact time between the feed and catalyst, thus improving conversion [6]. Increased contact time is related to residence time, which has throughput advantages [6]. A liquid phase outlet is in the correct conditions for downstream purification of ethylene, an advantage to vapor outlet, as a phase change is not necessary [7].

Another research interest is the use of hydrous feedstocks in ethanol dehydration, as anhydrous feedstocks can be very energy intensive due to the separation processes necessary to get it to high purity levels [6]. Biological feedstock is traditionally formed through fermentation of sugars by yeast cells, resulting in ethanol and carbon dioxide. However, as the ethanol concentration increases in the batch there is observed inhibition of yeast growth [8]. The fermentation process with the *Saccharomyces cerevisiae* species of yeast typically produces an ethanol broth of 6-8%, which is a mostly hydrous feedstock [9]. While distillation can be performed, water’s large specific heat capacity makes distillation expensive in terms of cost and energy [5]. A proposed advantage of hydrothermal media is allowance for variability in water content, which could make lack of distillation a more viable option [10, 11]. High temperature pressurized water is a clean solvent for organic reactions, which means its environmentally friendly [12-14]. Additionally, reduction in mass transfer limitation has been observed in hydrothermal media, resulting in faster reaction rates [15-18]. Specifically, in the case of zeolite
catalyzed ethanol dehydration, increased steady state activity and selectivity has been observed with a hydrous ethanol feed [19].

1.3 Types of Catalysts

An ample amount of research has been conducted into the types of catalysts used in the ethanol dehydration reaction. A catalyst is a material that increases the rate of reaction or lowers the energy requirements of a reaction. Because ethanol dehydration is so highly endothermic, catalysts are a necessity to reduce energy costs by reducing the temperature at which the reaction takes place. Many different types of catalyst can be used in ethanol dehydration reaction, such as alumina, silica, sulfuric acid, zeolites, and more. Every type of catalyst is evaluated by the temperature at which it maintains the best selectivity and ethanol conversion, otherwise known as, activity. However, factors such as the catalyst stability also play a role in the viability for industry.

Prior to the growth of the petrochemical industry, raw catalysts such as phosphoric acid were the primary catalyst used by the industry. Phosphoric acid causes many process issues due to corrosion and low productivity, but was a necessity in the early chemical industry because of the high selectivity for ethylene, producing a high purity product [1, 19].

Phosphoric acid was replaced in industry by activated alumina, which has now become one of the most used and investigated catalysts for the reaction. Alumina and its variants demonstrate great conversions of over 99% at selectivities between 97% and 99% at temperatures between 450-500 °C [1]. Alumina also maintains good stability, but is hindered by the formation of coke at catalyst active sites. Zeolites are another type of catalyst that show promise due to high selectivity
and stability, but have not been proven in industry. Our experiment utilizes HZSM-5, a specific type of zeolite catalyst.

**Experimental**

2.1 Safety

Standard safety precautions were taken throughout the entire series of experiments conducted. Personal protective gear was used at all times, which included safety glasses and gloves. Safety shields were employed around the reactor as the typical operating temperature was approximately 375°C with pressures reaching as high 3600 psig. All gas tanks were secured to a vertical edge using chains to prevent tipping.

2.2 Equipment

The ethanol dehydration reaction in both liquid and vapor phases were carried out through the schematic shown below, Figure 5:

![Figure 5: Ethanol Dehydration Equipment Schematic](image-url)
The reactants, water and ethanol, were stored in plastic containers and pumped to the reactor. Before reaching the oven, the two streams are mixed. The water-ethanol mixture was pumped through a coiling wire, such that the mixture reaches the preferred temperature before reaching the packed bed. The outlet end of the reactor was blocked with a porous frit that allowed products to exit but retained the HZSM-5 packed bed. Products flow from the reactor to a glass collection chamber. Liquid products were collected through releasing a valve at this chamber, while the vapor products bubbled out of the mixture into a series of pipes that led to the in-line gas chromatograph. The piping that delivers product to the gas chromatograph was insulated with aluminum foil and heated to prevent condensation in the piping. A photograph of the equipment can be seen below in Figure 6:

![Figure 6: Picture of Process Unit](image)

2.3 Procedure

The catalyst was calcined in batches prior to the trials in accordance with the next section. The reactor was loaded with 0.75 g of catalyst and secured in oven of the retrofitted gas chromatograph. The oven was then turned on and allowed to reach 375 °C. If the trial was to be in the liquid phase, the system would be pressurized to 3600 psi. Once the oven reached the desired
temperature, the pumps and GC-FID were turned on. Gaseous product activity was measured with the GC-FID for the duration of the trial. The glass collection column for liquid products was emptied as needed. Liquid product samples were retained for further analysis, as well as oil substances formed before reaching steady state. At the conclusion of the experiment, coked catalyst was collected.

2.3 Catalyst Preparation

ZSM-5 was prepared for each reaction through calcination, or a period of high temperatures to cause a chemical change. Calcining ZSM-5 decreases the moisture content of the catalyst and removes impurities, allowing for the reactants to more easily access the active sites within the ZSM-5. The catalyst was initially calcined in a low temperature oven for one hour at 100˚C, and the catalyst was then moved to a 550 ˚C oven for approximately 12 hours. The catalyst was removed from the oven by using long metal tongs to decrease proximity to the heat source, and heat resistant gloves were used to prevent burns and other injuries from occurring in the case of skin contact with the hot crucible. The crucible and catalyst were cooled and then stored in a sealed plastic container until use.

Figure 7: Calcined catalyst to be loaded into reaction vessel.
2.4 Reactor Assembly

Before connecting the reactor to the inlet feed line, a semi-porous metal frit was secured on the outlet of the micro-reactor. Once the frit was fitted, the desired amount of catalyst was loaded into the micro-reactor using a small plastic funnel and metal spatula. Once the reactor was loaded, the reactor was connected to the inlet and outlet piping of the unit using a wrench. Below is a picture of the reactor tube:

![Figure 8: Micro Reactor Used for Experiment](image)

2.5 Reactor Startup

After installing the loaded reactor, the oven door was closed, and the desired temperature was entered as the set point for the oven. For experiments in the vapor phase, no pressurization was necessary. For liquid phase dehydration, the reaction was run at 3600 psi to keep the reactants in liquid phase despite a temperature of 375 °C. To accomplish this, the valve on the nitrogen tank was opened and set to 3600 psi to pressurize the system. Once the correct temperature and pressure conditions were met, the pumps were set to the desired flow rates. Below is a picture of the micro reactor in the oven attached to the inlet and outlet streams.
Special care was taken to ensure that the reactor was very tightly secured to the inlet and outlet blocks. A tight connection was needed to prevent reactants, zeolite and products from being lost when the equipment was pressurized. Occasionally, lubricant was applied to allow for a tight connection without destroying the threading.

2.6 Gas Chromatograph Continuous Gaseous Product Analysis

Immediately after the feed pumps were turned on, the Gas Chromatograph-FID (GC-FID) analysis was initiated via a data collection software. Helium was used as a carrier gas to inject the gaseous product through the GC-FID. Over the course of the reaction, gaseous product was injected into the instrument (every 10 minutes). Chromatographic data was collected and analyzed at the conclusion of the experiment. The chromatogram shows the retention time on the x-axis and intensity on the y-axis. The area under the curve of each peak is proportional to the concentration of the product. An example of this is shown below as Figure 10:
A calibration curve was created by injecting samples of known concentrations and measuring the corresponding area. This allowed for determination of concentration of unknown samples in an experiment. The calibration curve is shown below:

Figure 10: Example Gas Chromatogram

Figure 11: Ethylene calibration curve used to amount of ethylene produced
2.7 Liquid Product Analysis

Liquid product was collected in a glass column until removal. This collection column can be seen below in Figure 12:

![Glass Collection Column for Reactor Outlet](image)

**Figure 12: Glass Collection Column for Reactor Outlet**

Liquid product samples were collected as the column filled. Special care was taken to ensure that the glass column was not being emptied at the same time a gas sample was being auto-injected to the GC-FID. Collection of liquid samples changed the pressure in the product line which could cause an artificially low activity peak. The sample was collected in a graduated cylinder to determine the volume and also the mass. The time over which the sample was generated was recorded and used to determine the mass flow rate and volume flow rate exiting the reactor. Samples were collected and stored in a refrigerator. Multiple liquid samples were collected in each experiment to ensure an accurate measurement. A calibration curve was created for batch analysis of the liquid samples. This allowed for determination of ethanol concentration in the samples, which is ultimately the ethanol conversion of the experiment. The calibration curve used is shown below. All samples were diluted to ensure that the area is in the range of the curve.
Figure 13: Ethanol calibration curve used to find the amount of unreacted ethanol in the liquid sample.

2.8 Oil Analysis

Oil samples were collected during the experiments and refrigerated until analysis. An example of oil can be seen below:
The oil samples were diluted with acetone and analyzed through tandem gas chromatography-mass spectrometry (GC-MS). A mass spectrometer allows for identification of a species based on a spectral library. Thus, the contents of oil samples from both liquid and vapor phase runs can be identified and then compared.

Results and Discussion

4.1. Effect of water loading on ethanol conversion

From the liquid samples collected, a weight-percentage of ethanol was found using a gas chromatograph. This weight percentage was converted to a molar flow rate and a total ethanol conversion was calculated. The conversions of ethanol are shown below in Figure 15. Our data shows that over the range of water flow rates tested, the vapor phase reaction resulted in higher conversions in the range of 91 ± 9% to 98 ± 3%, compared to the conversion range of the liquid phase of 80 ± 2% to 91 ± 6%. These results are consistent with previous work done by Deanna Poirier where she found that at the same WHSV and a water loading of 33% that ethanol
conversion was 99% for the vapor phase and 77% for the liquid phase. While the conversion for vapor phase was higher, we observed that the overall conversion had no clearly discernible relationship with an increase or decrease in water loading.

Figure 15: Ethanol conversion as a function of water loading.

4.2. Effect of water loading on ethylene yield

From the gaseous product analysis, we were able to quantify an amount of ethylene produced by using data from another gas chromatograph and the wet test meter in aggregate. This amount of ethylene was converted to a molar flow rate to calculate ethylene yield. These values were plotted below in Figure 16. Figure 16 shows that water loading has a strong, positive relationship with ethylene yield in the liquid phase, but negligible effect in the vapor phase. At a water loading of 0%, ethylene yield in the liquid phase averaged at 16 ± 3% compared to the vapor phase at 95 ± 6%. This difference in yields decreases for every incremental increase in water
loading, until at 30% water loading, the liquid phase achieves a yield of 90 ± 4% compared to the vapor phase 88 ± 8% yield.

![Figure 16: The effect of water loading on ethylene yield in the vapor and liquid phase.](image)

The difference in yield between the two phases was attributed primarily to a reduced selectivity for ethylene at lower water loading levels. At the lower water loading levels, we observed that there was an increase in secondary peaks following the main peak for ethylene. One of these peaks was identified to be butene, a higher carbon number olefin, indicating that further chain-building reactions to make higher alcohols which then can be dehydrated to the higher olefins. This finding was discussed in Phillips et al. where researchers found that the presence of water increases selectivity towards ethylene by moderating the acidity of catalytic sites [19].
Figure 17 and 18: Proposed Water Mechanism. On the left in low water loading scenarios, ethanol can bond to two adjacent catalyst acid sites, which leads to dimerization chemistry that can form many different products via a carbonium intermediate. On the right, water molecules can hinder ethanol molecules adsorbing to reaction sites, forcing unimolecular reactions which increases selectivity for ethylene, the desired product.

We believe that this difference in selectivity may be due to a molecular hindrance by water at the catalyst surface. As shown above in Figures 17 and 18, water molecules may cause hindrance at the catalyst active sites, forcing unimolecular dehydration pathways instead of bimolecular dehydration. In bimolecular dehydration, common products such as ethers form via a carbocation intermediate. The carbocation is an extremely reactive intermediate, particularly with alcohol and olefin mixtures. This can form many different types of compounds, such as a main byproduct of ethanol dehydration, diethyl ether, as well as other chain and branched hydrocarbons. The
hindrance by water forces the unimolecular pathway which avoids this reactive intermediate, and therefore is more selective towards our desired product, ethylene.

4.3. Oil Precursor Analysis

On reactor startup, the first hour of our trials produced oil in the liquid samples, as seen below in Figure 19:

![Liquid Oil Samples](image)

Figure 19: Liquid Oil Samples

Qualitatively, it can be observed that the liquid sample on the right from a 90% liquid phase run has a darker amber hue compared to the sample on the left from a 90% vapor phase run. This phenomenon was consistent for all runs done for this project. These oil samples were run on a GC in order to evaluate the presence of higher hydrocarbon substances in the oil (Figure 20). As the darker amber hue in the photograph suggests, the liquid phase oil reports a higher intensity and more varied types of oligomers.
Figure 20: GCMS Data from a 70% vapor phase (top) and 70% liquid phase (bottom) reaction.

The GC-MS data shows high intensity peaks in the liquid phase that are not significant in the vapor phase (large signal to noise ratio). Methyl hexane and methyl heptane are higher carbon alkanes seen exclusively in the liquid phase oil samples. There are also branched aromatics, such as diethyl benzene and ethyl dimethyl benzene that are only seen with significant intensity in the liquid phase. Thus, the GC-MS data supports conclusions from the color of the oil that there is more oligomerization in the liquid phase oil. This suggests a more rapid coking process in the liquid phase.
Conclusions and Recommendations

The results of our project are potentially powerful in legitimizing liquid phase catalytic dehydration as a means of producing ethylene. The primary takeaways from our findings are that within our water loading range, overall ethanol conversion is negligibly affected, vapor phase does not diminish in ethylene yield at higher water loading, and finally, and perhaps most importantly, the presence of water enhances ethylene selectivity and yield substantially in the liquid phase reaction to the point where it is competitive with the vapor phase reaction.

For the first two takeaways, the fact that vapor phase ethanol conversion and ethylene yield are not negatively affected by the presence of water is beneficial for the process already in place, even without exploring the lesser known liquid phase process. We have shown that in our water loading range, an ethanol feedstock of 100% or 70% quality can be pumped into a reactor with negligible difference in terms of activity, showing that it is not necessary to purify the ethanol-water broth from fermentation up to and beyond the azeotrope, which requires specialty distillation techniques. Removing this process step can lead to reducing the cost of the overall process, and therefore, reducing the cost of green polyethylene.

For the third take away, along with the benefits covered in the last paragraph, we have shown that the liquid phase reaction can actually be competitive in terms of yield at the highest water loading. This suggests that at the higher water loadings, we may be able to reap, not only the benefits of the lower separation costs from feeding a lower quality feedstock into the reactor, but also the proposed benefits of the liquid phase reaction that were covered in the background such as improved phase separation post-reaction, better mass-transfer characteristics on the catalyst surface, and improved heat-transfer in the liquid phase. These benefits in aggregate may improve the overall process cost and make the process more attractive to other industries.
In answering our questions, we revealed several new questions that may be of interest for future research. Our studied water loading range was at the low end of the spectrum from 0-30%. It would be interesting to see how the yield and conversion shift beyond 30% and approaching original fermentation broth qualities of about 90%. Additionally, the precursor oil and coked catalyst were not main focuses of this study, but the small qualitative step shows that there is some peculiar behavior between the vapor and liquid phase in terms of coke and oil color as well as the chemical species present in the oil.
References

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15. A Loppinet-Serani, C. Aymonier, F. Cansell, Supercritical water for environmental technologies, Journal of Chemical Technology * Biotechnology 85 (2010) 583-589
16. H. Machida, M. Takesue, R.I. Smith Jr., Green chemical processes with supercritical fluids: properties, materials, separations and energy, Journal of Supercritical Fluids 60 (2011) 2-15


### Appendix A: Table of Trials

<table>
<thead>
<tr>
<th>Run</th>
<th>Phase</th>
<th>Ethanol Flow Rate (mL/min)</th>
<th>Water Flow Rate (mL/min)</th>
<th>Ethanol Conversion (mol%)</th>
<th>Ethylene Yield (mol%)</th>
</tr>
</thead>
<tbody>
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<td>C2</td>
<td>Vapor</td>
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<td>Vapor</td>
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</tr>
</tbody>
</table>

*Indicates a run that no data was obtained due to instrumentation errors or unforeseen circumstances