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# Innovation and Development of Biofuel Technologies

An Undergraduate Honors College Thesis

in the

Ralph E. Martin Department of Chemical Engineering  
College of Engineering  
University of Arkansas  
Fayetteville, AR

by

Nicole Lorenz

April 29, 2011

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## **Abstract**

The need for viable alternatives to gasoline has lead researchers to explore various options for renewable energy resources. This research study focuses on two major options for renewable energy. The first is biodiesel, which is a fuel that can be made from vegetable oils or animal fats. In this study, biodiesel was made from tall oil, a paper byproduct. A novel reaction method was used, employing high temperature methanol rather than acid or base catalysis. The second option that was investigated is butanol, which is an alcohol with advantages over ethanol. First, a two-step fermentation was examined to improve the productivity of butanol fermentation. After this, the electrically-driven separation method of electrodeionization (EDI) was explored in order to further increase the final butanol product yield after the two-step fermentation.

# **Innovation and Development of Biofuel Technologies**

## **Introduction**

The unrestrained use of petroleum-derived fuel in this country has led to a critical need for gasoline alternatives. Oil reserves are being depleted and the country has developed a dependence on foreign oil, often from politically unstable countries. Of the 102 quadrillion Btus of energy consumed in the United States in 2007, 40% was petroleum and two-thirds of this petroleum was imported (Joyce, 2009). In contrast, almost 100% of the renewable energy used in the U.S. was produced in this country (Joyce, 2009). Biofuels are currently the leading source of renewable energy in the U.S. and show great potential for providing a reliable and long-lasting energy supply. This research study focuses on multiple aspects of biofuel technology and investigates ways to improve both diesel and alcohol based biofuels.

## **I. Biodiesel Production by Supercritical Methanol Reaction**

### **I.1 Literature Review**

Biodiesel is a fuel source that can be produced from various vegetable oils and animal fats. Biodiesel is lead-free, has little sulfur, and is biodegradable (McIntyre, 2009). It also has a higher flash point than diesel fuel, which results in greater transportation and storage safety (Knothe, 2005). Biodiesel is made up fatty acid alkyl esters and is typically produced by the transesterification of triglycerides with short chain alcohols, producing glycerol as a byproduct (Knothe, 2005) (Figure 1). It can also be produced by esterification of free fatty acids. Esterification of fatty acids is the main reaction that occurs with tall oil fatty acids, which is the

oil feedstock that will be used in this study. The reaction of biodiesel is traditionally done using an acid or base catalyst, but an enzyme catalyst can also be used. A catalyst-free method, called the supercritical fluid method, also exists and can have advantages in the conversion of algae oil to biodiesel. This is the method that will be used in this project.

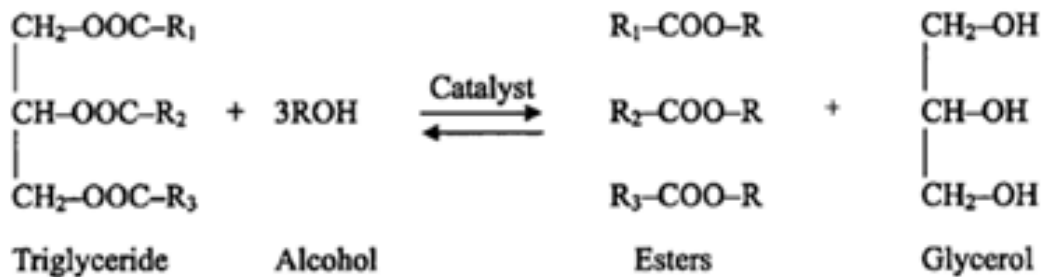


Figure 1 - Transesterification of Triglycerides with and Alcohol (Dermirbas, 2005)

The supercritical phase of a fluid is reached at very high temperatures and pressures. In this phase, the fluid will act as both a liquid and a gas. This allows the reaction to proceed without the use of a catalyst since it eliminates the usual two-phase mixture of oil and methanol and allows for a single-phase mixture, allowing enough contact to react without a catalyst (Dermirbas, 2005). In this project, static mixers have been added to the reactor to improve contact between reactants when the reactor is not in a fully single-phase supercritical state.

The disadvantages of the supercritical reaction method include high capital costs due to the high temperature and pressure of the reactor (Lim et. al., 2009). However, these costs can be offset by the elimination of the cost of the catalysts and the need to separate out catalysts after the reaction (Lim et. al., 2009). In addition to this, traditional catalytic reactions are inhibited by water and free fatty acids due to soap formation and catalyst hindrance (Dermirbas, 2009).



Algae oil typically contains a mixture of oils and its composition varies depending on species (Dermirbas, 2009). A group of University of Arkansas seniors on the 2009 P<sup>3</sup> design team working on this project found that a sample of algae from an algae turf scrubber system in Florida contained 5% free fatty acids and 95% triglycerides. Supercritical reactors have been proven successful in converting a variety of oils, both free fatty acids and triglycerides, into biodiesel.

## I.2 Materials and Methods

### *I.2.1 Equipment and Experimentation*

This project used a continuous supercritical biodiesel reactor (Figure 2). The reactor has heaters with power supplied by variable AC power adaptors, which allow the temperature of the reactor to be changed. The pressure can be controlled by an adjustable pressure let-down valve. Two graduated cylinders supply oil and methanol to the reactor. Two pumps that can be varied from 1-9 mL/min control the volumetric flow rates of the oil and methanol. The reactor has been tested with tall oil fatty acids (TOFA), which is a byproduct of the pulp and paper industry. It has been tested at varying pressures, temperatures, and oil to methanol molecular flow rate ratios.

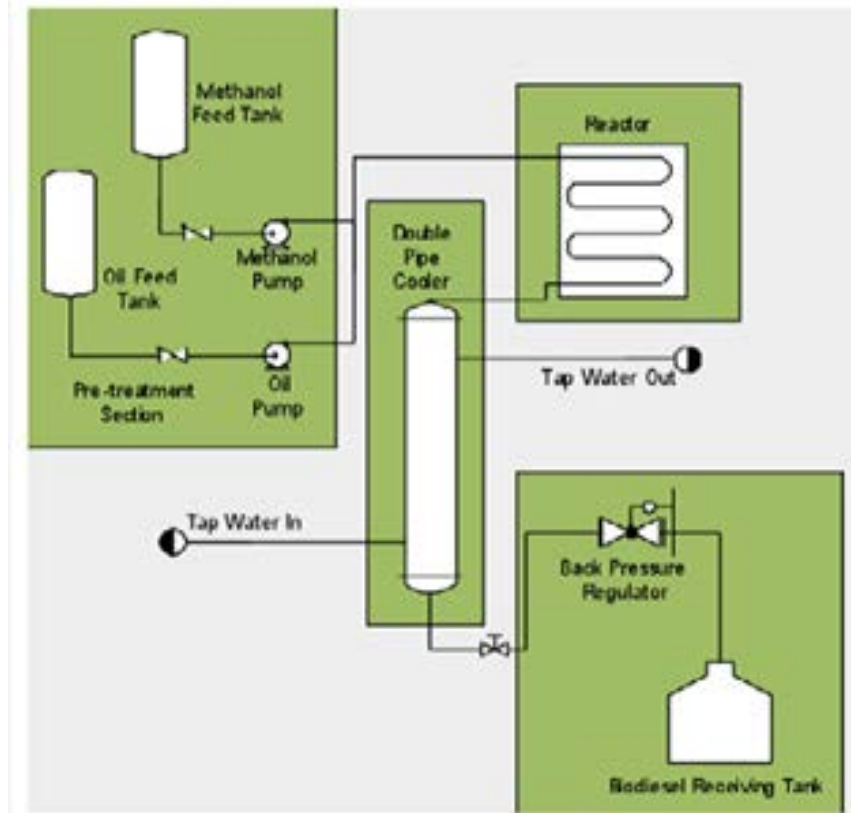


Figure 2 - Diagram of Biodiesel Experimental System (Magie et. al., Final P3 Report)

## 1.2.2 Analysis

### 1.2.2.a Theory

The reaction between TOFA and methanol proceeds by esterification (Figure 3). The products of the reaction are fatty acid methyl esters (FAME) and water. Unreacted methanol and TOFA will also be present in the product stream.

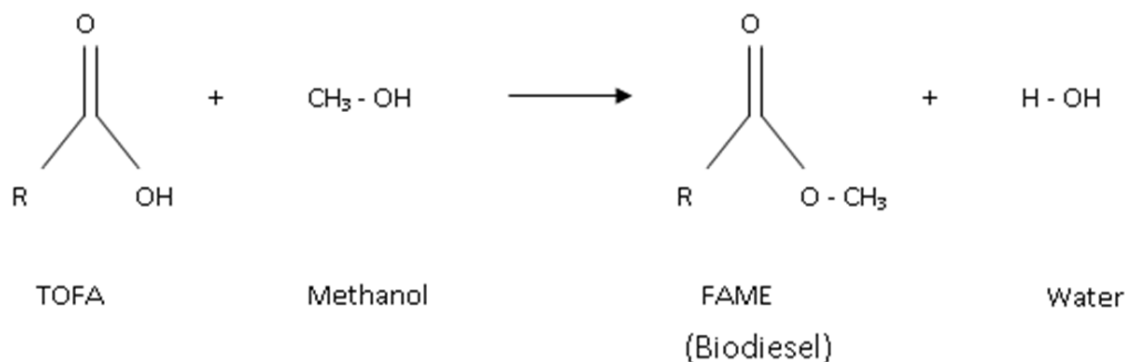


Figure 3 – Esterification Reaction of TOFA

### *1.2.2.b Biodiesel Separation*

After the products exit the reactor, they are allowed to sit overnight in a separatory funnel. The bottom layer contains mostly biodiesel (FAME) with some unreacted methanol and water. The top layer contains mostly methanol with some water and unreacted TOFA. The two layers are separated using the separatory funnel and the mass and volume of each layer are measured. The bottom layer is then distilled up to 103 °C to separate methanol and water from the biodiesel. The mass and volume of the biodiesel and methanol-water mixture from the bottom layer are then measured.

### *1.2.2.c Density*

In order to determine whether the biodiesel that is produced is within national biodiesel standards, certain physical properties must be measured. The density of each sample was measured with a pycnometer on an analytical scale. The pycnometer ensures a constant volume so that the mass of a sample can be compared to the mass of a liquid with a known density (this experiment used water) and the density of the sample can be calculated.

#### *1.2.2.d Viscosity*

The viscosity of the samples at 40 °C was also measured. The samples were placed in a hot water bath at 40 °C for at least 15 minutes. Then the viscosity of each sample was measured using a Cannon-Fenske viscometer.

#### *1.2.2.e Calculations*

The percent conversion for each experiment was calculated by dividing the moles of FAME product that exited the reactor by the moles of TOFA product that entered the reactor. The moles of tall oil entering the reactor can be calculated using the volumetric flow rate of the oil and the molecular weight of the tall oil:

$$\frac{(\text{Flow Rate TOFA}) \times (\text{Time Collected}) \times (\text{Density TOFA})}{\text{Molecular Weight TOFA}} = \text{Moles TOFA In}$$

The moles of biodiesel out were calculated using the mass of biodiesel left in the bottom layer after distillation and the molecular weight of the FAME products:

$$\frac{\text{Mass FAME out}}{\text{Molecular Weight FAME}} = \text{Moles FAME Out}$$

The molecular weight of the TOFA was calculated based on the composition of typical TOFA in the Southeastern United States (Figure 4). Likewise, the molecular weight of the FAME product was calculated based on each of the free fatty acids in the TOFA replacing a hydrogen molecule with a methyl group.

Table 1. Composition of tall oil fatty acids (Southeastern U.S.), adapted (Schulte, 2007)

<b>Compound</b>	<b>Mass Percent</b>
Palmitic acid	0.4%
Palmitoleic acid	0.7%
Stearic acid	2.3%
Oleic acid	46.0%
Linoleic acid	46.2%
Eicosadienoic acid	2.4%
Abietic Acid	2.0%

### I.3 Results

#### *I.3.1 Physical Property Results*

Table 2 shows the density, viscosity, and percent conversion results for all experiments. The physical properties of the biodiesel produced are very important since the U.S.A. has quality standards regarding the biodiesel that can be used. For example, the U.S. viscosity standard for biodiesel at 40 °C is 1.9-6.0 mm<sup>2</sup>/s (Shahidi, 2005). The viscosities of the samples from these experiments were slightly higher than what is acceptable. This indicates that biodiesel produced from tall oil would have to be blended with less viscous types of biodiesel to obtain the required viscosity. Most countries also specify that the density of biodiesel be between 0.85-0.90 g/mL (Shahidi, 2005). Every sample except for one was between these values. There are other

physical properties such as cetane number, flash point, and impurity content that were not able to be tested in this study, but are included in biodiesel standard specifications.

Table 2. Comparison of Results for Varying Conditions

Trial	Temperature (°C)	Pressure (Psi)	Methanol:Oil Molecular Flow Ratio	Density (g/mL)	Viscosity (mm <sup>2</sup> /s)	% Conversion
1	330	1775	7.75	0.8782	7.04	81.24
2	320	1850	7.75	0.8801	6.72	78.23
3	350	2050	7.75	0.8818	7.3	75.22
4	350	1550	7.75	0.8821	7.5	84.24
5	350	1050	7.75	0.8812	8.36	78.23
6	340	1500	15.5	0.8804	7.18	63.94
7	345	1500	31	0.9049	24.94	52.65
8	300	1550	7.75	0.8869	9.21	81.24
9	310	2000	7.75	0.8878	9.43	81.24
10	390	2000	7.75	0.8916	9.49	76.73
11	395	1500	7.75	0.8965	12.66	70.79

### *1.3.2 Results of Varying Methanol to Oil Flow Ratio*

Increasing the methanol to oil molecular flow rate ratio (Figure 4) resulted in an overall decrease in the percent conversion. Increasing the flow ratio from 7.75 to 15.5 resulted in a 24.1% decrease in percent conversion. Increasing the flow ratio from 15.5 to 31 resulted in a 17.6% decrease. This result is interesting, since similar studies have shown that increasing the methanol to oil ratio has a positive effect on the percent conversion due to increased contact of

oil and methanol (He et. al., 2006) (Wen et. al., 2008). However, a study by a recent masters student at the University of Arkansas at Fayetteville using tall oil also showed a decrease in percent conversion with increasing methanol to oil flow ratios (Schulte, 2007). A possible explanation for these results is that the free fatty acids in tall oil could be acting as both reactants and acid catalysts in the reaction (Minami & Saka, 2006).

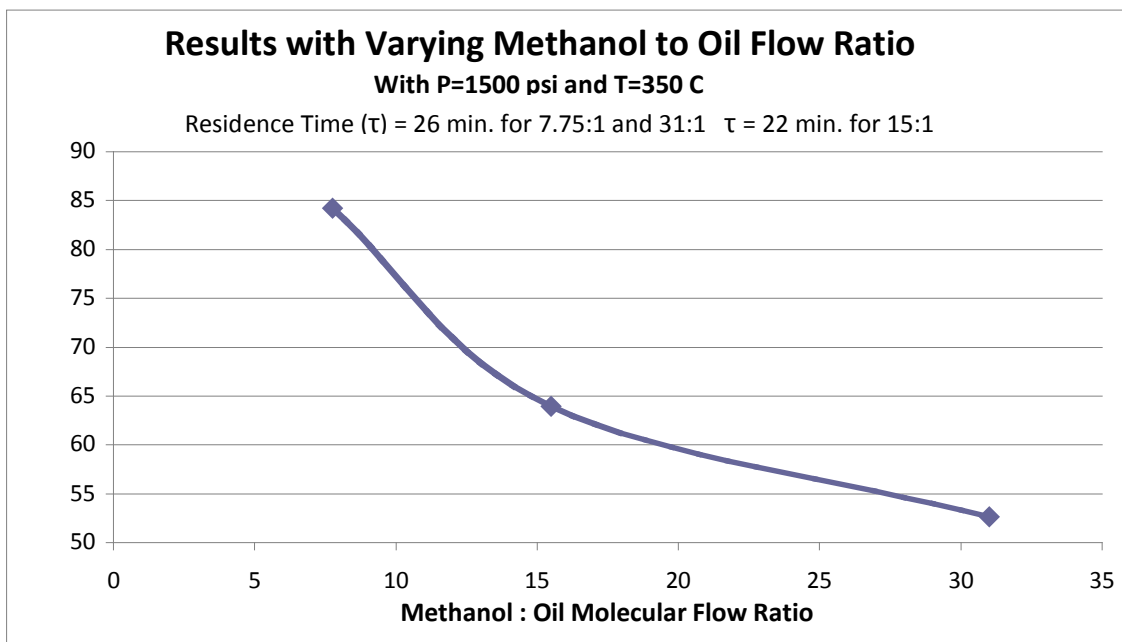


Figure 4 - Comparison of results with varying methanol to oil molecular flow rate ratio at a pressure of 1500 psi and a temperature of 350 °C

### 1.3.3 Results of Varying Temperature

The results of varying temperature are shown in Figure 5. At 1500 psi, there was a peak of percent conversion around 350 °C. This agrees with most available literature, where a peak has occurred somewhere between 300 and 350 °C (He at. al., 2006). However, at 2000 psi, there

was a slight minimum at 350 °C. Replicates of these experiments should help with the interpretation of results.

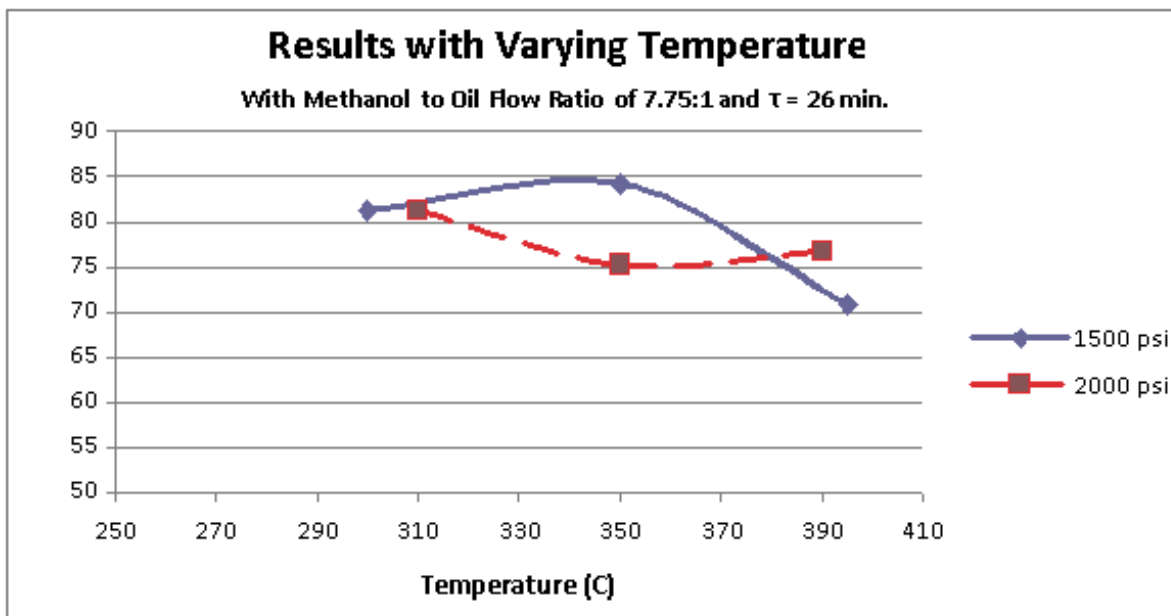


Figure 5 - Comparison of results of varying temperature with a methanol to oil molecular flow rate ratio of 7.75:1 and pressures of 1500 psi and 2000 psi

#### 1.3.4 Results of Varying Pressure

The results of varying pressure show a slight peak at 1500 psi. The percent conversion had a 7.7% increase from 1000 to 1500 psi and a 10.7% decrease from 1500 to 2000 psi. Since there is not a large difference between supercritical ( $P > 1173$  psi) and subcritical ( $P < 1173$  psi), this may be an indication that completely supercritical conditions are not required to obtain the desired percent conversion in this reaction.



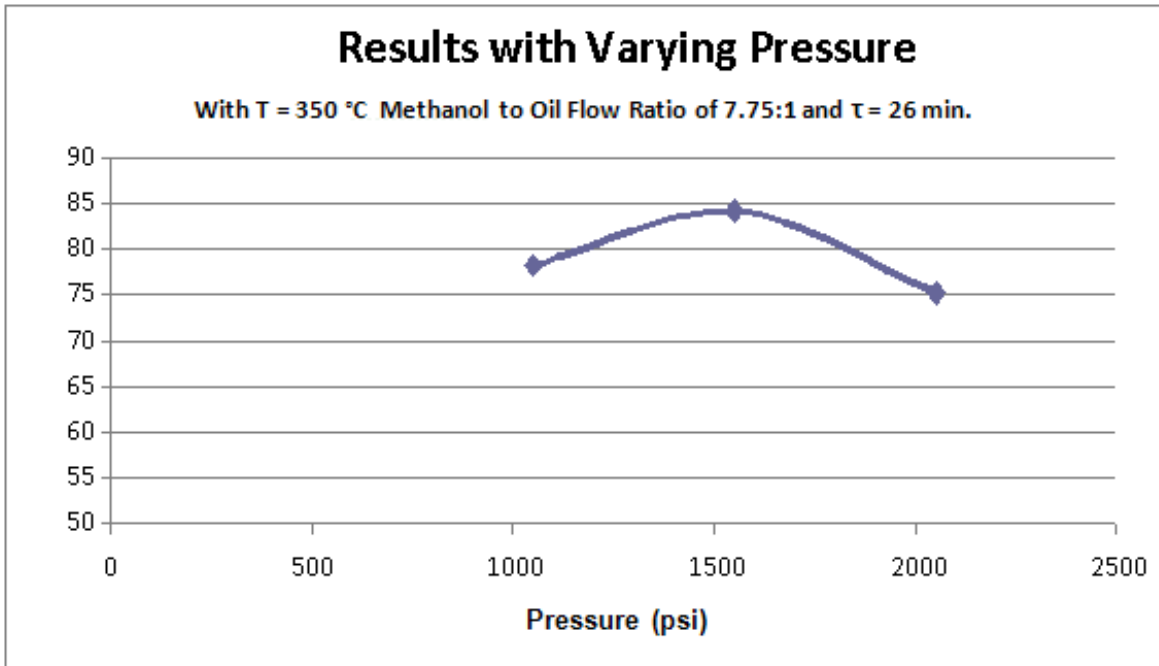


Figure 6 - Comparison of results of varying pressure with a methanol to oil molecular flow rate ratio of 7.75:1 and a temperature of 350 °C

#### I.4 Conclusions

A supercritical biodiesel reactor was tested at varying pressures, temperatures, and methanol to oil flow ratios. It was found that percent conversion decreased with increasing methanol to oil flow ratio and that there was a slight peak in percent conversion at a pressure of 1500 psi. The temperature results showed a slight peak at 350 °C when the reactor was run at 1500 psi and a slight minimum at 350 °C when the reactor was run at 2000 psi. Pressure results show that it may be possible to run this reactor below supercritical conditions.

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## II. Continuous Butyric Acid Fermentation in a Two-Step Butanol Production Process

### II.1 Literature Review

#### II.1.1 Butanol

Butanol is a renewable fuel that can be mixed with gasoline. It can be made from sugars in renewable and waste materials and it has some advantages to ethanol. It releases more energy per unit mass than ethanol, can be mixed with gasoline in higher concentrations, and can potentially be shipped through existing pipelines (Smith & Workman, 2004). Although butanol has many desirable qualities, it is not currently used as a fuel. This is mainly because of low product yields. The traditional single-step ABE process typically produces butanol, acetone, and ethanol in a ratio of 6:3:1 (Qureshi & Blaschek, 2001). Therefore, the maximum production of the process is 60% butanol.

#### II.1.2 Two-Step Butanol Fermentation

For this project, a two-step method of butanol production was used, which has been shown to produce higher yields of butanol (Ramey, 1998). In the first step, glucose is converted to hydrogen, carbon dioxide, and butyric, acetic, and lactic acid using a bacterium. In our project, the fermentation was carried out using *Clostridium tyrobutyricum*. After this, the organic acids from the first step can be converted to butanol, acetone, and ethanol using another bacterium such as *Clostridium acetylbutylicum*. This two-step process is shown in Figure 7. Since butyric acid is converted to butanol in the second fermentation, a pure stream of butyric acid fed to the second step will produce a pure butanol product - a result which is not possible with A.B.E. fermentation. In addition to its use in butanol production, butyric acid itself has many uses, particularly in the food and beverage industry (Zhu, 2003).

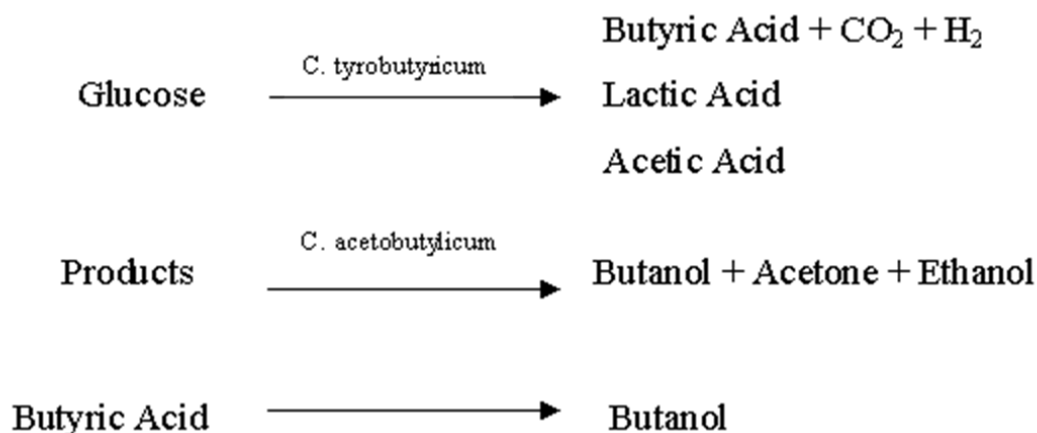


Figure 7 - Diagram of two-step butanol fermentation reactions

Researchers have tried various methods of increasing butyric acid productivity in the past. These methods include using immobilized or mutant cells (Liu & Yang, 2005), using a continuous fermentation with a cell recycle to increase the amount of bacteria present (Zhu, 2003), and using extraction methods after the fermentation (Zhu, 2003). However, continuous reaction experiments have been rare since it is difficult to prevent contamination within the reactor. Since continuous production involves a constant product stream, it has the potential to both be inexpensive and have a high production rate. For this reason, I worked on the improvement of the butyric acid yield by continuous production in the first fermentation step of the two-step butanol production process.

## II.2 Materials and Methods

### II.2.1 Equipment

This research used a continuous fermentation with a membrane filter to recycle bacteria back into the fermenter (Figure 8). An Appikon® 1L fermenter and a Romikon® Koch

Membrane with a 100,000 MW cutoff will be used. A standard PYG (peptone, yeast extract, and glucose) media will be used as feed for the fermentation and nourishment for the bacteria. The system will be operated at a pH of approximately 6.9.

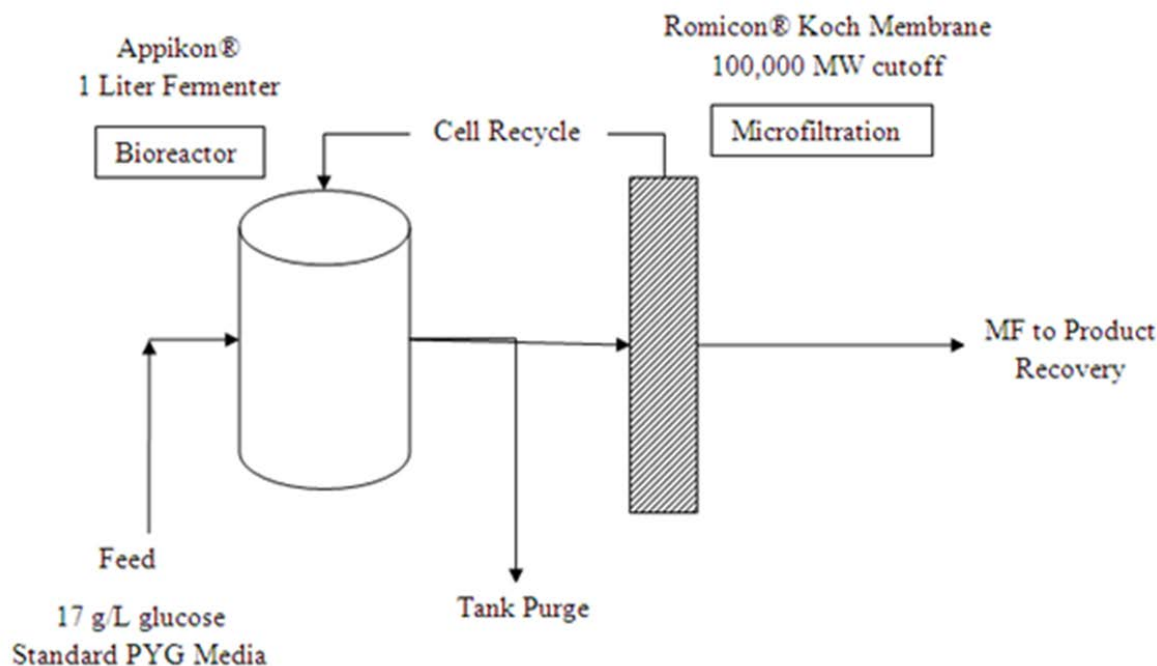


Figure 8 - Diagram of Experimental System

### *II.2.2 Data Analysis*

For the analysis of results, samples were collected at the fermenter outlet stream. These samples were prepared and analyzed in a high performance liquid chromatograph (HPLC). The chromatograph peaks of the test solutions were compared to the peaks of known standard solutions and the concentration of each organic acid in the samples were determined. The optimum conditions were those that had the highest concentration of butyric acid in the outlet stream.

### *II.2.3 Calculations*

Important measurements and calculations used in analyzing data included:

- Dilution rate (D) – This is the rate that media in the fermenter is replaced with fresh media. It is calculated by dividing the volumetric flow rate by the volume of the fermenter, and at steady state the dilution rate is equal to the specific growth rate of cells.
- $Y_{P/S}$  – This is the amount of glucose that is converted to organic acid products and is one measure of fermentation efficiency. It is calculated using the balanced chemical equations for the conversion of glucose to products. First, the amount of glucose that is required for each product is calculated using the chemical equations and summed to determine the total amount of glucose required. Next the amount of glucose used during the fermentation is calculated by subtracting the amount of glucose exiting the fermenter from the amount that was fed into the fermenter. The  $Y_{P/S}$  is then calculated by dividing the glucose required to make products by the glucose used during fermentation. Inefficiency of glucose used is due to factors such as glucose being used for cell growth.
- Productivity (P) – This is the total concentration of organic acids produced on a basis of time. It is calculated by multiplying the concentration of organic acids exiting the fermenter by the dilution rate.
- Normalized cell mass – This is a measure of the amount of *Clostridium tyrobutyricum* cells present in the fermenter. The normalized cell mass is measured by an instrument that quantifies optical turbidity in the fermenter. The optical turbidity can then be correlated to the amount of cells present in the fermenter.
- Recycle rate – This is the flow rate of the recycle stream divided by the total flow rate through the fermenter and multiplied by 100.

## II.3 Results

### II.3.1 Results of Varying Dilution Rate without Cell Recycle

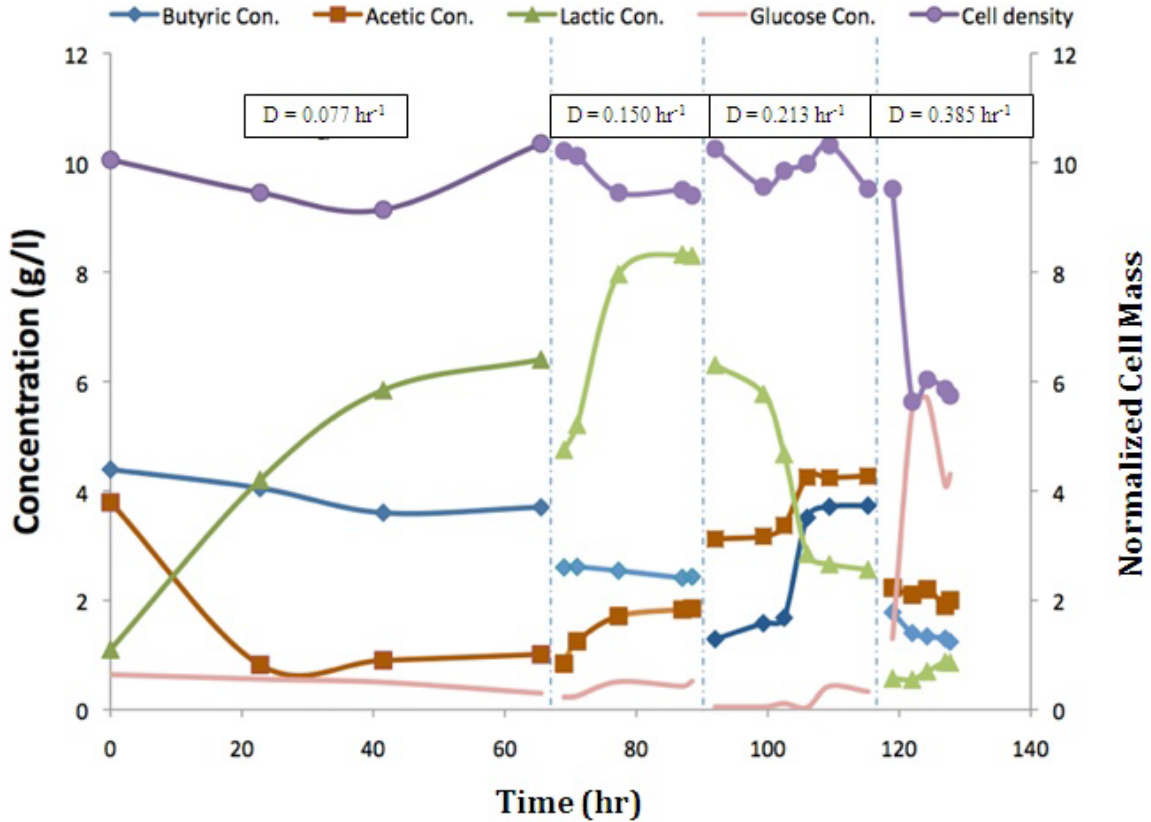


Figure 9 – Results of Varying Dilution Rate without Cell Recycle

Table 3 – Steady State Results for Varying Dilution Rate without Cell Recycle

D, hr <sup>-1</sup>	% butyric	% acetic	% lactic	P, g/L hr	Butyric, g/L hr	N. Cell Mass	Yp/s
0.077	33.3	9.1	57.6	0.85	0.28	10.3	0.91
0.150	19.3	14.7	66	1.88	0.36	9.5	0.91
0.213	35.3	40.4	24.2	2.25	0.79	9.52	0.87
0.385	30.2	48.8	21	1.58	0.48	8.52	0.42

First, the dilution rate was examined without adding a cell recycle in order to determine the optimum dilution rate for the system. Higher dilution rates allow for greater productivity, but



may affect other aspects of the fermentation such as butyric acid selectivity. Also, if the dilution rate is too high, the cell growth rate will not be fast enough and cells will start to be “washed out” of the fermenter. For this fermentation, wash out occurs at a dilution rate of  $0.385 \text{ hr}^{-1}$ . At this dilution rate,  $Y_{P/S}$  drops significantly, cell mass drops, and glucose remaining at the reactor exit increases. These are all indications that the fermentation is not running efficiently. The highest productivity occurs at a dilution rate of  $0.213 \text{ hr}^{-1}$ , which is the highest dilution rate before wash out occurs at  $0.385 \text{ hr}^{-1}$ . It was also found that butyric acid selectivity is not greatly affected by dilution rate.

### II.3.2 Results with Varying Cell Recycle

Table 4 – Steady State Results with Cell Recycle at a Dilution Rate of  $0.213 \text{ hr}^{-1}$

D, $\text{hr}^{-1}$	% cell recycle	% butyric	% acetic	% lactic	P, g/L hr	Butyric P, g/L hr	N. Cell Mass	$Y_{p/s}$
0.213	0	35.3	40.4	24.2	2.25	0.79	9.52	0.87
0.213	47	23.4	17.3	59.3	2.78	0.65	12.56	0.96
0.213	80	70.9	16.3	12.7	1.65	1.17	29.35	0.8
0.213	95	53	14.6	32.4	2.11	1.12	22.45	0.91

At a dilution rate of  $0.213 \text{ hr}^{-1}$ , it was found that butyric acid selectivity and productivity increase with recycle rate up to 80% recycle. The normalized cell mass also increases with percent recycle up to 80% recycle, indicating that the cell density may be related to butyric acid selectivity and productivity. It was found that total productivity was not greatly affected by the recycle rate.

Table 5 – Steady State Results with Cell Recycle at a Dilution Rate of 0.385 hr<sup>-1</sup>

D, hr <sup>-1</sup>	% cell				P g/L hr	Butyric P, g/L hr	N. Cell	
	recycle	% butyric	% acetic	% lactic			Mass	Yp/s
0.385	0	30.2	48.8	21	1.58	0.48	5.7	0.42
0.385	26	9.5	14.4	76.1	4.52	0.43	9.8	0.76
0.385	43	5.8	11.1	83.2	5.64	0.33	10.8	0.98

At the higher dilution rate of 0.385 hr<sup>-1</sup>, total productivity increases with recycle rate, but butyric acid selectivity decreases. This is possibly due to the fact that the recycle rate and cell density were not as high as they were at the dilution rate of 0.213 hr<sup>-1</sup>.

#### II.4 Conclusions

A continuous butyric acid fermentation using *Clostridium tyrobutyricum* was carried out for five months. The greatest dilution rate achieved without cell recycle was 0.213hr<sup>-1</sup>. The greatest butyric acid selectivity and productivity were 70.9% and 1.17 g/L hr, respectively, and occurred at D = 0.213hr<sup>-1</sup> and 80% cell recycle. The productivity and selectivity were lower than batch system results, so future work in the research group will involve increasing these in the continuous system.

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### III. Electrodeionization Separation for Improved Butanol Production

#### III.1 Literature Review

##### III.1.1 Electrodialysis and Electrodeionization

The separation process of electrodialysis (ED) is done using an electric potential difference across an ED cell (Figure 10). The feed stream enters the cell and is separated by a positively charged anion exchange membrane (AEM) and a negatively charged cation exchange membrane (CEM). The AEM will allow anions to pass through, but not cations. Likewise, the CEM will only allow cations to pass. The positioning of alternating CEMs and AEMs will trap ions in concentrate streams. An electrode rinse (ER) is needed on either side of the cell to prevent chemical build up. The exiting feed stream is then reduced in ion concentration and is called the diluate stream.

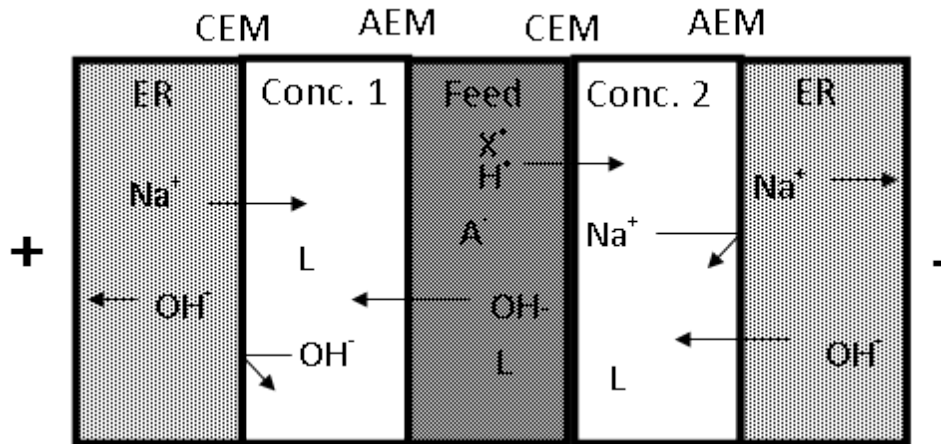


Figure 10 - Diagram of an Electrodialysis Cell

Electrodeionization (EDI) is similar to ED, but in an EDI system, electrically charged ion-exchange resin beads are placed in the feed stream chamber. These resin beads increase conductivity in the stream and facilitate ion transfer through the system (Xu & Huang, 2008). This allows separation to occur at much lower ion concentrations than would occur in a

traditional ED system (Feng, X. et. al., 2008). This is very important in this research project since the organic acid concentrations are often quite low in the EDI system. However, the addition of ion-exchange beads has caused problems in past EDI systems. Loose beads in the feed chamber can cause leaks in the system and make it difficult to take apart the system for cleaning. This is not a major problem in the desalination of water since the product is low value and severe fouling rarely occurs. However, the separation of organic acids requires a maximum product recovery and occasional cleaning of the EDI system.

The ion-exchange wafer was invented at Argonne National Laboratory and addresses many of these problems associated with loose resin beads (Datta et. al., 2002). In the ion-exchange wafer, resin beads are loosely held together and form a media through which the feed stream may flow (Datta et. al.). The types of beads have been found to have an effect on the separation of different weak acids.

Electrodeionization has many benefits over other separation techniques. It does not involve the use of harsh chemicals, which can be harmful to the environment after disposal (Fedorenko, 2004). It typically only produces streams of slightly higher ion concentrations than the feed stream. These concentrate streams can usually be disposed of without needing further treatment. EDI also provides a very pure diluate stream. It is often used at the end of a line of purification to reach the final product (Fedorenko, 2004).

### *III.1.2 Electrodeionization as Part of a Butanol Fermentation System*

The major application of electrodeionization in this project was to improve overall butanol production in the two-step butanol fermentation process described in section II.1.2. Electrodeionization can be used to separate butyric acid from acetic and lactic acid so that a more

pure stream of butyric acid can be fed to the second fermentation, resulting in a higher butanol concentration in the final product.

Adding the EDI to a continuous system could also increase the initial production of butyric acid. The first fermentation has product inhibition, particularly by butyric acid (Michel-Savin et. al., 1989). After separating butyric acid from the product stream, the remaining product stream with lactic and acetic acid could be fed back into the continuous reactor. This would theoretically lead to an increased productivity of butyric acid.

## III.2 Materials and Methods

### *III.2.1 Ion-Exchange Wafer Production*

The ion-exchange wafers used in this project were composed of cation and anion exchange beads, polyethylene, and sucrose. The materials were mixed together and pressed between two plates at a temperature of 248 °C and 10,000 psi. Two different wafers were used in these experiments. Wafer #1 contained Amberlite IRA-400 (Cl) as the anion exchange beads and Amberlite IRA-120 (plus) as the cation exchange beads. Wafer #2 contained Amberlite A-21 as the anion exchange beads and Amberlite IRC-76 as the cation exchange beads.

### *III.2.2 Experimental Design*

Experiments were run in a batch EDI system (Figure 11). Solutions with initial concentrations of 10 g/L sodium butyrate and 10 g/L sodium acetate were fed into the feed chamber of the EDI system. Samples were taken at the concentrate and diluate chambers once an hour for five hours during experiments and analyzed using an HPLC.

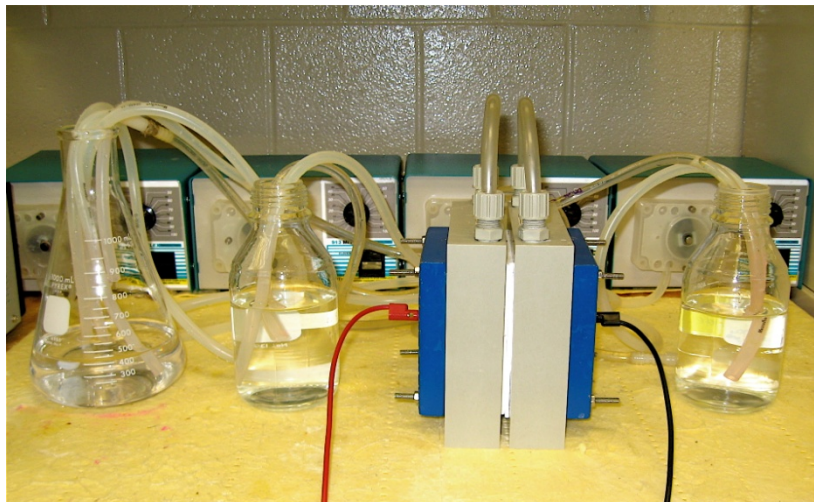


Figure 11 – Experimental EDI System

### III.3 Results

#### III.3.1 Results with Varying Current

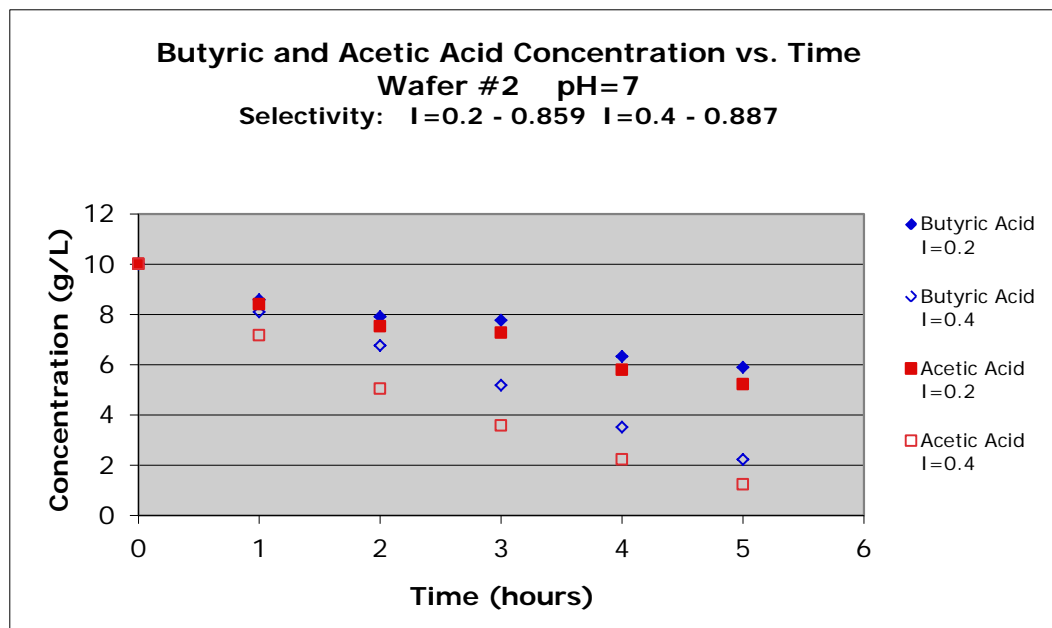


Figure 12 – Concentration vs. Time for Varying Current

It can be seen in Figure 12 that as the current increases, the concentration of both the butyric acid and the acetic acid in the diluate decrease. This is due to the fact that the current is a driving force in the EDI separation process. However, the selectivity for butyric acid vs. acetic acid is not greatly affected by the current.

### III.3.2 Results with Varying pH

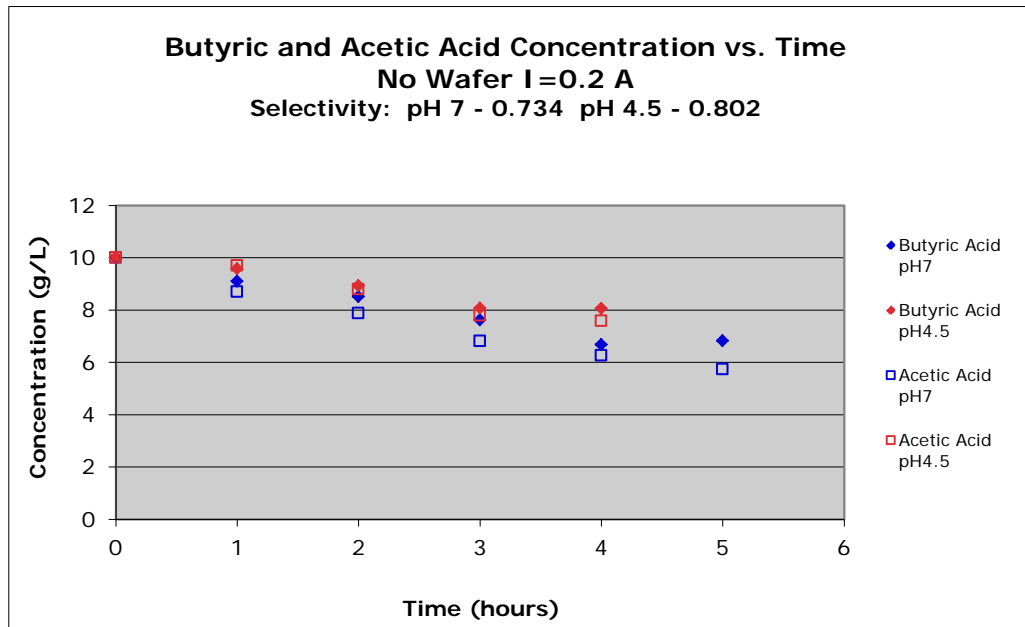


Figure 13 – Concentration vs. Time for Varying pH

Figure 13 shows that the selectivity and the final concentration were not greatly affected by changing the pH in the system. However, the final concentration of both organic acids were found to be slightly lower at a pH of 7 than at a pH of 4.5. This is possible due to the fact that both butyric and acetic acid are weak acids and will therefore be more dissociated at a pH of 7 than at a pH of 4.5. More free ions will allow for a greater degree of removal.



### III.3.3 Results with Varying Ion-Exchange Beads

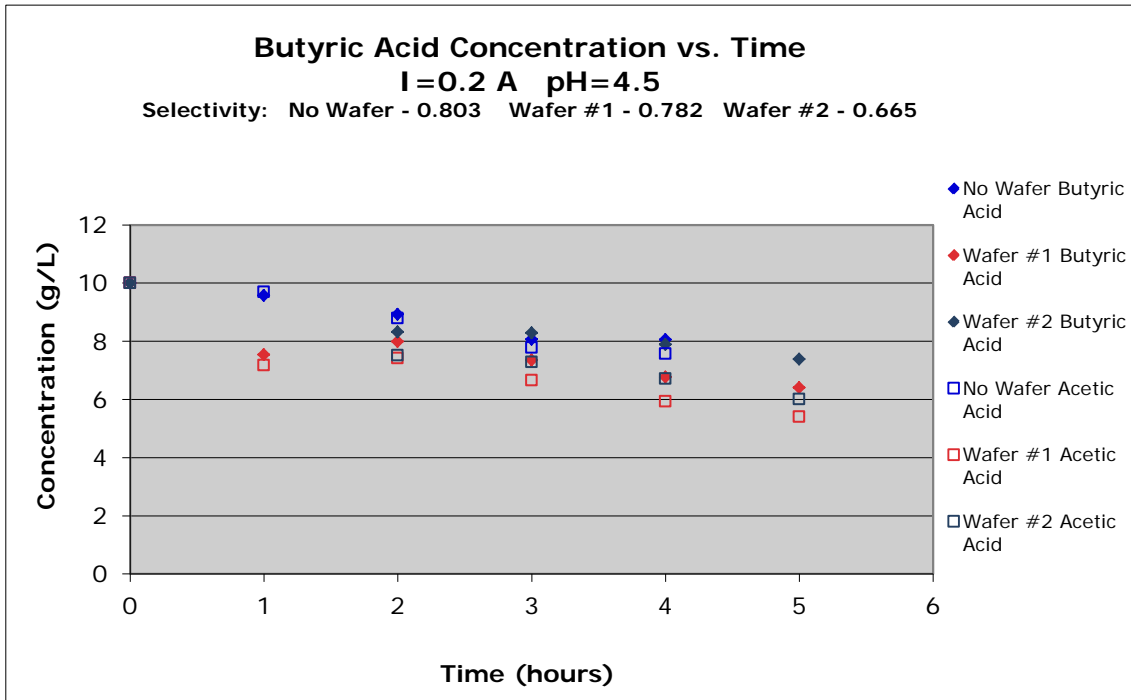


Figure 14 – Concentration vs. Time for Varying Ion-Exchange Beads

Figure 14 shows that the presence of an ion-exchange wafer and the type of ion exchange beads used does not have a great effect on the final organic acid concentration, but does have an effect on the selectivity of the separation. However, more experiments are needed to determine the exact relationship between the types of ion-exchange beads used and the selectivity of the separation.

### III.4 Conclusion

A batch EDI system containing butyric and acetic acid was used to simulate the fermentation broth exiting the first step of a two-step butanol fermentation process. It was found that higher currents and higher pH resulted in a lower final overall organic acid concentration, while the types of ion exchange beads affected the selectivity of the separation.

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