BIOdiesel Tech NOTES

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ION EXCHANGE RESINS FOR CLEANING BIODIESEL: HOW DO THEY WORK?

After biodiesel is made, it must be cleaned to remove impurities, including soap and glycerin. The traditional water wash method causes several problems, including possible emulsions and degraded biodiesel if the fuel is not dried adequately. It also creates a lot of waste water. Waterless methods of purifying biodiesel have been introduced into the marketplace, such as ion exchange resins and synthetic magnesium silicate. A number of different companies manufacture ion exchange resins (which are small polymer beads) to clean biodiesel. Although the products are similar, the companies' explanations of how the products work are sometimes very different. For example, many companies say the beads work by exchanging ions (the sodium or potassium ions from the soap in the biodiesel are exchanged with hydrogen ions on the bead surfaces). However, one company selling similar beads claims they work via glycerin and soap interaction. University of Idaho conducted a series of experiments on ion exchange resins to determine how they work, including how long they remain effective. Three types of beads were tested: Amberlite BD10Dry from Rohm and Haas, and T45BD and T45BD Macro from Thermax.

The tests were conducted using clean biodiesel that had been additized with specific amounts of glycerin, sodium methoxide, and methanol, to produce the desired levels of soap and glycerin. (Sodium methoxide will react with methyl esters to produce soap).

Four possible modes of cleaning

The researchers hypothesized that the ion exchange resins might work in four different ways.

The beads are presumed to work via ion exchange: they exchange a hydrogen ion with the sodium or potassium ion in the soap. Because the sodium or potassium portion of the soap is being held by the resin, the fatty acid portion is released into the effluent biodiesel, which will therefore have a higher percentage of free fatty acids. If the soap level in the biodiesel is higher than 2500 ppm, the biodiesel's acid value will likely exceed the ASTM limit of 0.5 mg KOH/g (the amount of KOH required to neutralize one gram of fuel).

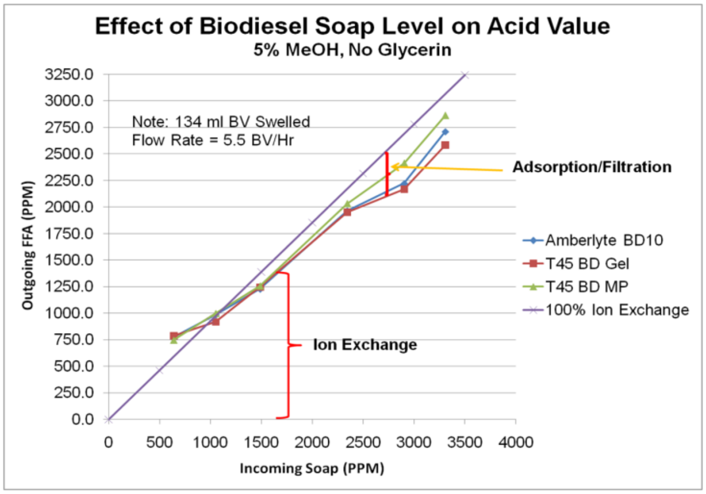
Another possible method of cleaning involves filtration. The ion exchange bed can act as a filter. If soap and glycerin have precipitated from the solution, which they are prone to do if the cosolvent methanol is removed, the soap and glycerin can be removed by simple filtration.

Adsorption is a third possible cleaning mode. Adsorption occurs when polar contaminants attach themselves to the bead surface due to the attraction of intermolecular forces. In fact, synthetic magnesium silicate, another popular waterless method of cleaning biodiesel, is known to work through adsorption: binding the polar soap or glycerin molecules to its surfaces. Perhaps the ion exchange beads also work partially in this way. This is probably an important mechanism for glycerin removal.

The fourth possible mode of cleaning is the soap-glycerin interaction. Glycerin is thought to be removed from biodiesel through adsorption or filtration. Because glycerin is a highly polar molecule, it is held on the surface of the adsorbent by attraction to polar groups already on the surface. Soap, being soluble in glycerin, would be dissolved into the glycerin and removed from the biodiesel with it.

Modes of cleaning: test results

Tests showed that, at lower soap levels (less than 1,000 ppm), the beads worked almost completely through ion exchange. At higher soap levels, the beads worked mostly through ion exchange, but not entirely. Other modes of cleaning appear to be operating at these high soap levels—possibly a combination of the other three modes.



The straight line on the graph represents an ideal ion exchange curve, where all of the soap entering the column of beads is converted to free fatty acids. It is apparent that at soap levels above 1,000 ppm, the free fatty acids in the effluent biodiesel are lower than the predicted amount, even though the soap was removed from the biodiesel. Therefore, some other modes of cleaning must have been operating in addition to ion exchange.

Glycerin is not removed through ion exchange at all, since there are no relevant ions to exchange. Instead, glycerin removal probably happens through adsorption and filtration. For example, the precipitated soap material that collects at the bed surface also contains glycerin and trapped biodiesel.

Manufacturers of these products sometimes claim that the products work well until they are exhausted, at which point they stop working suddenly. This research showed, instead, that the products had a gradual decline of effectiveness. As one mode of operation stopped working (such as ion exchange), other modes continued to work (such as filtration, or soap and glycerin interaction). Therefore, the products did not show a sudden drop in effectiveness. Rather, the effectiveness gradually degraded until the soap or glycerin levels exceeded the specification limits.

How long do the beads remain effective?
Tests were also conducted tests to determine how long the beads remained effective. Biodiesel with an initial soap level of 2000 ppm was cleaned to a soap level of 50 ppm or less (to maintain compliance with the ASTM specification of no more than 0.02% sulfated ash), up to 250 bed volumes. With an initial soap level of 1,000 ppm, the beads remained effective up to 400 bed volumes. In other words, a higher soap level caused the beads to lose their effectiveness more quickly.

(Note: the term "bed volume" is a common way for resin manufacturers to rate the capacity of their product. A bed volume corresponds to a volume of fluid equal to the expanded volume of the bead bed.)

To translate this into a real-life situation, at a soap level of 1000 ppm, about 1 kilogram of beads is needed to purify 500 kg of biodiesel. This is a lower effectiveness rate than some bead manufacturers advertise.

Do different kinds of beads work equally well?
Two types of gel resins were tested, which are the most common type, as well as a new "macroporous" resin manufactured by Thermax. All three worked equally well to remove soap, but we found that the macroporous resin (T45BD Macro) was not effective at removing glycerin. More testing is needed to verify whether macroporous resins remove glycerin.

Tips for working with ion exchange resins

1. The glycerin will need to be washed from the beads several times during the lifetime of the beads. Note that glycerin can be washed (or "desorbed") from the beads with methanol, but the sodium or potassium ions from soap cannot be removed by simple washing. Various strategies have been proposed for washing with methanol. Some involve extended soaking, and others use slow flow through the bed, but all require at least 4 hours of contact time. Once used, this methanol may need to be distilled to remove water.
2. Each time the bed is replaced, the new beads need to be "classified." This means that clean biodiesel (or sometimes methanol) is pumped through the column from bottom to top to fluidize the bed and allow it to settle so there are no voids, and so the beads are surrounded by other beads of similar size. This creates biodiesel that might need to be reprocessed. We have seen situations where this biodiesel ended up high in sulfur due to residual sulfuric acid from the bead manufacturing process.
3. The soap and glycerin levels at the exit of the column need to be monitored regularly—possibly hourly—to watch for breakthrough of these contaminants.
4. Some plants have noticed that a layer of soap can accumulate on top of the resin bed. This may need to be removed periodically. The amount of soap will depend on the amount of methanol in the biodiesel when it enters the column. Generally, you want the methanol percentage to be about 2%. Less than this and you can have soap precipitation that will plug the column.

For more information, see "Comparison of Methods for the Purification of Biodiesel" at: BiodieselEducation.org