Technical Article

Portable IR Analyzers: The Ideal Measurement Solution for Biofuels Blend Quality and Wastewater Testing

by Sandra Rintoul

Two challenges facing the biofuels industry involve compliance with blend quality standards and wastewater regulations. According to a study done by the National Renewable Energy Laboratory,[1] the chief problem found with biodiesel blends was inaccurate blend ratios. Retail customers and fleet managers do not typically worry about whether the blend ratio is correct until a problem occurs. For fleet managers, this can mean a total shutdown of operations. Since bad news often spreads faster than good news, fleet-stopping events do not help to promote public acceptance of biofuels.

Environmental upsets also hurt the public image of the biofuels industry. Last year, several biodiesel plants in the U.S. were fined for illegally discharging vegetable-based oil and grease and polluting nearby streams. The U.S. EPA has established limitation guidelines for discharges of "oily wastes" from facilities utilizing any type of oil and grease in their manufacturing process. While biofuels plants are new to the industrial community, they need to be good neighbors and properly dispose of and comply with regulations regarding oily wastes. Current limits on oil and grease concentration levels require producers to monitor their waste byproducts more closely prior to discharging, which means measuring the oil and grease to ensure compliance.

While illegal discharges of oily waste can have far-reaching environmental effects, the blend ratio can affect cold weather performance, tax incentives, engine performance, and warranty issues. Portable infrared analyzers offer a quick analytical method capable of determining the biodiesel and ethanol blend ratio or the amount of oil in wastewater.

Biofuels blending

There are basically two ways to blend biodiesel: splash blending (either in a tank or in the delivery truck) and in-line blending. The fact that biodiesel is typically denser than petroleum diesel and has different cold flow properties is an additional challenge to getting an adequate mix during blending. Probably the biggest concern with the biodiesel blends is what happens in cold weather. The cold filter plug point (CFPP) is the temperature at which the crystals begin to form in the biodiesel. These crystals can then plug the fuel filter. The amount of biodiesel in a blend is often reduced in the winter to avoid filter plugging. Blending in more biodiesel than specified can stop an engine.

Splash blending

The most common and least accurate method of blending used for biodiesel is splash blending. Diesel fuel and biodiesel are pumped by the distributor directly into the delivery truck when it is loaded. The hope is that the blend will be adequately mixed by the time the truck gets to the delivery site.

During a demonstration with a portable fixed-filter infrared analyzer (see *Figure 1*) at a splash blending distribution facility, a sample was taken from a delivery truck destined to deliver B20 (20% biodiesel in diesel) and the reading was determined to be 8.7% biodiesel. The analyzer accuracy was checked with a B20 standard, and the reading was 20%. After much questioning, the truth came out: The facility had run out of biodiesel and the truck had been topped off with diesel. In another demonstration test, 5 min after splash-filling the truck for a B20 blend, a sample taken from the top was 11.9% and from the bottom was 24.1%. The first delivery was less than four miles away, offering little chance for a thorough mix. Efforts to convince a driver to draw a sample at each delivery to check the blend have not yet been successful.



*Figure 1 InfraCal Biodiesel Blend Analyzer (**Wilks Enterprise, Inc.**, South Norwalk, CT).*

Due to the difference in densities between diesel and biodiesel, blending fuels in cold weather with nonheated biodiesel reduces the chance of an adequate blend prior to delivery. If biodiesel is loaded first into an empty delivery truck on a very cold day, there will be little or no mixing. Residual diesel or biodiesel left in the truck from prior deliveries can also skew the blend.

Splash blending has inherent difficulties that lead to inaccurate mixing. Infrared analysis, described in detail below, offers a quick on-site test method for verifying the blend ratio and avoiding offending problems.

In-line (injection) blending

In-line blending is not new to pipeline terminals and racks, especially for blending ethanol in gasoline. On the other hand, relatively few fuel biodiesel distributors are using in-line blending. With in-line blending, the biofuel is metered into the petroleum fuel as it travels through a pipe. Although this method offers better blend consistency for biodiesel than splash blending, density and viscosity changes in the biodiesel require adjustments to the meters for an accurate blend.

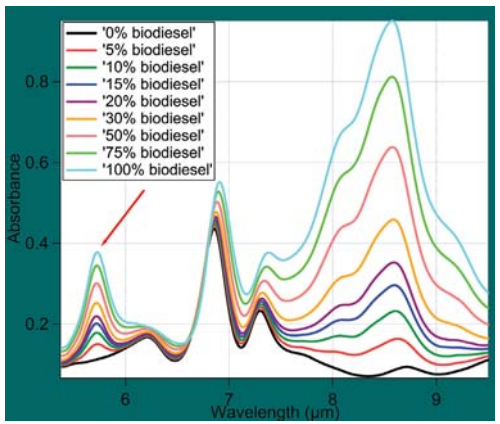

Figure 2 Midinfrared spectra of different concentrations of biodiesel in diesel.

Volumetric Standards % Biodiesel in Diesel	InfraCal Biodiesel Blend Analyzer	FTIR-EN Method 14078
17.00	17.02	19.90
25.00	24.57	28.30
47.00	46.97	52.00
63.00	63.22	77.30
76.00	74.55	82.00
100.00	100.00	99.85

Figure 3 Comparison of EN Method 14078 and an InfraCal biodiesel blend analyzer.

As more mandates for a minimum of ethanol in gasoline come into effect, a large number of major oil companies are blending higher percentages of ethanol at their terminals. Although manufacturers of in-line blending systems claim indisputable accuracy, a quick check for the correct blend gives real data to a claimed assumption.

Infrared measurement of biodiesel and ethanol blend ratios

EN Method 14078 and the recently passed ASTM Method D7371 both specify midinfrared for the biodiesel blend ratio. In the midinfrared region, the biofuel ester has characteristic absorption due to the carbonyl band at 5.7 µm or 1745 cm^{-1} (see *Figure 2*). Inexpensive filter-based analyzers that select the 5.7-µm wavelength (Figure 1) allow for portable and easy analysis needed by regulatory agencies, blenders, and fleet managers. The data in *Figure 3* show a comparison of volumetrically mixed standards tested by a fixed-filter infrared analyzer and with an FTIR using EN Method 14078. The fixed-filter analyzer's ease of use reduces operator error compared to the more complicated EN method. As the data show, in this comparison, the fixed-filter analyzer matched the volumetric standard numbers more closely than the FTIR EN method.

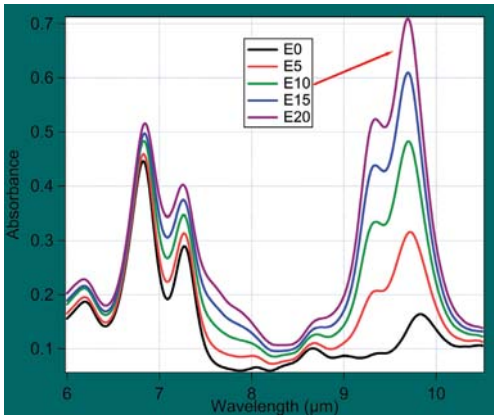

Figure 4 Midinfrared spectra of different concentrations of ethanol in gasoline.

Ethanol also has an infrared absorbance band that is unique to gasoline at 9.6 µm (1042 cm^{-1}), as shown in *Figure 4*. Again, a filter-based infrared analyzer selecting the 9.6-µm wavelength offers a compact and rugged solution for on-site measurements.

Oil and grease compliance

Biofuels producers discharging into a sewer line or waterway or applying industrial sludge to the soil are faced with strict oil and grease limits as part of the Clean Water Act initiated in 1972. When industries discharge high levels of oil and grease into a sewer line, a clog can form and result in a sanitary sewer overflow (SSO). The runoff from an SSO is a major source of pollution for our waterways. It is estimated that 23–28% of SSOs are due to fats, oils, and grease (FOG) or as much as 19 million gallons from 1998 to 2001 (State of North Carolina, 2002).[2] Regulations for oil and grease lim-

its vary by state and local sanitization departments. Effluent limits of oil and grease entering a sewer from industries can be as low as 100 ppm. Limits for oil and grease going directly into a waterway can be as low as 4 ppm. To ensure compliance, industries need an accurate on-site analysis.

Infrared analysis of oil and grease in water

Infrared analysis of oil and grease has been used in the petroleum industry on highly regulated off-shore oil platforms for over 35 years. The measurement by infrared absorption makes use of the fact that hydrocarbons such as fats, oil, and grease can be extracted from water through the use of an appropriate solvent. The extracted hydrocarbons absorb infrared energy at a common infrared wavelength, and the amount of energy absorbed is proportional to the concentration of the oil/grease in the solvent. The infrared absorbance can be converted to a direct readout in ppm of oil in the original effluent sample.



Figure 5 On-site use of an InfraCal TOG/TPH analyzer.

Oil and grease measurement procedure

Portable infrared analyzers such as the InfraCal TOG/TPH analyzer (*Figure 5*) allow for on-site analysis by regulators or industrial pretreatment personnel. The extraction and measurement procedure involves several simple steps, permitting an operator with minimal training to



perform the analysis. First, the effluent sample is collected in a container. Next, a solvent such as hexane, perchloroethylene, or S-316 is added and the sample is shaken. The solvent will separate, carrying dissolved oil with it. The solvent extract is then placed in the analyzer, and after a couple of minutes the result is displayed. The analysis from sample collection to final result is complete in less than 10 min. If the same sample were sent to a laboratory, the result would possibly not be known for a week—that could be a week of effluent with oil levels over the regulatory limit being released.

Conclusion

With the public image vacillating between food and fuel issues and the environmental advantage of biofuels, it is important to keep quality and environmental standards high in order to further the acceptance of biofuels. Analytical testing equipment is essential to this goal. Portable infrared analyzers offer a quick analytical method to assess the blend ratio, and can be a valuable asset for fuel distributors, engine manufacturers, fleet operators, and regulatory agencies. They also provide biofuels producers with an easy way to measure oil and grease in their wastewater. Effluent that is above the regulatory limits can be detected before it stops the flow of the sewer line or is discharged into a waterway, avoiding fines and negative headlines.

References

1. Kinast, J.A. *Production of Biodiesels from Multiple Feedstocks and Properties of Biodiesels and Biodiesel/Diesel Blends*; NREL/SR-510-31466, Mar 2003.
2. State of North Carolina, Easley, M., Governor; Ross, W., Jr., Secretary of the Department of Environment and Natural Resources; Hunt, G., Director of the Division of Pollution Prevention and Environmental Assistance; *FOG Task Force: Considerations for the Management of Discharge of Fats, Oil and Grease (FOG) to Sanitary Sewer Systems*: DPPEA-FY01-22, Jun 2002.

Ms. Rintoul is Product Manager, ***Wilks Enterprise, Inc.****, 140 Water St., South Norwalk, CT 06854, U.S.A.; tel.: 831-338-7459; fax: 831-338-3393; e-mail: srintoul@wilksir.com.*