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THE ADVANTAGES OF WATER WASHING BIODIESEL

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When biodiesel is produced, the methyl esters need to be purified before the fuel is suitable for use in engines. The fuel is likely to contain methanol, soap, and free glycerin, all of which should be removed. Years ago, producers would debate whether removing these contaminants was really necessary. Today, there is uniform agreement that for the fuel to provide trouble-free operation in an engine and to meet the national quality specification (ASTM D 6751), purification to remove these contaminants is essential.

Water washing is one of the best-known purification techniques and, although no survey results are publicly available, is probably the most widely practiced technique. This discussion will compare water washing with alternative techniques and explain why it is so frequently used.

Except for distillation, all of the techniques used to purify biodiesel rely on the difference in molecular polarity between the methyl esters in biodiesel and the contaminants. Methanol, soap, and glycerin are all polar and are thus strongly attracted to each other and polar solvents such as water. Methyl esters are only slightly polar and thus have limited solubility with water and with the contaminants. Only about 4-6% methanol is soluble in methyl esters, depending on the temperature. The solubilities of soap and free glycerin are much less although they are higher when methanol is present to act as a co-solvent. When water is added to biodiesel, it generally forms a separate phase, and since methanol, soap, and free glycerin are more strongly attracted to the water, they selectively partition into the water phase. If the water phase is removed, either by gravity settling or centrifugation, the concentrations of the contaminants will be reduced. Frequently, multiple cycles of washing are required to achieve sufficiently low levels of the contaminants. Some producers have avoided water washing because of: 1) the desire to minimize waste water production; 2) when natural surfactants such as soap and monoglycerides are present they may form emulsions, and 3) if methanol is dissolved in the water it is more complicated to recycle.

The problem with methanol contamination of the wash water can be overcome if the methanol is removed before the washing step. However, without the methanol, the soap may precipitate from the methyl esters as a highly viscous gelatinous material that plugs filters, screens, and pipes.

Adsorbents are an alternative to water washing and generally consist of high porosity powders such as magnesium silicate that are treated to attract polar compounds. The surface of the adsorbent has locations on its surface that attract polar compounds, known as active sites. When the polar sites on the powder are filled, the adsorbent is exhausted and cannot be reused or recycled. Since the material is non-toxic, some biodiesel producers have sold the spent adsorbent for use in animal feed. Methanol is usually removed before adsorbents are used since the highly polar methanol will rapidly fill the active sites on the adsorbent, thus leaving most of the other contaminants in the fuel. However, when the methanol is removed, soap rapidly precipitates and collects on the surface of the adsorbent, blocking further passage of liquid. These solid adsorbents are most effective for low soap concentrations and at elevated temperatures. They can be used as a polishing step and may help to remove monoglycerides and sterol glucosides as an added benefit.

Ion exchange resins are small plastic beads coated with a material that attracts polar compounds such as glycerin and soap. The beads are more expensive that adsorbents, but they can be used for more produce and can be regenerated to restore glycerin removal by washing with methanol although regeneration for soap removal is more complicated and is generally not performed at the plant level.

Distillation is becoming more popular as a biodiesel purification technique because it produces a visibly clear product with very low levels of monoglycerides. These monoglycerides are responsible for many of the low-temperature operability problems seen with biodiesel. While distillation is highly energy intensive, its greatest expense may be the 3 – 10% loss of material lost as bottoms from the high-temperature region of the distillation column. It should also be noted that distillation does not eliminate the need for purification because while the process removes monoglycerides and soap, free glycerin has boiling properties that are close enough to methyl esters that it will not be removed by distillation. Although most free glycerin is removed by settling tanks or centrifugation, the amount that remains with the methyl ester, either dissolved or as small droplets, exceeds the allowable specification of 0.02%. This free glycerin must be removed before distillation by either water washing, adsorbent, or by an ion exchange resin.

Water washing has the disadvantage that it utilizes water supplies that might be in short supply, especially in the western United States. In addition, it may produce large amounts of wastewater with a high biological oxygen demand that can be expensive to treat before it can be released to the environment. However, plant designs are available that recycle the water within the plant and thus have minimal waste water discharge.

Perhaps the most frustrating aspect of water washing can be the formation of emulsions between the water and the methyl esters. Soap and monoglycerides seem to be the most prominent surfactants that stabilize these emulsions. Emulsions due to soap seem to be shorter-lived while emulsions created by an excess of monoglycerides may be permanent. If emulsions occur, they can usually be broken with the addition of acid, but the resulting product will usually require reprocessing.

To use water washing effectively requires that free fatty acid (FFA) and water levels of the incoming feedstock oil be as low as possible to minimize soap formation during the transesterification process. FFA less than 0.5% and water less than 0.1% is desirable. Similarly, to minimize monoglycerides residue in the finished fuel requires a good quality reaction. This means adequate time and temperature as well as sufficient catalyst and excess methanol. Processing high FFA feedstocks are possible but require special procedures whose description is beyond the scope of this TechNote.

Water washing requires that initial washing steps be conducted with a minimum of agitation and without air entrainment to prevent emulsion formation. Later wash stages can be more vigorous when soap levels are lower (< 1000 ppm). The use of a dilute acid mixed with the wash water can also help to minimize emulsion formation. However, strong acids will split the soap back to a salt and FFA, and when the soap level is high (> 2500 ppm), the resulting acid value will exceed the level allowed by the ASTM specification.

Water washing has an important advantage over ion exchange resins. If some process upset occurs in the plant, such as a pump failure or a feedstock quality variation, the soap production can become very high. If this material is supplied to a bed of ion exchange resin, it can overwhelm the active sites on the resin beads and exhaust the entire bed requiring very expensive replacement. So, a mistake that might have just cost a few hours of production could end up costing much more.

While water washing can be troublesome, when properly conducted it is a robust technique that uses no costly materials, can handle high contaminant levels, and produces biodiesel that meets all requirements of the ASTM specification. If patience and proper care are used, it can be executed with minimal problems even in high volume production operations.