COMPARISON OF METHODS FOR THE PURIFICATION OF BIODIESEL

A THESIS
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ABSTRACT

Biodiesel is a proven alternative to petroleum diesel fuel. Once produced, biodiesel contains several impurities such as soap and glycerin. The free fatty acids in the oil react with the sodium or potassium catalyst to form soaps. After the biodiesel and by product glycerin are separated, trace amounts of glycerin remain in the biodiesel. Soap and glycerin impurities in the biodiesel can lead to engine wear and fuel storage problems.

Traditionally, soap and glycerin are removed from the biodiesel by water washing. Water washing has several disadvantages such as producing large amounts of waste water that requires treatment and causing plant operational problems such as emulsion. Recently, several alternative “waterless” purification procedures have been used, such as ion exchange resins and Magnesol, a brand-named adsorbent.

The objective of this study was to compare these two “waterless” purification methods by their mode of operation, effectiveness, life, and its ease of use. Experiments were developed in order to compare each purification method. Ion exchange resins were tested in packed bed columns and Magnesol was tested by mixing and filtering.

During this research it was found that soap and glycerin can be removed by a combination of four modes. These modes are filtration, physical adsorption, ion exchange and soap removal by glycerin affinity. It was found that the four mode theory was supported by the experimental data.
It was also found that ion exchange resins can reduce soap levels from 1200 ppm to below 50 ppm for about 550 BV of processed biodiesel. Ion exchange resin resins can reduce glycerin levels from 0.08% to below 0.02% for about 200 BV of processed biodiesel. Magnesol can reduce soap levels from 1000 ppm to below 50 ppm and glycerin levels from 0.08% to below 0.02% at a Magnesol concentration of 1%.
I thank my major professor, Dr. Jon Van Gerpen for the opportunity to investigate a practical problem in the biodiesel production process. I would like to thank my committee members Dr. Brian He and Dr. W. Daniel Edwards for their guidance and support. I would like to thank Dr. Joseph C. Thompson for his ideas and support. I also want to mention his help with the development of equipment and procedure to make this project possible. I would like to thank my lab assistants Sweta Khanal and Sohana Khanal for their help preparing for and conducting the experiments. I would like to thank Jim Sabzali and Vivek Naik from the Thermax Company for their visits and technical and financial support.

I, especially, want to thank my wife Christina Wall for her patience and support.
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ABBREVIATIONS

The following abbreviations were used throughout this thesis:

FFA: Free fatty acid
GC: Gas Chromatography
PPM: Parts per million
BV: Bed volume
CHAPTER 1. INTRODUCTION

Biodiesel is a well known and proven alternative to petroleum diesel fuel. It can be used in most diesel engines with few modifications. Biodiesel has been shown to reduce engine exhaust emissions leading to less pollution of the environment. (McCormick et al., 1998)

Biodiesel is typically produced using a transesterification reaction. Plant oils or animal fats are mixed with alcohol and a base catalyst, such as sodium hydroxide, and heated until a separation occurs between the biodiesel and the glycerin. The majority of the glycerin is then removed from the solution, by phase separation.

After the transesterification reaction has been completed and the glycerin has been separated and removed, the raw biodiesel still contains a small percentage of free glycerin and soap. Soap is the product of saponification reactions that occur in parallel to transesterification. Figure 1.1 depicts the saponification reaction.

![Saponification reaction](image)

Figure 1.1: Saponification reaction (Bruice, 2004)

Soap is generally formed because of free fatty acids reacting with the catalyst. If the oil contains free fatty acids, these will be converted to soap by the
saponification reaction. The water contained in the reactants of transesterification causes an increase in free fatty acids by hydrolysis of the oil and therefore more soap will be created. (Ma et al., 1999)

Traditionally, the soap and trace amounts of glycerin are removed by washing with water. This involves mixing water with the biodiesel, agitating them gently, and then allowing them to separate. The soap and glycerin are extracted into the water phase and removed when the water is separated from the solution.

The use of water to wash the biodiesel feedstock causes many problems.

- Water washing produces a large amount of waste water that must be treated.
- Water washing introduces water to the fuel that can cause it to degrade.
- After water washing, the fuel must be dried. This causes an increased energy cost.
- Water washing with a high soap level biodiesel can lead to emulsions that can cause significant yield loss and other plant operational problems.
- Water washing can require a great deal of time for drying, multiple washes and water-biodiesel separation.

Prior to use, wash water must be deionized to remove metal ions, such as calcium and magnesium that could be transferred to the fuel causing the fuel to be out of specification for those compounds. (Bryan, 2008)

As an alternative to water washing, several methods are available to remove soap and glycerin from biodiesel. These impurities can be removed by passing the fuel through a bed of ion exchange resin. Other methods for removing impurities
involve the use of adsorbent compounds such as magnesium silicate (Berrios et al., 2008; Kucek et al., 2007).

The object of this research is to compare ion exchange resins to adsorbents for the purification of biodiesel. Each method will be compared by its mode of operation, effectiveness, life, and ease of use. The operating parameters and recommendations for use will also be presented.
CHAPTER 2. Literature Review

Various purification methods have been proposed in the literature to purify biodiesel. Researchers have used water washing, filtration with a membrane, adsorbents and ion exchange resins to remove impurities such as soap and glycerin (Berrios et al., 2008; Predojevic et al., 2008; He et al., 2006; Wang et al., 2009; Kucek et al., 2007; Yoris et al., 2008). Silica gel, magnesium silicate and ion exchange resin are the common materials used in these studies. This chapter discusses the results of these studies in purifying biodiesel.

Crude biodiesel contains impurities that can cause problems in its use and storage. The impurities contained in crude biodiesel include free fatty acids, water, methanol, glycerides, free glycerin, and metal compounds such as soap and catalyst. Table 2.1 shows how the impurities affect the biodiesel and engines.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Fatty Acid (FFA)</td>
<td>Corrosion, low oxidative stability</td>
</tr>
<tr>
<td>Water</td>
<td>Formation of FFA, corrosion, bacterial growth (filter blockage)</td>
</tr>
<tr>
<td>Methanol</td>
<td>Low density and viscosity, low flash point, corrosion</td>
</tr>
<tr>
<td>Glycerides</td>
<td>High viscosity, injector deposits, crystallization</td>
</tr>
<tr>
<td>Metals (soap, catalyst)</td>
<td>Injector deposits, high sulfated ash (filter blockage), abrasive engine deposits</td>
</tr>
<tr>
<td>Free Glycerin</td>
<td>Settling problems, Increases in aldehydes and acrolein exhaust emissions</td>
</tr>
</tbody>
</table>
2.1 Water Wash

Washing the crude biodiesel with water is the traditional way to remove impurities. There are several variations to water washing, including washing with deionised water, washing with acidified water, and using a membrane to prevent emulsions with water washing. Studies by Van Gerpen et al. (2003, 2005) have shown that adding acid to the wash water aids in removing soaps. Also, multiple washes are required to achieve satisfactory soap removal. Some cases required as many as six individual washes (Van Gerpen et al., 2003).

Berrios et al. (2008) tested water washing with deionised water and acidified water and found that acidified water performed better in removing soaps. However, glycerin removal required longer wash times with acidified water compared to deionised water. Their results showed that increased wash water temperatures improved soap removal but glycerin removal was not significantly improved by temperatures elevated above ambient.

Predojevic et al. (2008) compared water washing with hot distilled water to a 5% phosphoric acid solution. In this study, the effect of wash method on the biodiesel density, kinematic viscosity, acid value, iodine number, water content, saponification number, cetane index and yield loss were evaluated. It was found that there was no significant change in density, kinematic viscosity, iodine number, water content, saponification number, cetane index between a distilled water wash and a phosphoric acid wash. It was found that the phosphoric acid wash decreased the acid value to a greater degree, and the phosphoric acid wash produced higher yields than the distilled water wash.
He et al. (2006) conducted experiments using several methods of water washing. These wash methods included distilled water, HCl acid wash, solvent extraction, and hollow fiber membrane extraction. This study compared yield loss for each method but did not give information about impurity removal.

The distilled water wash involved adding a 1:1 volume ratio of water to biodiesel. The solution was agitated in a water bath oscillator for 20 min, allowed to phase separate, and then the water was removed. This process was repeated three times. The solution was then dried over sodium sulfate. It was found that the highest biodiesel yield was achieved at a water temperature of 50°C and an agitation rate of 125 rpm.

The HCl wash was performed by adding a 1:1 volume ratio of HCl (pH =1) to biodiesel and agitated and separated similar to the distilled water wash. The biodiesel was then washed with distilled water two additional times and then the solution was dried over sodium sulfate. It was found that the addition of acid led to reduced biodiesel yield loss compared to a distilled water wash at the same temperature. The acid value increased due to the addition of acid.

The solvent extraction was performed by adding petroleum ether to biodiesel at a 1:1 volume ratio. The solution was then water washed three times. Then, the solvent was removed and the solution was dried over sodium sulfate. Addition of solvent led to a yield loss due to emulsion formation at the biodiesel/water interface. Evaporation of the solvent also lead to yield loss.

The hollow fiber membrane extraction involved using a 1 m long by 1 mm diameter hollow fiber membrane. Two membranes were tested, a hydrophilic
polysulfone membrane and a hydrophobic polyacrylonitrile membrane. Each membrane was placed in a beaker filled with distilled water and biodiesel was pumped through it. The purified biodiesel was then dried over sodium sulfate.

It was found that when using membrane separation, the mass transfer occurred without phase mixing with each other. The hydrophilic polysulfone membrane provided the lowest yield lost of the study, 8.1% weight, whereas washing with 20°C distilled water provided the highest yield loss of 15.2% weight. (He et al., 2006)

2.2 Filtration

Wang et al. (2009) found that soaps and glycerin could be removed by filtration using a membrane. This study involved passing raw biodiesel through a ceramic membrane after methanol removal. To test the effectiveness of the ceramic membrane, filtration pore sizes of 0.1 µm, 0.2 µm, and 0.6 µm were evaluated. The membrane was configured in a tube shape with an outside diameter of 26 mm and a length of 250 mm. The inside of the tube contained 19 three mm channels giving a total filtration area of 0.045 m².

Figure 2.1 shows the setup for filtration using the ceramic membrane tubes. To begin the test, methanol at 30 °C was passed through the membrane to provide initial cleaning. Biodiesel was then passed through the membrane at 60 °C. After 3 minutes, a sample was collected and analyzed for potassium, sodium, calcium, magnesium, and free glycerin. These results were compared for each membrane pore size used. The effects of temperature and transmembrane pressure were also tested at the 0.1 µm pore size.
Table 2.2 shows the results comparing the three pore sizes and water washing for the crude biodiesel. From this table it can be seen that as the pore size decreases the effectiveness of removal of potassium and free glycerin were enhanced significantly. The potassium was in the form of soap and catalyst.

Table 2.2: Results of purification with a ceramic membrane. (Wang et al., 2009)

<table>
<thead>
<tr>
<th></th>
<th>Metals Content (mg/kg)</th>
<th>Free Glycerin (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Potassium</td>
<td>Sodium</td>
</tr>
<tr>
<td>Crude Biodiesel</td>
<td>160</td>
<td>8.98</td>
</tr>
<tr>
<td>Pore: 0.6 µm</td>
<td>4.25</td>
<td>0.68</td>
</tr>
<tr>
<td>Pore: 0.2 µm</td>
<td>2.2</td>
<td>0.88</td>
</tr>
<tr>
<td>Pore: 0.1 µm</td>
<td>1.7</td>
<td>1.36</td>
</tr>
<tr>
<td>Water Wash</td>
<td>2.46</td>
<td>1.41</td>
</tr>
</tbody>
</table>

2.3 Adsorbents

Solid adsorbents have shown success in the removal of impurities from biodiesel. Magnesium silicate and silica gel were the materials used. Kucek et al.
(2007) conducted a study on analyzing the use of the commercial magnesium silicate product, Magnesol. In this study biodiesel was produced in a two stage reaction. The first stage involved producing biodiesel with ethanol and KOH or NaOH. After the first stage, the solution was allowed to separate and the glycerin was drained off and the ethanol was removed. Next, 2% by weight of Magnesol was added to the biodiesel and stirred continuously for 20 min at 65°C. After the Magnesol was filtered from the biodiesel, a second reaction was performed and the biodiesel was water-washed.

Using this procedure it was found that the use of Magnesol provided a significant reduction in monoglycerides and bound glycerin compared to a two stage reaction with a water wash between the stages. Use of Magnesol provided no significant yield loss. All other biodiesel impurities were below the Brazilian biodiesel standard. Table 2.3 shows the reduction in monoglyceride and bond glycerin obtained from this study.

Table 2.3: Monoglyceride (MAG), bonded glycerin content from a two step reaction. (Kucek et al., 2007)

<table>
<thead>
<tr>
<th></th>
<th>MAG (wt%)</th>
<th>Bonded Glycerin (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>1.65</td>
<td>0.42</td>
</tr>
<tr>
<td>KOH</td>
<td>1.89</td>
<td>0.48</td>
</tr>
<tr>
<td>NaOH-Magnes</td>
<td>0.97</td>
<td>0.25</td>
</tr>
<tr>
<td>KOH-Magnes</td>
<td>1.19</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Berrios et al. (2008) evaluated the use of Magnesol for the purification of biodiesel. Biodiesel fuels from two different sources were compared. The Magnesol was mixed with the biodiesel fuels for 30 min and removed by filtration. The biodiesel fuels were sampled after 10, 20 and 30 min of agitation to determine
the effect of residence time on purification effectiveness. It was found that soap and glycerin were removed satisfactorily by the 10 min case. Four experiments were conducted using 0.25, 0.5, 0.75 and 1 % by weight of Magnesol in the biodiesel. Each of the samples was evaluated for methanol content, free glycerol, soap, acid value and oxidative stability. Table 2.4 shows the averaged performance of Magnesol purification on the properties of raw biodiesel. It can be seen that the free glycerin, soap, and methanol content are reduced significantly.

Table 2.4: Effect of Magnesol purification on biodiesel properties (Berrios et al., 2008)

<table>
<thead>
<tr>
<th></th>
<th>Raw Fuel</th>
<th>Magnesol Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Biodiesel 1</td>
<td>Biodiesel 2</td>
</tr>
<tr>
<td>Methyl Ester Content (%(m/m))</td>
<td>95.3</td>
<td>90.1</td>
</tr>
<tr>
<td>Free Glycerol (%(m/m))</td>
<td>0.11</td>
<td>0.1</td>
</tr>
<tr>
<td>Monoglyceride ((%(m/m))</td>
<td>0.46</td>
<td>0.73</td>
</tr>
<tr>
<td>Diglyceride ((%(m/m))</td>
<td>0.21</td>
<td>1.21</td>
</tr>
<tr>
<td>Triglyceride ((%(m/m))</td>
<td>0.43</td>
<td>5.69</td>
</tr>
<tr>
<td>Methanol ((%(m/m))</td>
<td>1.4</td>
<td>1.32</td>
</tr>
<tr>
<td>Soap (ppm)</td>
<td>909</td>
<td>1240</td>
</tr>
<tr>
<td>Water (mg/kg)</td>
<td>1050</td>
<td>1050</td>
</tr>
<tr>
<td>Oxidative Stability (h)</td>
<td>1.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Acid Value (mg KOH/g sample)</td>
<td>0.18</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Predojevic et al. (2008) evaluated the use of silica gel in a column with bed dimensions of 2 cm by 2 cm. To dry the biodiesel, a 1 cm layer of sodium sulfate was placed above the silica gel. This study analyzed the biodiesel density, kinematic viscosity, acid value, iodine number, water content, saponification number, and cetane index and yield loss. It was found that there was no significant change in density, kinematic viscosity, iodine number, water content, saponification number or cetane index due to purification by silica gel. This study compared the results from purification with silica gel to that of water washing. It was found that silica gel produced yields of about 94% compared to 90% from water washing with
distilled water. Silica gel reduced the acid value by greater than 90% compared to a 75% reduction by distilled water washing.

Two studies were conducted by Yoris et al. (2007, 2008) to evaluate the effectiveness of silica gel for the removal of glycerin from biodiesel. In the first study, a test solution was prepared by adding glycerin to clean biodiesel with no methanol. A column of 0.25 inch inside diameter and 30 cm in length was loaded with silica gel. Biodiesel containing glycerin levels of 0.1 - 0.2% was passed through the bed at a space velocity of 3-11 cm$^3$/min. Tests were conducted to regenerate the bed by washing with methanol.

For this test, a breakthrough curve was generated. From this curve it was found that the maximum adsorption capacity was 0.139 grams glycerin per grams silica gel. The breakthrough time, which is the time needed to reach the ASTM standard for glycerin, was found to exceed 1 hour at a space velocity of 14 cm$^3$/min. It was also found that the glycerin adsorption capacity could be restored by flushing the bed with 4 bed volumes of methanol.

In the second study, test solutions were created by adding glycerin to clean biodiesel and also solutions prepared containing water, methanol, monoglycerides and soaps in addition to glycerin. Sodium stearate and Glycerol monostearate were used to simulate soap and monoglycerides. After the test solution was prepared, 3 grams of silica gel were added to the solution. Stirring was performed at 25°C for 2 hours. The silica gel was then allowed to settle and the liquid phase was sampled for analysis.
The samples were analyzed to determine the effect of soaps, water, methanol and monoglycerides on the adsorption of glycerin. It was found that soaps and water did not affect the adsorption of glycerin. Methanol and monoglycerides were shown to reduce the adsorption capacity of the silica gel for glycerin.

2.4 Ion Exchange

Berrios et al. (2008) tested the use of ion exchange resins on the purification of biodiesel. The ion exchange resins were tested their ability effect methanol, glycerin, soap, acid value and oxidative stability parameters of the biodiesel. Two raw biodiesel fuels were used for testing, as was shown in Table 2.4. Berrios et al. (2008) evaluated ion exchange resins from Purolite and Rohm and Haas to determine their effectiveness.

Two ion exchange columns were tested in parallel. The 3 cm diameter resin columns were loaded with 80 grams of dry resin and flow rates of 0.25 L/h or 2.5 bed volumes per hour were used.

From this test it was found that ion exchange resin has little effect on methanol concentration after the bed has reached equilibrium. Purification with the ion exchange resin caused the acid value of the purified biodiesel to increase slightly. Oxidative stability did not seem to be affected. Soap and glycerin were reduced significantly. The two resins were found to perform similarly and the purification capacity was found to be 500 L biodiesel/kg resin for the biodiesel #1 and 720 L biodiesel/kg resin for the biodiesel #2. In table 2.4, it can be seen that biodiesel fuels #1 and #2 had about the same glycerin content but biodiesel fuel #2
had about 300 ppm more soap. This difference in initial soap level is the reason why the resin had longer life processing biodiesel fuel #1.
CHAPTER 3. Theory

The production of biodiesel produces byproducts that can have a negative impact on the biodiesel's end use; these byproducts are mainly soap and free glycerin. This chapter discusses theory behind the removal of these impurities.

3.1 Four Mode Theory

In the course of the research conducted for this project, the authors proposed that the removal of trace amounts of soap and free glycerin from biodiesel involves four different operating modes. The various media and methods of purification take advantage of at least one of these modes. The four modes of purification are:

1. Filtration: Filtration is the removal of impurities that are insoluble in biodiesel by a mechanical action. This mechanical action can take the form of surface filtration or depth filtration. In most cases, both types of filtration are involved. Filtration can be used to remove both insoluble soap and glycerin. Filtration is most effective when biodiesel methanol levels are low.

2. Adsorption: Adsorption is the removal of soluble impurities by a chemical action. The pores on the adsorbent are charged and attract the impurities. The impurities become chemically bonded to the charged surface of the adsorbent. Adsorption can be used to remove both soluble soap and glycerin. The soap and glycerin adsorption capacity of ion exchange resins can be regenerated using a methanol wash.

3. Ion Exchange: Ion exchange is the removal of impurities by exchanging an ion from the ion exchange material, for the metal portion of the impurity
contained in the raw solution. Ion exchange is the chemical breakdown of
the impurity. Ion exchange can be used to remove soap from biodiesel by
exchanging the hydrogen ions from the ion exchange material for the sodium
or potassium ion on the soap molecule. After the exchange takes place, the
free fatty acid portion of the soap molecule is allowed to pass through the
resin bed.

4. Glycerin/Soap Interaction: Soap has a stronger affinity for the
glycerin portion of the biodiesel, therefore glycerin can aid in the removal of
soap. As glycerin becomes adsorbed on the surface of the purification
media, soap is entrapped in the glycerin layer and removed from the
biodiesel stream.

These four modes of biodiesel purification encompass the mechanisms and
interactions that allow impurities to be removed from biodiesel. In the technical
literature there is no consensus about the mechanisms that are active in biodiesel
purification. This theory clarifies the way impurities are removed from biodiesel.

3.2 Purification Processes

Purification of biodiesel involves a series of separation processes that may
occur in combination. These separation processes include filtration, physical
adsorption, and ion exchange adsorption.

Filtration is a mechanical process where insoluble particles are removed from
a fluid-particle suspension. The filtration media is placed in a column and the fluid-
particle suspension is passed through the column and the particles become
attached to the external surface of the filtration media, removing them from
the fluid. In the crude biodiesel solution, insoluble soap and glycerin particles can be filtered.

There are two main types of filtration, surface filtration and depth filtration. Surface filtration occurs on the surface of the filtration media layer. Depth filtration occurs when multiple layers of filtration media are available and provides a greater surface area for particle removal.

Physical adsorption is a process where molecules in the fluid bond onto the internal surface of the adsorbent media and are removed. Adsorption differs from absorption in that adsorption is the accumulation of solute molecules on the surface of the adsorbent media. Absorption is the accumulation of solute molecules in the bulk volume of the absorbent media.

Adsorption uses interactions similar to van der Waal bonds, to attract and bind solute molecules to the surface of the adsorbent. Van der Waal bonds are formed by a series of repulsive and attractive forces that reach a point of equilibrium when adsorption occurs. Adsorption bonding occurs when there is a concentration gradient between the fluid and the adsorbent. This bonding is weak and can be reversed by washing the adsorbent with a clean solvent (Cooney, 1998).

Figure 3.1 depicts the mechanics of physical adsorption. In this figure it can be seen that an adsorbent particle is surrounded by a fluid film layer. The solute molecules must first diffuse into the fluid film layer and then transfer onto the adsorbent particle surface. The diffusion from the fluid is driven by a difference in concentration. If the fluid has a relatively high concentration of solute, diffusion will occur toward the particle and adsorption will occur. If the concentration of solute is
high on the particle, then desorption will occur. Desorption is the process used to regenerate adsorbent materials.

![Physical adsorption mechanics](image)

**Figure 3.1: Physical adsorption mechanics (Cooney, 1998)**

Ion exchanging is a special type of separation process where ions are adsorbed from the fluid surrounding the ion exchange material. This adsorption releases ions of the same charge from the ion exchange material into the fluid. Figure 3.2 depicts the mechanics of an ion exchange resin.

In figure 3.2 it can be seen that the basic adsorption mechanics for ion exchange are similar to the physical adsorption depicted in figure 3.1. A diffusion film layer surrounds the ion exchange particle which is suspended in a homogeneous fluid. In the ion exchange adsorption, sodium ions diffuse from the fluid flow into the film layer and then onto the ion exchange particle. The sodium
ions are exchanged with the hydrogen ions from the ion exchange particle. The hydrogen ion diffuses into the film layer and then into the fluid flow. (Arden 1968)

![Image](https://example.com/image.png)

**Figure 3.2 Ion exchange mechanics (Arden, 1968)**

There are four categories of ion exchange resins: Strong and weak acid cation exchange resins and strong and weak base anion exchange resins. Strong acid cation exchange resins are the type used to purify biodiesel.

Strong acid cation exchange resins are manufactured by the sulphonation of styrene-divinyl benzene copolymers. The process is performed by agitating a suspension of styrene, divinyl benzene and a stabilizer such as polyvinyl alcohol. The rate of agitation determines the size of the resin beads that polymerize. The resin beads are then sulphonated using sulfuric acid. Figure 3.3 shows the process of strong acid cation exchange resin manufacture (Osborn, 1956).
Ion exchange resins have several important properties that affect their performance. Ion exchange resins swell or shrink with adsorption or desorption of solvents. The internal cross-linking of the resin’s structure controls the extent of swelling. Cross-linking improves the resin’s mechanical properties but reduces its ion exchanging rate and capacity (Inczedy, 1966). Figure 3.4 shows the structure of a strong acid cation exchange resin.

Manufacturers primarily make two types of ion exchange resins for purification of biodiesel, “gel” and macroporous resins. Gel resins are the most common and are made by Purolite, Dow, Thermax, and Rohm and Haas. Gel resins have low cross-linking and have a translucent appearance. Macroporous resins have higher cross-linking and are opaque in appearance. Thermax currently is marketing a macroporous resin specifically for purification of biodiesel.
Figure 3.4: Structure of a strong acid cation exchange resin. -----, Polystyrene chain; ------, divinyl-benzene cross-link. (Albright and Yarnell, 1987)
Chapter 4. Experimental Methods and Equipment

Two main approaches were used to compare media for the purification of biodiesel. The first involves passing raw biodiesel through a packed bed of purification media. The second involves mixing a purification media with the biodiesel for a period of time and then pumping it through a filter to separate the material from the biodiesel. Ion exchange resins were tested using the packed bed method. Adsorbents were tested by the mix and filter method.

4.1 Packed Bed Purification

The equipment used to evaluate the packed bed method consisted of glass columns ranging from 1 to 3 inches in diameter. In the bottom of the column was an 80 mesh screen that contained the purification media but allowed biodiesel to pass through. At the top of the column was an inlet and overflow outlet. The fuel level was maintained by a float switch controller and a peristaltic pump to provide a constant head over the bed. Flow rate was controlled by a needle valve and measured by a rotameter. The cleaned biodiesel was then collected in a separation funnel. A Sigma 900 Max automatic water sampler was used to pump the cleaned biodiesel from the separation funnel into sample bottles at a set time interval. Figure 4.1 shows the equipment used in the packed bed purification experimentation.
4.2 Adsorbent Purification

Adsorbents, such as magnesium silicate, were tested by first removing the methanol from the crude biodiesel. Two percent by weight of adsorbent was mixed into the crude biodiesel. The biodiesel adsorbent mixture was then agitated for 10 min at a temperature of 60°C and then poured into a Büchner funnel containing a #4 Whatman filter. Vacuum was applied to suction the biodiesel through the filter. The equipment used for this process is depicted in figure 4.2.

4.3 Feedstock Preparation

The biodiesel used in this experiment was prepared from crude mustard seed oil and canola oil crushed at the University of Idaho pilot plant. Biodiesel was prepared in a large batch using sodium hydroxide and methanol. The biodiesel was then water washed to remove impurities. This was used as the test fuel.
For each test, the clean biodiesel was treated with glycerin, sodium methoxide and methanol to produce the desired level of soap and glycerin. The test fuel was prepared in 5 and 10 gallon batches and was typically used within 1 to 2 days. Appendix B shows the soap and glycerin addition calculation.

![Figure 4.2 Adsorbent purification equipment](image)

**Figure 4.2 Adsorbent purification equipment**

### 4.4 Purification Media

The adsorbent media used in this study was Magnesol from the Dallas Group. The ion exchange resins used in this study were T45BD and T45BDMP from the Thermax Company and BD10Dry from Rohm and Haas. Table 4.1 shows the product data from several ion exchange resin manufacturers.
Table 4.1 Comparison of ion exchange resin product data.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Type</th>
<th>Matrix Structure</th>
<th>Functional Groups</th>
<th>Ionic Form</th>
<th>Particle size</th>
<th>Density (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermax</td>
<td>Gel</td>
<td>Polystyrene</td>
<td>Sulfonic acid</td>
<td>Hydrogen</td>
<td>0.4-1.2 mm</td>
<td>80 g/ml</td>
</tr>
<tr>
<td>Thermax</td>
<td>Macroporous</td>
<td>Polystyrene</td>
<td>Sulfonic acid</td>
<td>Hydrogen</td>
<td>0.4-1.2 mm</td>
<td>40 g/ml</td>
</tr>
<tr>
<td>Purolite</td>
<td>Gel</td>
<td>Polystyrene</td>
<td>Sulfonic acid</td>
<td>Hydrogen</td>
<td>Not available</td>
<td>80 g/ml</td>
</tr>
<tr>
<td>Dowex</td>
<td>Gel</td>
<td>Polystyrene</td>
<td>Sulfonic acid</td>
<td>Hydrogen</td>
<td>0.3-1.2 mm</td>
<td>80 g/ml</td>
</tr>
<tr>
<td>Rohm &amp; Haas</td>
<td>Gel</td>
<td>Polystyrene</td>
<td>Sulfonic acid</td>
<td>Hydrogen</td>
<td>Not available</td>
<td>80 g/ml</td>
</tr>
</tbody>
</table>

4.5 Measurement Techniques

In order to determine the effectiveness of purification, measurements were performed on the soap level, free fatty acid value, and free glycerin percentage before and after the processing. Soap level was determined using AOCS method Cc 17-79. One hundred ml of acetone containing 2% deionised water was used as a solvent for each sample. To provide a blank, each batch of acetone solvent and bromophenol blue indicator was titrated with NaOH or HCl to the point of a slight color change to faint yellow prior to adding the biodiesel. Then, after adding a measured quantity of fuel, the mixture was titrated with 0.001 N HCl to the blue-to-yellow endpoint of the bromophenol blue. Soap level was calculated using the following equation:

\[
Soap \ (\text{ppm} \ as \ sodium \ oleate) = \frac{HCL \ (ml) \times Normality \ (HCL) \times 304,400}{Sample \ Mass \ (g)}
\]

Later in the test program, an automated method was developed to determine the soap level using a Metrohm 848 Titrino Plus Autotitrator (Herisau, Switzerland). The autotitrator uses an electrode to measure the pH of the solution, and then it adds small increments of 0.01 or 0.001 normality HCl. As the solution
becomes neutralized, a titration curve is generated. The titrator then analyzes the second derivative of the titration curve to determine the equivalence point, which is the point where all the soap is neutralized. The point on the titration curve that has the largest second derivative is considered to be the equivalence point.

Acid value was measured using the ASTM D974 method. A mixture of 50% toluene, 0.5% water and 49.5% isopropyl alcohol was used as a solvent for each sample. Phenolphthalein was added to a sample of solvent and biodiesel and then titration was performed with 0.1 KOH in iso-propanol to the clear-pink endpoint of the phenolphthalein. An automated method was developed to determine the acid value using the Metrohm autotitrator. Acid value was calculated using the following formula:

$$\text{Total Acid Number (mg KOH/g)} = \frac{\text{KOH (ml)} \times \text{Normality (KOH)} \times 56.1}{\text{Sample Mass (g)}}$$

Free glycerin was measured using gas chromatography with an Agilent 6890N gas chromatograph, according to the ASTM D6584 GC method. 0.1 gram of biodiesel was mixed with 100 µL each of Butanetriol, Glycerol-tridecanoate, and N-Methyl-N-trifluoroacetamide (MSTFA) and the solution was allowed to set for 20 min. 8 mL of heptane was then added as a solvent to the solution. 1 µL of this solution was then injected to perform the GC analysis.
4.6 Experimental Procedures

In order to evaluate the effectiveness of packed bed media such as ion exchange resins, several tests were developed. Resin life tests were developed to determine how the resin performs as it becomes exhausted. Dry resin was weighed and poured into the column. Clean biodiesel or methanol was pumped into the outlet of the column to classify the resin bed. Classification of the resin bed caused the resin to be distributed with larger resin beads on the bottom and smaller beads on the top. Air pockets are also removed by classification.

After classification was completed, the biodiesel was drained until it was level with the top of the resin bed. Raw biodiesel was then pumped into the column. 1000 ml samples were taken at 1 to 2.5 hour intervals for flow rates of 2 to 4 bed
volumes per hour. Samples were analyzed to determine the effectiveness of purification at intervals of 5 to 10 liters. To determine the effectiveness of purification, the soap level, acid value and free glycerin level were measured before and after passing through the bed.

When free glycerin levels leaving the resin bed exceeded the ASTM specification level of 0.02%, the resin bed was washed with clean methanol to regenerate the resin bed. Methanol washing involved passing 5 to 10 bed volumes of methanol through the resin bed to remove the glycerin bonded to the resin. This washing was performed at flow rates ranging from 2 to 4 bed volumes per hour.

Soap levels were monitored to determine when 50 ppm soap in the product was reached. Soap levels above 50 ppm cause the biodiesel ASTM specification for sulfated ash (0.02% weight) to be exceeded. The column was run until soap levels were well above the specification levels. Acid values were also measured to determine the amount of soap removal due to ion exchange in the resin.

The effect of flow rate and bed height was measured by varying the bed height from 1 to 3 inches in several columns. For each column, the flow rate was varied from 1 to 7.5 bed volumes per hour. Samples were taken at each flow rate and soap levels were determined.

The effect of processing biodiesel with ion exchange resin on the acid value was determined by passing biodiesel through the resin at several soap levels. For each soap level, the acid value of the outgoing fuel was measured.

To determine the effectiveness of purification of biodiesel with adsorbents such as magnesium silicate or diatomaceous earth, the mass of the adsorbent was
varied, and for each treatment level, the soap and glycerin levels were measured.

The experimental setup was similar to that used in ion exchange resin experiments.
CHAPTER 5. Results and Discussions

This chapter discusses the experimental results of tests conducted to validate the four mode theory of soap and glycerin removal. It also describes the operating parameters needed to achieve optimal performance from biodiesel purification products. The performance of adsorbents, filtration media, and ion exchange resins for their ability to purify biodiesel are compared.

5.1 Four Mode Theory Validation

Experiments were conducted to validate the four mode theory of soap and glycerin removal from biodiesel which was discussed in chapter 3. The four mode theory states that soap and glycerin can be removed by a combination of filtration, physical adsorption, ion exchange and purification by the interaction between soap and glycerin.

5.1.1 Filtration Mode

The first mode that was tested was soap removal by filtration. Figure 5.1 shows the effect of filtration on soap removal. In this experiment, the particle retention size of the filters was varied from 2 to 40 µm and the soap levels after filtration were found to vary from 600 to 1200 ppm. In this initial test, the biodiesel feedstock contained no methanol or glycerin and was at room temperature. The sodium-catalyzed biodiesel feedstock contained 1500 ppm of soap and the potassium-catalyzed biodiesel feedstock contained 1300 ppm.
The results of this experiment show that as the filter particle retention size increases, the amount of soap in the effluent also increases. This figure compares the filterability of sodium and potassium soaps. It can be seen that sodium soap can be filtered more effectively than potassium soap.

Figure 5.1 Effect of filter porosity on soap removal

A visual analysis was also performed to compare the amount of soap particulate in biodiesel samples which contained sodium and potassium soaps. This experiment involved the vaporization of methanol from two biodiesel samples containing sodium and potassium soaps. Since methanol acts as a cosolvent to keep soap in solution with the biodiesel, methanol removal should cause soap precipitation. Figure 5.2 shows the experimental setup for this analysis.
The visual analysis and filtration experiments show that there are distinct differences in the physical characteristics of sodium and potassium soaps. When methanol was removed it was found that sodium soaps formed a “gel-like” particulate layer in the biodiesel. Potassium soaps did not appear to form this particulate layer.

It was found that during methanol removal, the biodiesel samples with sodium soaps generated foaming, whereas, the potassium soaps did not. This foam is likely formed by methanol vapors bubbling through the sodium soap particulate layer. From the visual observations of the differences between sodium and potassium soaps in biodiesel and the soap filtration data, in figure 5.1, it appears that sodium soap is less soluble in biodiesel than potassium soap.

Figure 5.2 Methanol removal biodiesel containing sodium and potassium soap. (Left: Potassium, Right: Sodium)
5.1.2 Ion Exchange Mode

Experiments were conducted to determine the quantity of soap that is removed due to the ion exchange mode. An increase in free fatty acid (FFA) levels when soap is removed indicates that the sodium portion of the soap molecule is being held by the resin, releasing the FFA into the effluent biodiesel.

Figure 5.3 shows the effect of soap removal, by ion exchange, on the effluent biodiesel free fatty acid levels. The incoming soap level was varied from roughly 500 ppm to 3500 ppm. Free fatty acid measurements were taken on the effluent biodiesel at each soap level. From this figure it can be seen that as the crude biodiesel soap level is increased, the effluent biodiesel free fatty acid value also increases. Three ion exchange resins, Amberlyte BD10 by Rohm & Haas and T45BD and T45BDMP by Thermax, were tested.

In this experiment, the experimental data were compared to the theoretical 100% ion exchange curve. The 100% ion exchange curve is the case where all of the soap entering the column is converted to FFA. For each ion exchange resin, complete soap removal was achieved but 100% conversion from soap to free fatty acid was not achieved at soap levels greater than 1000 ppm. At soap levels below 1000 ppm the experimental data shows close to 100% ion exchange. At soap levels from 1500 to 3500 ppm, the experimental curve and the 100% ion exchange curve diverge. These data show that at lower soap levels, soap removal is performed primarily by ion exchange. At higher soap levels, soap removal is performed by a combination of ion exchange, filtration and adsorption.
Figure 5.3 Effect of biodiesel soap level on acid value.

To ensure that the difference between the experimental and 100% ion exchange curve was statistically significant, a 90% confidence interval was calculated. Figure 5.4 shows that the lines corresponding to the upper and lower confidence intervals fall below the 100% ion exchange curve. From this statistical analysis, it can be assumed, with 90% confidence that the experimental data falls below the 100% ion exchange curve.
5.2 Ion Exchange Resin Exhaustion

Tests were conducted to determine the ion exchange resin's effective life, the optimal operating parameters and the effect of the four modes over the resin life. Resin exhaustion tests were conducted for biodiesel feedstock containing soap only, glycerin only and a combination of soap and glycerin. The results from these tests were compared to the performance of other competitive products.

5.2.1 Soap Only

Figure 5.5 shows the resin soap exhaustion curve for Thermax's T45BD gel resin, with no glycerin present. In this test, a column with 200 ml of swelled resin was used to purify biodiesel containing 2000 ppm of soap, 5% methanol and no
glycerin. This test was conducted using a flow rate of 4 bed volumes per hour. Biodiesel was passed through the column until about 500 bed volumes (BV) were processed. The effluent soap level, after 500 BVs, was about 900 ppm. The effluent biodiesel soap level exceeded 50 ppm of soap after about 250 BVs. The small decrease in soap level at 100 BVs and 350 BVs and the acid value at 100 BVs was due to a fluctuation in flow rate and does not affect the overall results of this experiment. In figure 5.5, the effluent free fatty acid was also measured for samples up to about 500 BV. At 50 BVs, the FFA was measured to be about 2100 ppm and at 500 BVs the FFA measured 600 ppm.

The soap and acid curves in figure 5.5 were compared to determine the effect of the four mode theory over the life of the resin. There were two distinct regions where the mode of soap removal changed. These regions were from 0 to 225 BVs and 225 to 500 BVs.

It can be seen that the soap level is low from 0 to 225 BVs but the FFA values decrease, significantly, over this range of bed volumes, this trend shows that as the resin bed ages ion exchange gradually decreases and adsorption contributes more to soap removal. This shift in purification mode is likely due to the ion exchange sites being covered with soap particulate. From 225 to 500 bed volumes the soap level begins to rise in the effluent biodiesel and the FFA continues to drop, this indicates that ion exchange, adsorption and filtration capacity are being exhausted, allowing soap to pass with the effluent biodiesel.
Figure 5.5 Effect of resin age on soap removal (Resin: T45BD)

To summarize figure 5.5, the soap removal occurs in two phases over the life of the resin bed. As the resin bed ages, soap removal mode shifts from ion exchange to adsorption. The ion exchange gradually decreases due to the active sites being covered with soap particulate. In the second period, ion exchange, filtration and adsorption gradually become exhausted. As the ion exchange sites, adsorptive pores and bed filtration area are filled, more soap is allowed to pass, leading to complete bed exhaustion.

5.2.2 Glycerin Only

Figure 5.6 shows the resin exhaustion curve of the T45BD gel resin for glycerin removal with no soap present. In this test, biodiesel containing 0.08% free glycerin, 4% methanol and no soap was purified with 200 ml of swelled resin. The
flow rate for this test was about 3.5 BV/hour. Biodiesel was purified for about 316 bed volumes and then the resin bed was washed with methanol to test its regeneration capacity. The effluent biodiesel free glycerin level was measured over the life of the resin.

From figure 5.6, it can be seen that the effluent glycerin level increases gradually, at a relatively constant rate, as the resin bed ages. According to conversations with the Thermax Company, it is generally understood that glycerin is removed by adsorption in the ion exchange resin; this is supported by free fatty acid measurements that did not increase.

During this experiment the ability to regenerate the ion exchange resin for glycerin removal was tested. Figure 5.6 shows that washing the ion exchange resin
with methanol at 316 bed volumes, after glycerin exhaustion, can reduce effluent glycerin levels. In this figure, glycerin levels were reduced from 0.08% to 0.02% by washing with methanol.

5.2.3 Soap and Glycerin Combined

In normal production, crude biodiesel contains both soap and glycerin. Tests were conducted to determine the resin life and active modes for biodiesel containing soap and glycerin. These tests compared gel and macroporous resins, from different manufacturers, to determine if resins from different manufacturers perform differently.

5.2.4 Macroporous Resin Test

Figure 5.7 shows the resin exhaustion curve for soap removal and the corresponding free fatty acid value, for Thermax’s T45BDMP macroporous ion exchange resin. For this test, crude biodiesel containing 1200 ppm of soap, 0.08% glycerin and 4% methanol was purified by 180 ml of swelled resin, at a flow rate of 2.5 BV/hour. This test was conducted until about 1000 bed volumes had passed through the resin at which time the incoming and outgoing soap levels were approximately equal. At 50 BV, the soap and FFA values were 27 ppm and 1800 ppm, respectively. At 1000 BV, the soap and FFA values were 1070 ppm and 1260 ppm, respectively. A soap level of 50 ppm was exceeded at about 550 BV.
Comparing the soap exhaustion curve in figure 5.7 to the 0% glycerin curve in figure 5.5, it can be seen that similar soap removal characteristics were achieved. To compare these curves the initial soap level must be taken into consideration.

The crude biodiesel in figure 5.5 contained 2000 ppm of soap, whereas, in figure 5.8, a soap level of 1200 ppm was used. From these figures, it can be seen that the 50 ppm soap level is reached at 250 BV for the 2000 ppm case and at 550 BV for the 1200 ppm case. Basically, if the soap level is doubled the number of bed volumes needed to achieve a given soap level appears to be halved.

The relationship between the soap removal and free fatty acid values for purification of crude biodiesel containing soap and glycerin follows roughly the same pattern as the 0% glycerin case. From figure 5.7, it can be seen that most of the
soap is removed but the acid value gradually decreases as the influent increases from 0 to about 500 BV. This region corresponds to the shift from ion exchange to adsorption that occurs as the resin ages. From 550 to 1000 BV, the FFA value continues to drop and the soap level climbs rapidly. This region is the phase where ion exchange, adsorption and filtration are all becoming exhausted and soap is allowed to pass into the effluent. The fluctuations in FFA value occurring at 50, 580 and 650 BV volumes are due to a decrease in flow rate leading to more efficient ion exchange causing an increase in FFA.

An important difference between the ion exchange resin exhaustion curves depicted in figures 5.5 (soap only) and 5.7 (soap and glycerin) is the slope and final value of the free fatty acid curve. In figure 5.5, the FFA curve has a much steeper slope and the final FFA value is around 500 ppm. In figure 5.7, the FFA curve has a smaller slope and the final FFA value is around 1300 ppm. These differences indicate that when glycerin is present, the ion exchange sites may become blocked off during the purification process reducing the ion exchange action.

The glycerin removal tests were also performed with the macroporous resin. Glycerin removal was not found to be effective compared to the gel resin tests. Macroporous resins are used in industry for biodiesel purification and are claimed to be effective. Additional experiments should be conducted to whether verify glycerin removal occurs with macroporous resins.

5.2.5 Parallel Gel Resin Test

Figure 5.8 shows the soap exhaustion curve of the T45BD and Amberlyte BD10 gels resins, for combined soap and glycerin removal. In this test, biodiesel
containing 1000 ppm of soap, 4% methanol and 0.08% glycerin was purified, at a flow rate of 2 BV/hour, by 200 ml of swelled resin. At about 400 bed volumes, each resin bed was washed with methanol to test the resin’s ability to be regenerated for glycerin removal.

Figure 5.8 Comparison of gel resins for soap removal (BD10, T45BD).

In figure 5.8, the effluent biodiesel soap level was measured for samples up to about 700 BVs. From 0 to 400 BVs the soap level gradually increased to about 50 ppm. The resins of the two manufacturers performed in a similar manner for this region of the curve. At 400 BVs, a methanol wash was conducted. The methanol wash was performed at too fast of a flow rate on the Amberlyte BD10 column causing the column to partially fluidize and become unstable. Soap particulate was dislodged and leached into the effluent biodiesel raising the soap level during the
400 to 600 BV region of the Amberlyte BD10 curve. After 600 BV, the column stabilized and the performance of the two resin columns became similar again.

The resin soap removal exhaustion curve from crude biodiesel, containing both soap and glycerin, is similar to the soap exhaustion curve from biodiesel containing only soap. The crude biodiesel used in the soap-only test, depicted in figure 5.5, contained soap levels of about 2000 ppm. The effluent biodiesel soap level exceeded 50 ppm at about 225 BV in this test. The crude biodiesel used in the soap and glycerin combination test, depicted in figure 5.8, contained soap levels of about 1000 ppm. The effluent biodiesel soap level exceeded 50 ppm at about 400 BV in this test. From these figures, it can be seen that doubling the soap level of the crude biodiesel entering the column will reduce the number of bed volumes that can be treated, for a given effluent soap level, by approximately half.

Comparing figures 5.5, 5.7 and 5.8 it can be seen that the resin exhaustion curves are of roughly the same shape. In figures 5.7 and 5.8, the crude biodiesel contained about half the soap level as was used in figure 5.5, therefore, about double the bed volumes are needed to achieve the same effluent soap level. From this comparison, it appears that the presence of glycerin in the crude biodiesel does not affect the resin’s soap removal life.

Figure 5.9 shows the glycerin exhaustion curve from the same test as figure 5.8. In this test, biodiesel containing 1000 ppm of soap, 4% methanol and 0.08% glycerin was purified, at a flow rate of 2 BV/hour, by 200 ml of swelled resin. At about 400 bed volumes, each resin bed was washed with methanol to test the resin’s ability to be regenerated for glycerin removal.
In figure 5.9, the glycerin level was measured from 17 to 700 BV. The glycerin values after the methanol wash are not typical due to incorrect wash procedures. Effluent glycerin values varied from about 0% at 75 BV to 0.01% at about 150 BV. The ASTM specification level of 0.02% was exceeded at about 200 BV. It was found that the flow rate of methanol during regeneration has a significant effect on the effectiveness of washing. From figure 5.6, it can be seen that the methanol wash flow rate should be roughly the same as the biodiesel run flow rate of 2 to 5 bed volumes per hour.

**Figure 5.9: Comparison of gel resins for glycerin removal. (BD10,T45BD)**

The glycerin exhaustion curves of the two gel resins were of roughly the same shape and their performance can be considered comparable. The slight variability between the two curves is likely due to differences in the flow rate and
flow dynamics through the resin bed. These parameters were different due to variability in the flow control valves and differences in methanol evaporation between the two columns.

The manufacturer's estimate of the life of the ion exchange resin, at an initial soap level of 1000 ppm, is 1 kg of resin is needed to purify 1600 kg of biodiesel. In this study, it was found that, at an initial soap level of 1000 ppm, 1 kg of resin is needed to purify 500 kg of biodiesel. This discrepancy might be due to differences in the expectations for quality of the purified biodiesel since these are not stated by the manufacturers.

5.3 Ion Exchange Resin Operating Parameters

Tests were conducted to determine the proper flow rate and bed aspect ratio parameters to achieve optimal performance of the ion exchange resins. Figure 5.10 shows the effect of flow rate and bed aspect ratio on soap removal. For this test, the flow rate was varied from 0 to 250 unswelled bed volumes per hour, for unswelled bed heights of 1 to 3 inches in 0.5 inch increments. The crude biodiesel that was used for this test contained 1000 ppm of soap, 5% methanol and glycerin. The exact amount of glycerin was not measured.

This data shows that as flow rate increased, soap removal decreased and as the bed height increased, the soap removal increased. It can be seen that for this range of flow rates and 2-3 inches bed heights, the soap removal is roughly the same. Breakthrough of soap, as indicated by elevated outgoing soap levels, occurs almost immediately with the 1 inches bed height and at about 75 BV/hour for the 1.5 inches height. It can be assumed that if additional tests were conducted with
greater flow rates, breakthrough would occur in the larger bed heights in the same way it occurs in the 1 and 1.5 in bed heights. It was not possible to run these tests with the current equipment because it would have required pressurizing the bed and this was not possible.

From this figure, it can be seen that for a dry resin bed aspect ratio of 2 to 1 or greater, the flow rate should be kept below 100 bed volumes per hour to obtain outgoing soap levels of below 50 ppm. The Thermax company recommends that a flow rate of about 2-5 swelled or 4 to 10 unswelled BV/hour be used. This data shows that the manufacturer's flow rate recommendations are conservative.

![Flow Rate, Bed Aspect Ratio Effect on Soap Removal](image)

**Figure 5.10** Effect of flow rate and aspect ratio on soap removal.

Figure 5.11 shows the effect of flow rate on glycerin removal. In this test, crude biodiesel containing 0.09% glycerin, 4% methanol and no soap was passed
through 140 ml of swelled resin. The flow rate was varied from about 0 to 30 BV/hour. It can be seen that as the flow rate increased, the glycerin breakthrough increased. These data show that the ASTM specification for glycerin was not reached for the maximum flow rate tested, which was significantly greater than the manufacturer’s recommended flow rate of 2 to 5 swelled BV/hour.

![Glycerin Breakthrough with Varying Flow Rate](chart)

**Figure 5.11 Effect of flow rate on glycerin removal (Resin: T45BD)**

### 5.4 Adsorbent Media Effectiveness

Tests were conducted to determine the effectiveness of adsorbents, such as Magnesol in removal of soap and glycerin from biodiesel. Crude biodiesel, at 60°C, containing 1200 ppm of soap, 0.08% free glycerin and no methanol, was treated with Magnesol and diatomaceous earth. Magnesol is specially treated by the manufacturer to have the ability to adsorb polar compounds. Diatomaceous earth is
not supposed to have the ability to attract or adsorb compounds but merely acts as a depth filter as it accumulates on the surface of the media.

Before testing the adsorbents, the crude biodiesel was passed through a paper filter to determine the filter’s ability to removal soap and glycerin. The filtered biodiesel contained soap and glycerin levels of 700 ppm and 0.06%, respectively. For this test, the weight percentage of purification media was varied from 0.1 to 5% and the soap and glycerin values were measured. The details of this experimental setup were discussed in more detail in chapter 4.

Figure 5.12 Soap removal by adsorption and filtration

In figure 5.12, it can be seen that Magnesol, the commercial magnesium silicate adsorbent media, removed soap to a lower concentration than diatomaceous earth. Magnesol reduced the effluent soap levels to 100 ppm at
0.1% weight. From 1 to 5% weight, the soap level was consistently about 30 ppm. Diatomaceous earth reduced the effluent soap levels to about 375 ppm at 0.1%. The effluent soap level gradually decreased as the weight percentage was increased from 0.1% to 2%. From 2 to 5% weight, the soap level was consistently about 70 ppm.

In figure 5.13, it can be seen that Magnesol is more effective at removing glycerin than diatomaceous earth. Magnesol reduced the effluent glycerin levels to 0.045% at 0.01%. The glycerin level decreased from 0.045% to undetectable levels as the Magnesol percentage was increased from 0.1 to 2%. From 2 to 5%, the glycerin level was below the detection threshold and considered to be 0.005%. The apparent increase in glycerin level from 0.25 to 0.5% was due to experimental error and should not be considered significant.

Diatomaceous earth reduced effluent glycerin levels to 0.05% at 0.1% weight. From 0.1 to 0.5% of diatomaceous earth the glycerin levels reduced from 0.05% to 0.03%. Increasing the percentage of diatomaceous earth from 0.5% to 5% did not reduce glycerin levels below 0.03%. The increases in glycerin levels at 1 and 2% were probably due to experimental error and should not be considered significant.

Figure 5.14 shows the effect of Magnesol on the acid value. This figure corresponds to the same test as figures 5.12 and 5.13. For this test, the Magnesol percentage is varied from 0.5% to 5% and the FFA over this range decreased from about 800 to 300 ppm. This figure shows that Magnesol can have a significant effect in improving the quality of biodiesel, by reducing its free fatty acid value.
Figure 5.13 Glycerin removal by adsorption and filtration.

Figure 5.14 Reduction in acid value by processing with Magnesol.
The comparison and evaluation of Magnesol and diatomaceous earth found that Magnesol is significantly more effective at removing soap and glycerin from biodiesel than diatomaceous earth. It was found that Magnesol can also significantly reduce biodiesel free fatty acid values. All of the testing in this experiment was conducted using biodiesel at 60°C. Lower temperatures would likely produce better soap removal due to the soaps being less soluble in the biodiesel, thus making them easier to filter.

5.5 Sulfur

Table 5.1 shows the effect of purification by ion exchange resins and Magnesol on the biodiesel sulfur levels. Magnesol purification did not have a significant effect on sulfur levels. Ion exchange resin produced a significant increase in sulfur level in the initial fuel processed. The ion exchange resin increased sulfur levels from 12.5 ppm to 22 ppm for the gel resin and up to 35 ppm for the macroporous resin after 5 BV. After 24 BV, the ion exchange resin did not make a significant change in sulfur level, sulfur levels returned to about 12.5 ppm.

In order to determine if the differences were significant between each purification method and the crude biodiesel, statistical analysis using the SAS software package was performed. The procedure used for this analysis was the t-test (LSD) Least Significant Difference. Using a 95% confidence level it was found that each sample had a significant difference in sulfur level as compared to the crude biodiesel except for the Macroporous resin after 24 BV, therefore, it can be assumed that ion exchange resins do not provide a significant change in sulfur levels after 24 BV.
Biodiesel sulfur levels are high in the low BV period due to sulfur residue leaching from the resin. Sulfur levels reduce after all the sulfur residue is leached from the resin. This sulfur residue is a by-product from the sulphonation process used in the manufacturing of the ion exchange resins.

Table 5.1: Effect of purification media on biodiesel sulfur level

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfur (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude Biodiesel</td>
<td>13.11</td>
</tr>
<tr>
<td>Gel Resin (5 BV)</td>
<td>22.05</td>
</tr>
<tr>
<td>Macroporous Resin (5 BV)</td>
<td>35.26</td>
</tr>
<tr>
<td>Macroporous Resin (24 BV)</td>
<td>12.29</td>
</tr>
<tr>
<td>Magnesol</td>
<td>10.02</td>
</tr>
</tbody>
</table>
CHAPTER 6. CONCLUSIONS

6.1 Conclusions

This chapter discussed the purification of biodiesel with ion exchange resins and adsorbents. Results supporting the four mode theory of soap and glycerin removal were presented and discussed. Tests were conducted to determine the operating parameters such as the bed aspect ratio and flow rate required to produce optimal performance. Ion exchange resin exhaustion curves were generated for the gel and macroporous resins. The performance of adsorbents were evaluated and compared.

Two tests were performed to validate the four mode theory of soap and glycerin removal. It was found that soap can be removed by a paper filter and that increasing the filter’s fineness produces more soap removal. Sodium soaps were found to be more filterable than potassium soaps.

Ion exchange resins were evaluated to determine the modes that are active in their operation. It was found that at low crude biodiesel soap levels ion exchange resins remove soap predominately by the ion exchange mode. At higher soap levels, soap is removed by a combination of ion exchange, adsorption and filtration. This test also showed that as the crude biodiesel soap level is increased the effluent free fatty acid value increases.

Ion exchange resin exhaustion curves were generated for gel and macroporous resins from two manufacturers. These curves were generated for crude biodiesel containing only soap, only glycerin and a combination of soap and
glycerin. It was found that, as the ion exchange resin ages, the effluent free fatty acid value decreases and the effluent soap level increases. It was observed that there are two phases of soap removal that occur sequentially during the exhaustion of a resin. First, ion exchange gradually decreases and combines with adsorption. Second, ion exchange, adsorption and filtration all gradually become exhausted leading to more soap passing into the effluent biodiesel.

Glycerin was found to be removed by a combination of adsorption and filtration. Glycerin levels increase at a relatively constant rate over a glycerin exhaustion curve; upon reaching the incoming level, the effluent glycerin content levels off. Glycerin removal capability can be regenerated by washing the ion exchange resin with methanol. This process was found to be sensitive to high methanol flow rate. High methanol flow rate does not allow time for the glycerin to be desorbed into the methanol. The recommended methanol flow rate for glycerin regeneration is 2-5 BV/hour.

The shape of the soap exhaustion curve is roughly the same, regardless of the crude biodiesel glycerin levels. It was found that there is a linear relationship between the crude biodiesel soap level and the number of bed volumes that can be processed to reach exhaustion. If the crude biodiesel soap level is doubled, the exhaustion bed volume is halved.

Tests were conducted to compare ion exchange resins of different types and different manufacturers. Gel and macroporous resins were found to provide similar performance for soap removal. Gel resins from Rohm and Haas and Thermax were found to have similar performance for soap and glycerin removal.
Tests were conducted to determine the bed aspect ratio and flow rate to obtain optimal performance. Bed aspect ratio has a significant effect on the optimal flow rate through the ion exchange resin bed. It was found that as the flow rate increased, the effluent soap and glycerin levels increased. As the bed aspect ratio increased, the effluent soap levels decreased. For the range of flow rates tested it was found that aspect ratios from 2 to 1 through 3 to 1 performed similarly.

Tests were conducted to evaluate and compare the effectiveness of adsorbents and filtration media, such as diatomaceous earth, Magnesol and saw dust, in removing soap and glycerin. It was found that paper filters alone, can reduce soap levels significantly. Magnesol is more effective in removing soap and glycerin than diatomaceous earth. Magnesol can reduce the free fatty acid value of biodiesel. Saw dust was also found to be effective in removing soap and glycerin from crude biodiesel.

Tests were conducted to determine the effect of biodiesel purification products on biodiesel sulfur levels. When ion exchange resins are first used the initial biodiesel contained increased sulfur levels. After about 20 bed volumes, this value decreases to the crude biodiesel level. Magnesol was found to have a small effect in reducing crude biodiesel sulfur levels.

6.2 Recommendations for Future Work

Future studies on this topic should develop methods to obtain better control of process variables. Biodiesel methanol concentration was found to be a difficult variable to control due to the volatility of methanol. The columns and biodiesel reservoir should be designed to minimize methanol leakage. A new column design
should be used that incorporates flow rate control using a feedback loop and
temperature control.

Soap and glycerin measurements should be taken as soon as possible after
processing with the purification media. Samples were found to change over time
when stored. Soap and glycerin measurements should be performed at least three
times and averaged to obtain sound values.

Additional tests should be conducted to compare purification performance
using potassium and sodium catalyst. Tests should also be conducted comparing
several different initial soap, glycerin and methanol levels. The effects of
temperature should also be tested on resin performance and life.


A. Saw dust tests

Figure A.1 shows the effectiveness of saw dust in removing soap from crude biodiesel. Crude biodiesel containing 2000 ppm of soap, 4% methanol and no glycerin was passed through the saw dust and the outgoing soap level was measured. The saw dust used in this experiment was fine saw dust obtained from a cabinet shop.

This experiment found that soap was reduced to levels below the detection limit of about 10 ppm, up to a biodiesel to saw dust ratio of about 45 gram biodiesel to 1 g saw dust. An additional large scale test was conducted and it was found that sufficient soap and glycerin removal was achieved for about 14.6 g biodiesel per g saw dust.

Saw dust is able to remove soap and glycerin from crude biodiesel due primarily to filtration. When packed in a column, fine saw dust acts as an excellent surface filter and depth filter. Surface filtration is the particulate deposition on the top surface of a filter. Depth filtration is the particulate deposition throughout the volume of multiple layers of filtration media.
Figure A.1 Soap removal with saw dust
B. **Soap and Glycerin Addition Calculations**

**Problem Statement:**

How much sodium methoxide, methanol and glycerin should be added to obtain 500 ppm of soap and 0.05% glycerin?

**Assumptions:**

Initial soap and glycerin levels are 0. MW of sodium soap = 304.4, use 25% sodium methoxide (NaOCH₃).

**Soap:**

\[
500 \, (\text{ppm}) = \frac{500 \, \text{g soap}}{10^6 \, \text{g biodiesel}} \times \frac{1 \, \text{mole soap}}{304.4 \, \text{g soap}} = \frac{1.643 \, \text{mole soap}}{10^6 \, \text{g biodiesel}}
\]

\[
\frac{0.25 \, \text{g NaOCH}_3}{\text{g catalyst mix}} \times \frac{1 \, \text{mole NaOCH}_3}{54 \, \text{g NaOCH}_3} \times \frac{1 \, \text{mole soap}}{1 \, \text{mole NaOCH}_3} = \frac{0.00463 \, \text{mole soap}}{\text{g catalyst mix}}
\]

\[
\frac{1.643}{10^6 \, \text{g biodiesel}} \times \frac{\text{mole soap}}{0.00463 \, \text{mole soap}} = 354.9 \, \frac{\text{g catalyst mix}}{10^6 \, \text{g biodiesel}} = 0.355 \, \frac{\text{g catalyst mix}}{\text{kg biodiesel}}
\]

**Glycerin:**

\[
\text{Mass Glycerin} = \frac{\% \text{Glycerin}}{100 \times \text{Mass Biodiesel}}
\]
C. **Autotitrator Procedure**

1. Prepare samples  
   a. Label  
      i. Weight  
      ii. Sample number  
      iii. Test (ie. T45BD)  
   b. Weigh fuel into cup  
   c. Add acetone

2. Sampler  
   a. Put cups into sampler

3. Titrator  
   a. Menu/enter/sample table  
   b. Sample table  
      i. Method-Soap or Acid  
      ii. ID1 – Sample Number  
      iii. ID2- Test  
      iv. Weight  
   c. Esc to main screen

4. Starting titration  
   a. Press start on sampler  
      i. Number of samples  
      ii. Starting sample position

**Run calibration daily**

1. Titrator  
   a. Sample table  
      i. 1 entry, method “calibration”

2. Sampler  
   a. Start  
   b. 3 samples

**Purge buret-daily or when changing titrant (HCL or KOH)**

1. Put sampler on empty cup  
2. Titrator  
   a. Menu/manual control/dosing
D. GC Procedure

Step 1: Measure 0.1 g of biodiesel into sample bottle.
Step 2: Add 100 μL of S1, S2, MSTFA solutions then wait 20 minutes.
Step 3: Add 8 ml of heptane to sample bottle.
Step 4: Pipet 1000 μL of prepared sample into GC sample bottle.
Step 5: In GC program, go to Sequence/Sequence parameters/directory and select appropriate directory.
Step 6: Name vials in desired sequence in GC program.
E. Sample Titrator Calibration

Calibration was performed each day the titrator was used. Three buffers were used with pH values of 4, 7 and 10. The titrator was considered to be calibrated when the Slope was between 96.0% and 100%.

<table>
<thead>
<tr>
<th>848 Titrino plus</th>
<th>03176 5.848.0012</th>
</tr>
</thead>
<tbody>
<tr>
<td>2009-03-24 20:40:04</td>
<td></td>
</tr>
</tbody>
</table>

RESULT REPORT

Method CAL pH CALIBRATION
Determination time 2009-03-24 20:33:02
Sample number 30
Sample size 1.0 g
Cal. temp. (manual) 25.0 °C

<table>
<thead>
<tr>
<th>Buffer</th>
<th>pH</th>
<th>J/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buffer 1</td>
<td>4.000</td>
<td>215.4</td>
</tr>
<tr>
<td>Buffer 2</td>
<td>7.000</td>
<td>42.7</td>
</tr>
<tr>
<td>Buffer 3</td>
<td>10.000</td>
<td>-130.7</td>
</tr>
</tbody>
</table>

Slope 97.5 % pH(0) 7.737

Figure E.1 Sample titrator calibration
F. Sample GC Calibration

GC calibration was performed each time the GC column was replaced.
G. Ion Exchange Resin Bed Start-Up Procedure

1. Weigh resin into column.

2. Pump methanol or clean biodiesel into the outlet of the column. Resin should become fluidized.

3. Allow resin to settle and drain the methanol or clean biodiesel until it is just covering the top of the resin bed.

4. Fill column with crude biodiesel. Run several bed volumes through column to remove methanol before taking measurements.
H. Methanol Wash Procedure

1. Drain crude biodiesel until it is just covering the resin bed.

2. Fill column with methanol. Pass about 5 BVs of methanol through the column at a flow rate of 2 to 5 BVs per hour.

3. Drain methanol unit it is just covering resin bed. Fill column with crude biodiesel and continue processing. Allow several bed volumes to pass before taking measurements.