

SOAP AND GLYCERIN REMOVAL FROM BIODIESEL USING WATERLESS PROCESSES

J. Wall, J. Van Gerpen, J. Thompson

ABSTRACT. Biodiesel is a proven alternative to petroleum diesel fuel. During production of biodiesel, 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. These soap and glycerin impurities in the biodiesel can lead to engine operation 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 formation. Recently, several alternative “waterless” purification procedures have been developed, such as ion exchange resins and solid adsorbents. The objective of this study was to investigate the use of ion exchange resins and characterize their performance so that biodiesel plant operators can use them more effectively. Four different mechanisms were identified for soap and glycerin removal. These mechanisms are filtration, physical adsorption, ion exchange, and soap removal by glycerin affinity. It was found that ion exchange resins can reduce soap levels from 1200 ppm to below 50 ppm for about 550 bed volumes (BV) of processed biodiesel. Glycerin levels can be reduced from 0.08% to below 0.02% for about 200 BV of processed biodiesel.

Keywords. Absorbent, Biodiesel, Diesel, Ion exchange resin, Purification, Transesterification.

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 and Graboski, 1998).

Biodiesel is typically produced using a transesterification reaction. Plant oils or animal fats are mixed with alcohol and an alkali catalyst, such as sodium methoxide, and heated until a separation occurs between the biodiesel and the glycerin. After the transesterification reaction has been completed and the glycerin removed, the raw biodiesel still contains a small amount of free glycerin and soap. Soap is produced by saponification reactions that occur in parallel with transesterification.

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 (Van Gerpen 2005). The soap and glycerin are extracted into the water phase and removed when the water is separated from the biodiesel. The use of water to wash biodiesel causes many problems:

- Water washing produces a large amount of waste water that must be treated.
- 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, 2005).
- Water washing introduces water to the fuel, which can cause it to degrade by hydrolysis. After water washing, the fuel must be dried to remove the trace amounts of water. This causes an increased energy cost.
- If the biodiesel has a high soap level, then water washing can lead to emulsions that can cause significant yield loss and other plant operational problems.
- Water washing can increase the processing time because of the need for drying, multiple washes, and water-biodiesel separation.

Several alternative methods are available to remove soap and glycerin from biodiesel, such as passing the fuel through a bed of ion exchange resin and using adsorbent compounds such as magnesium silicate (Berrios and Skelton, 2008; Kucsek, 2007). Very little information is available on these products in this application, and most biodiesel plant operators develop their operating procedures by trial and error.

This article describes tests conducted with ion exchange resins to investigate the mechanisms by which they operate and to characterize their performance in purifying biodiesel so that biodiesel plant operators can use them effectively.

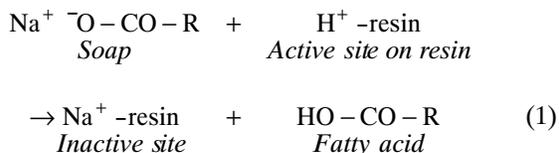
BACKGROUND

The types of ion exchange resins used for biodiesel processing consist of small (~0.5 mm) styrene beads that are coated with polar functional groups that can participate in ion exchange reactions with compounds from the surrounding

Submitted for review in March 2010 as manuscript number FPE 8475; approved for publication by the Food & Process Engineering Institute Division of ASABE in December 2010.

The authors are **Jacob A. Wall**, Research Assistant, **Jon H. Van Gerpen**, ASABE Member Engineer, Professor, and **Joseph C. Thompson**, ASABE Member Engineer, Research Support Scientist, Department of Biological and Agricultural Engineering, University of Idaho, Moscow, Idaho. **Corresponding author:** Jon H. Van Gerpen, Department of Biological and Agricultural Engineering, University of Idaho, P.O. Box 440904, Moscow, ID 83844-0904; phone: 208-885-7891; fax: 208-885-7908; e-mail: jonvg@uidaho.edu.

fluid. The usual explanation for how ion exchange resins remove soap from biodiesel involves the following reaction, which occurs on the surface or within the pores of the resin beads:



The resins studied here have sulfonic acid functional groups attached to their surface, which donate protons (H⁺) and capture Na⁺ ions. As a consequence of this reaction, the fatty acids created from the soap are added to the fuel stream.

Evaluating the performance of the ion exchange resins is complicated by the fact that this adsorption mechanism is only one of the ways that soap and free glycerin can be removed from biodiesel. There are at least four mechanisms of purification:

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 because methanol increases the solubility of soap and glycerin in the biodiesel. Methanol acts as a co-solvent to keep these contaminants dissolved in the biodiesel.

Adsorption: Adsorption is the removal of soluble impurities by chemical action. The surfaces and pores of the adsorbent particles are polar and attract the polar impurities. The impurities become chemically bonded to the charged surface of the adsorbent. Adsorption is the primary mechanism for glycerin capture with ion exchange resins and, as will be shown, may also be important for soap removal under some conditions. The glycerin adsorption capacity of ion exchange resins can be regenerated using a methanol wash.

Ion Exchange: As described above, 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 biodiesel solution. Ion exchange involves

the chemical breakdown of the impurity. Ion exchange removes soap from biodiesel by exchanging the sodium or potassium ion on the soap molecule for the hydrogen ions from the ion exchange material. After the exchange takes place, the free fatty acid portion of the soap molecule is soluble in the biodiesel and passes through the resin bed.

Glycerin/Soap Interaction: Soap has a strong affinity for glycerin; therefore, glycerin can aid in the removal of soap. As glycerin becomes adsorbed on the surface of the ion exchange resin, it forms a layer coating the resin. Soap is entrapped in this glycerin layer and is removed from the biodiesel stream.

These four mechanisms of biodiesel purification all appear to be active in the removal of impurities from biodiesel. As operating conditions and the properties of the ion exchange resins vary, one or more of these mechanisms may dominate the others.

EXPERIMENTAL METHODS AND EQUIPMENT

The equipment used to evaluate the resins consisted of glass columns filled with packed beds of resin ranging from 2.5 to 7.6 cm (1 to 3 in.) in diameter. In the bottom of the columns was an 80 mesh screen that trapped the purification medium 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 at the bottom of the column and was measured by a rotameter. The cleaned biodiesel was then collected in a glass separatory funnel. An automatic water sampler (Sigma 900 Max, Hach Co., Loveland Colo.) was used to pump the cleaned biodiesel from the separation funnel into sample bottles at set time intervals. Figure 1 shows the equipment used in the ion exchange resin bed purification experiments.

The biodiesel used in this experiment was prepared from crude mustard seed oil and canola oil crushed at the University of Idaho pilot plant. The biodiesel was prepared in a single batch using sodium methoxide and methanol. The biodiesel

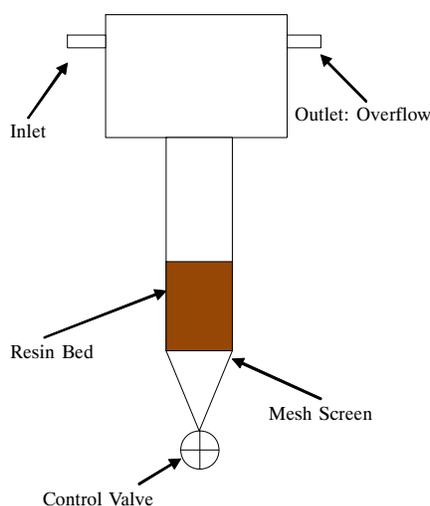


Figure 1. Ion exchange test setup.

Table 1. Comparison of ion exchange resin product data.

	Resin Type				
	T45BD	T45BDMP	PD206	DR-G8	BD10
Manufacturer	Thermax	Thermax	Purolite	Dowex	Rohm and Haas
Type	Gel	Macroporous	Gel	Gel	Gel
Functional groups	Sulfonic acid				
Ionic form	Hydrogen	Hydrogen	Hydrogen	Hydrogen	Hydrogen
Particle size	0.4 to 1.2 mm	0.4 to 1.2 mm	Not available	0.3 to 1.2 mm	Not available
Density	80 g mL ⁻¹	40 g mL ⁻¹	80 g mL ⁻¹	80 g mL ⁻¹	80 g mL ⁻¹

was then water washed to remove impurities. This was used as the clean test fuel.

For each test, the clean biodiesel was treated with measured amounts of glycerin and sodium methoxide dissolved in methanol to produce the desired levels of soap, glycerin, and methanol. The test fuel was prepared in 19 and 38 L (5 and 10 gal) batches and was typically used within 1 to 2 days. This approach was found to provide better consistency than blending a larger amount of fuel because of the tendency for glycerin and soap to settle or precipitate during storage.

The ion exchange resins used in this study were T45BD and T45BDMP from the Thermax Company (Northville, Mich.) and BD10Dry from Rohm and Haas (now Dow Chemical, Philadelphia, Pa.). Table 1 shows the product data from several ion exchange resin manufacturers. It can be seen that the products tested have properties that are typical of the range of products currently available in the market.

In order to determine the effectiveness of purification, the soap level, free fatty acid value, and free glycerin percentage were measured before and after processing. Soap level was determined using AOCs Method Cc 17-79 (AOCs, 2009), and 100 mL of acetone containing 2% deionized water was used as a solvent for each sample. To provide a blank, each batch of acetone solvent was titrated with NaOH or HCl to the point of a slight color change of bromophenol blue indicator to faint yellow prior to adding the biodiesel sample. Then, after adding a measured quantity of fuel, the solvent/sample 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:

$$\text{Soap (ppm) as sodium oleate} = \frac{\text{HCL (mL)} \times \text{Normality (HCL)} \times 304,400}{\text{Sample mass (g)}} \quad (2)$$

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

Acid value was measured by titrating with KOH to the phenolphthalein end point. 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 the titration was performed with

0.1 N KOH in isopropyl alcohol to the clear-to-pink endpoint of the phenolphthalein. An automated method was also developed to determine the acid value using the Metrohm autotitrator. The acid value was calculated using the following equation:

$$\text{Total acid number} \left(\frac{\text{mg KOH}}{\text{g}} \right) = \frac{\text{KOH (mL)} \times \text{Normality (KOH)} \times 56.1}{\text{Sample mass (g)}} \quad (3)$$

Free glycerin was measured using gas chromatography with a gas chromatograph (model 6890N, Agilent Technologies, Santa Clara, Cal.) according to the ASTM D6584 gas chromatographic method. In this process, 0.1 g of biodiesel was mixed with 100 μL each of butanetriol, glyceryl-tridecanoate, and n-methyl-n-trifluoroacetamide (MSTFA), and the solution was allowed to set for 20 min. Next, 8 mL of heptane was added as a solvent to the solution, and 1 μL of this solution was then injected to perform the GC analysis.

The tests described here were conducted using the glass columns discussed earlier. Dry resin was weighed and poured into the column. Either clean biodiesel or methanol was pumped back through the outlet of the column to “classify” the resin bed. Classification of the resin bed causes 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. Column preparation may also include swelling as the ion exchange beads absorb methanol. This can result in a doubling of the bead volume.

After classification was complete, the biodiesel or methanol was drained until it was level with the top of the resin bed. Raw biodiesel was then pumped into the top of the column. One liter samples were taken at 1 to 2.5 h intervals for flow rates of 2 to 4 bed volumes per hour (BV h⁻¹). To determine the effectiveness of purification, the soap level, acid value, and free glycerin level were measured at intervals of 5 to 10 L of throughput before and after passing through the resin bed.

When free glycerin levels leaving the resin bed exceed the ASTM specification level of 0.02%, the resin bed can be washed with clean methanol to regenerate its glycerin adsorption capacity. Methanol washing involved passing 5 to 10 bed volumes (BV) 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 BV h⁻¹. Initial tests with higher flow rates were performed but were shown to increase soap breakthrough, so flow rates were reduced. One of these cases is shown in the Results and Discussion section to illustrate this effect.

Soap levels were monitored to determine when 50 ppm soap in the effluent biodiesel was reached. Soap levels above 50 ppm will cause the biodiesel ASTM specification for sul-

fated ash (0.02% weight) to be exceeded. The fuel is also unlikely to pass the cold soak filtration test in the specification. For many of the tests, biodiesel was passed through the column until the soap levels of the effluent biodiesel greatly exceeded the specification levels. Acid values were also measured to determine the amount of soap removal due to ion exchange by the resin.

RESULTS AND DISCUSSION

One of the mechanisms for soap removal is filtration. Figure 2 shows the effect of filtration on soap removal. In this experiment, biodiesel was made using sodium and potassium catalysts. The biodiesel samples were passed through a series of filters that had varying particle retention size ratings. 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 test, the biodiesel feedstock contained no methanol or glycerin and was at room temperature. Since methanol acts as a cosolvent to keep soap in solution with the biodiesel, methanol removal should cause soap precipitation. The sodium-catalyzed biodiesel feedstock initially contained 1500 ppm of soap, and the potassium-catalyzed biodiesel feedstock contained 1300 ppm of soap.

The results of this experiment show that as the filter particle retention size decreased, the amount of sodium soap captured by the filter increased. The sodium soap was filtered more effectively than the potassium soap, which was not affected by the filter's particle retention size.

Sodium soaps are considered to be "hard" soaps, meaning they will solidify at room temperature, while potassium soaps are "soft" and will remain liquid. This tendency is probably responsible for the difference in filtration behavior between the two types of soap. Visual analysis and filtration experiments show that there were distinct differences in the physical characteristics of the sodium and potassium soaps. When methanol was removed, it was found that sodium soaps formed a gel-like layer in the biodiesel. Potassium soaps did not form this layer.

According to the manufacturers, ion exchange resins will remove both soap and glycerin. When the limiting value of glycerin removal has been reached, it is possible to wash the glycerin from the bed with methanol. However, when the limiting value of soap removal has been reached, then the resin bed must be replaced because regeneration of the bed in-

volves strong acid treatments that are beyond the usual scope of what can be done within the biodiesel plant. An important question addressed in this study was whether there is coupling between the soap and glycerin saturation levels. That is, if the bed is nearing saturation for soap, will that limit the amount of glycerin that can be adsorbed? To investigate this, tests were conducted with soap only in the biodiesel, with glycerin only, and then with both soap and glycerin. Biodiesel with controlled amounts of soap, glycerin, and methanol was passed through beds of resin for sufficient time (usually 3 to 5 days) to allow the bed to become saturated with at least one contaminant.

The ion exchange process can be identified by an increase in the free fatty acid (FFA) level of the biodiesel leaving the resin, which indicates that the sodium portion of the soap molecule is being held by the resin, releasing the FFA into the biodiesel. Figure 3 shows the effect of soap removal, by ion exchange, on the effluent biodiesel FFA levels. The incoming soap level was varied from roughly 500 to 3500 ppm with no glycerin present. The flow rate was held constant at 5.5 BV h^{-1} . In the adsorbent industry, expressing the flow rate in terms of the bed volume is common because it normalizes the liquid volumetric flow rate by the volume of the resin bed. It is similar to the space velocity that is frequently used in the catalyst industry. Free fatty acid measurements were taken on the effluent biodiesel at each soap level. Three ion exchange resins were tested: Amberlyte BD10Dry from Rohm and Haas, and T45BD and T45BDMP from Thermax. From figure 3, it can be seen that as the crude biodiesel soap level is increased, the effluent biodiesel FFA value also increases.

In this experiment, complete soap removal was attained at each test point, as indicated by zero soap levels in the biodiesel leaving the column. The experimental data were compared to the theoretical 100% ion exchange curve. The 100% ion exchange curve is the case in which all of the soap entering the column is converted to FFA. However, 100% conversion of soap to FFA was not achieved at soap levels greater than 1000 ppm. At soap levels below 1000 ppm, the experimental data show 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, although all of the soap was removed, the rise in FFA level was less than expected, indicating that some of the soap was removed by another mechanism. This is likely to be adsorption, since filtration is

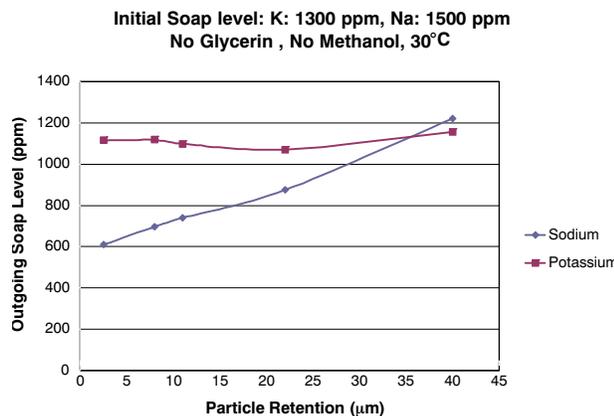


Figure 2. Effect of filter porosity on soap removal.

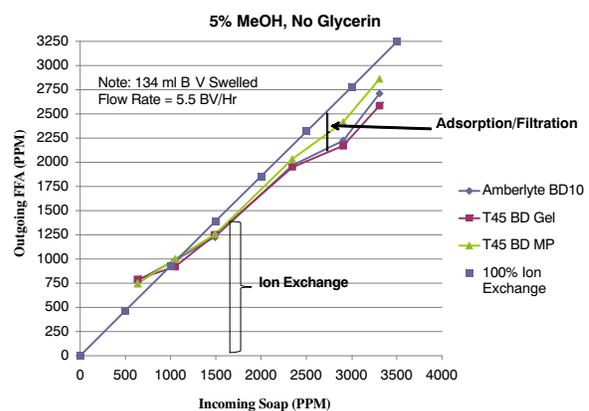


Figure 3. Effect of biodiesel soap level on acid value.

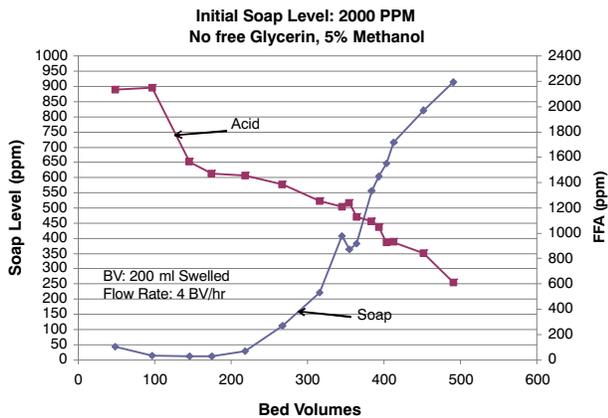


Figure 4. Effect of resin age on soap removal (resin: T45BD).

unlikely when methanol is present, keeping the soap in solution.

Figure 4 shows the performance curve for the Thermax T45BD gel resin, with no glycerin present over the resin’s entire useful life. 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 using a flow rate of 4 BV h⁻¹. Biodiesel was passed through the column until about 500 BV were processed. The effluent soap level, which was initially near zero, exceeded 50 ppm at about 250 BV and reached 900 ppm at 500 BV. The small decrease in soap level at 100 BV and 350 BV and in the acid value at 100 BV were due to a fluctuation in flow rate and did not affect the overall results of this experiment. The effluent FFA is also shown in figure 4. At 50 BV, the FFA was measured to be about 2100 ppm, and at 500 BV the FFA had decreased to 600 ppm.

It can be seen that the soap level is low from 0 to 225 BV, but the FFA values decrease significantly over this range of fuel volume. This trend suggests 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 exhausted or possibly covered with soap particulate. From 225 to 500 BV, the soap level begins to rise in the effluent biodiesel and the FFA continues to drop. This indicates that ion exchange and adsorption capacity are being exhausted, allowing soap to pass through with the effluent biodiesel.

Figure 5 shows the performance curve of the T45BD gel resin for glycerin removal with no soap present. In this test,

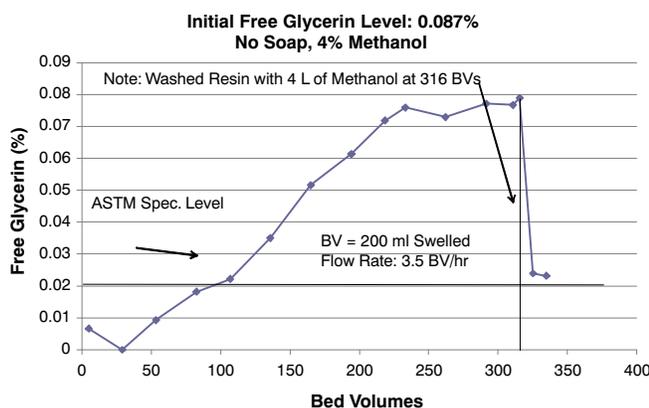


Figure 5. Glycerin removal with no soap present (resin: T45BD).

biodiesel containing 0.08% free glycerin, 4% methanol, and no soap was purified with 200 mL of swelled resin. This level of free glycerin (0.08%) was chosen because it is characteristic of free glycerin levels in crude biodiesel exiting a transesterification reactor. The flow rate for this test was 3.5 BV h⁻¹. Biodiesel was purified for about 316 BV, at which time the bed was passing virtually all of the glycerin that entered with the fuel. Then, the resin bed was washed with methanol to test its regeneration capacity.

It can be seen in figure 5 that the effluent glycerin level increased gradually, at a relatively constant rate, as the resin bed aged. According to the manufacturer of the resin, it is generally understood that glycerin is primarily removed by adsorption on the ion exchange resin. Glycerin is a highly polar compound, so it forms weak bonds with the polar sulfonic acid sites on the resin beads.

Figure 5 shows that washing the ion exchange resin with methanol at 316 BV, after glycerin exhaustion, reduced the effluent glycerin levels after the biodiesel flow was restarted. In this figure, glycerin levels were reduced from 0.08% to 0.02% by washing with methanol at a flow rate roughly equal to that of the biodiesel when it is being purified (2 to 4 BV h⁻¹). Other tests performed subsequent to this showed that the level of free glycerin recovery can be strongly affected by the manner in which the regeneration is performed. With slower flow rates and longer residence times, even lower values of free glycerin pass-through can be obtained.

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

Figure 6 shows the soap exhaustion curve of the T45BD and Amberlyte BD10Dry gel 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 h⁻¹, by 200 mL of swelled resin. At about 400 BV, each resin bed was washed with methanol to test the resin’s ability to be regenerated for glycerin removal.

From 0 to 400 BV, 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 BV, a methanol wash was conducted. The methanol wash was performed at too fast of a flow rate on the Amberlyte BD10

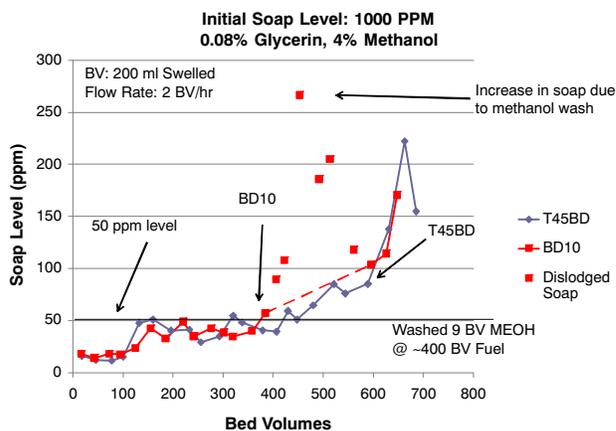


Figure 6. Comparison of gel resins for soap removal (resins: BD10 and T45BD).

column, causing the column to partially fluidize and become unstable. After the biodiesel flow was restarted, the soap level in the effluent biodiesel increased due to soap that was dislodged during the wash process. After 600 BV, the column stabilized and the performance of the two resin columns became similar again. This situation illustrates one of the challenges of maintaining consistently high fuel quality when using waterless processes.

The resin soap removal curve from biodiesel containing both soap and glycerin, shown in figure 6, is similar to the soap removal curve from biodiesel containing only soap, which is shown in figure 4. The crude biodiesel used in the soap-only test (fig. 4) contained soap levels of about 2000 ppm, and the effluent biodiesel soap level exceeded 50 ppm at about 225 BV. The crude biodiesel used in the soap and glycerin combination test (fig. 6) contained soap levels of about 1000 ppm, and the effluent biodiesel soap level exceeded 50 ppm at about 400 BV. From these figures, it can be seen that doubling the soap level of the crude biodiesel entering the column reduced the number of bed volumes that could be treated by approximately half. This also indicates that glycerin does not appear to affect the limiting value of the soap removal.

Figure 7 shows the glycerin exhaustion curve from the same test as figure 6. In figure 7, the glycerin level was measured from 17 to 700 BV. The glycerin values after the methanol wash are not typical because a high methanol flow rate was used for the washing. 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.

The glycerin exhaustion curves of the two gel resins were 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 beds. These parameters were different due to variability in the flow control valves and slight differences in methanol evaporation between the two columns. It was found that the flow rate of methanol during regeneration has a significant effect on the effectiveness of washing. From figure 7, it can be seen that when an excessive methanol wash flow rate is used, the glycerin removal is incomplete.

The manufacturer's estimate of the life of the ion exchange resin, at an initial soap level of 1000 ppm, is 1 kg of

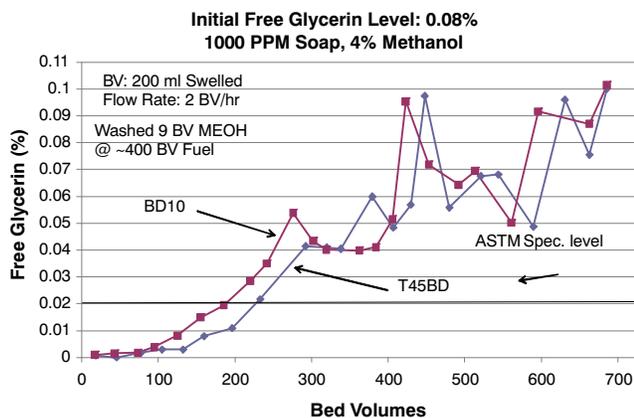


Figure 7. Comparison of gel resins for glycerin removal (resins: BD10 and T45BD).

resin 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 will 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.

Figure 8 shows the resin exhaustion curve for soap removal and the corresponding FFA values for Thermax's T45BDMP macroporous ion exchange resin. These resins, which utilize a more porous bead matrix, are attractive to some biodiesel producers because they cost less per unit of soap removal. For this test, crude biodiesel containing 1200 ppm of soap, 0.08% glycerin, and 4% methanol was purified with 180 mL of swelled resin at a flow rate of 2.5 BV h⁻¹. This test was conducted until about 1000 BV had passed through the resin, at which time the incoming and outgoing soap levels were approximately equal. 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 8 to the soap-only curve in figure 4, it can be seen that similar soap removal characteristics were achieved. To compare these curves, the difference in the initial soap level must be taken into consideration. The crude biodiesel in figure 4 contained 2000 ppm of soap, whereas, in figure 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, then the number of bed volumes needed to achieve a given soap level appears to be halved. These data indicate that the soap removal efficiency of the resin is not affected by the presence of glycerin, as was observed for the gel-type resins. The fact that the data show that almost all of the soap is passing through the bed after 1000 BV, while the acid value is still above 1200 ppm, is surprising and reinforces the challenge of collecting performance and life data for the resins. If all of the soap is passing through the bed, then the acid value should decrease to zero, and it probably will if sufficient time is allowed. It appears that the bed is releasing stored fatty acids that may have accumulated in the bed at some earlier time. This demonstrates that the resin beds are dynamic systems with the capability to store and release material. The time scale over which this behavior occurs is of the same order as the resin bed life, so it cannot be avoided by waiting for the bed to achieve steady state.

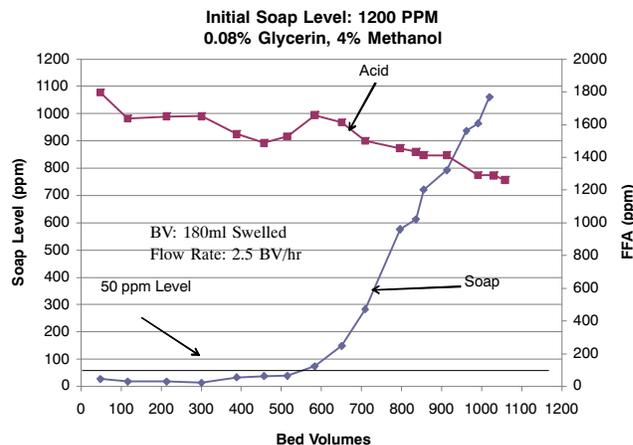


Figure 8. Soap removal from biodiesel containing soap and glycerin (resin: T45BDMP).

The relationship between the soap removal and FFA values for purification of crude biodiesel containing soap and glycerin also follows roughly the same pattern as the soap-only case. From figure 8, it can be seen that most of the soap is removed, but the acid value gradually decreases as the quantity of biodiesel processed approaches 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 where ion exchange and adsorption are becoming exhausted and soap is allowed to pass into the effluent. The fluctuations in FFA value occurring at 50, 580, and 650 BV correspond to temporary decreases in flow rate leading to more efficient ion exchange, causing an increase in FFA.

Comparing figures 4, 6, and 8, it can be seen that the resin exhaustion curves are of roughly the same shape. In figures 6 and 8, the crude biodiesel contains about half the soap level as in figure 4; 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.

An important difference between the ion exchange resin exhaustion curves depicted in figure 4 (soap only) and figure 8 (soap and glycerin) is the slope and final value of the FFA curve. In figure 4, the FFA curve has a much steeper slope, and the final FFA value is around 600 ppm. In figure 8, the FFA curve has a smaller slope, and the final FFA value is around 1300 ppm. These differences indicate a greater dependence on adsorption for soap removal. This may indicate that when glycerin is present, the ion exchange sites could be blocked off by the adsorbed glycerin, reducing the ion exchange action.

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

CONCLUSION

This research investigated the purification of biodiesel with ion exchange resins. Soap and glycerin can be removed by some combination of four mechanisms: filtration, physical adsorption, ion exchange, and soap removal by glycerin affinity. Ion exchange resin exhaustion curves were generated for both gel and macroporous resins.

It was found that when methanol is low, soap precipitation allows soap to 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 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 at low 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 and adsorption. This test also showed that as the crude biodiesel soap level is increased, the effluent FFA value also increases. It was found that, as the ion exchange resin ages, the effluent FFA 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 and adsorption gradually become exhausted, leading to soap passing into the effluent biodiesel.

Glycerin levels increase at a relatively constant rate over a glycerin exhaustion curve until the incoming level is reached. Glycerin removal capability can be regenerated by washing the ion exchange resin with methanol. This process was found to be sensitive to the methanol flow rate. High methanol flow rate does not allow time for the glycerin to be desorbed into the methanol and disrupts the bed, allowing soap precipitates to leave the bed. The recommended methanol flow rate for glycerin regeneration is 2 to 5 BV h⁻¹.

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, then 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 different manufacturers were found to have similar performance for soap and glycerin removal.

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