# Meeting the Challenges of Biodiesel Blend Measurements with Portable Mid-Infrared Analyzers

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*In a published paper on biodiesel blend quality submitted 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, an incorrect blend can mean a total shutdown of operations. On the regulatory side, the increase in fuel costs combined with the financial rewards of tax rebates and credits have allowed for shady characters to take advantage of inadequate testing programs by adding less biofuel than stated or adding other components to extend the fuel such as pure vegetable oil, jet fuel or kerosene.*

Cold weather performance, engine performance, warranty issues, and tax incentives are all motivations to having an accurate, portable and reliable biodiesel blend measurement. A quick analytical measurement method to assess the blend ratio can be a valuable asset for fuel distributors, engine manufacturers, fleet operators, and regulatory agencies.

## Blending Methods:

There are basically two methods of blending 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 the cold flow properties can change with different biodiesel feedstocks adds challenges to getting an adequate mix during blending.

## Splash Blending

The most common, and least accurate method of blending used for biodiesel is splash blending. Diesel fuel and B100 are pumped by the distributor directly into the delivery truck at the time it is loaded. The hope is that the blend will be adequately mixed by the time the truck gets to the delivery site. Obtaining measurement data on the blend ratio from a splash blender is not easy. As one (un-named) blender said, "What is in it for us except making our blending techniques look bad?"

Recently, a portable fixed filter infrared analyzer that measures percent biodiesel (*see figure 1*) was demonstrated at a splash blending distribution facility. A sample was taken from a delivery truck destined to deliver B20 and the analyzer indicated that the blend was only 8.7% biodiesel. The analyzer was checked with a B20 standard and the reading was 20.1%. After much questioning, it was discovered that they had run out of B100 and the truck had been topped off with diesel.

Splash blending also has the risk of inaccurate blend ratios if the delivery truck has not traveled far enough to provide adequate mixing. In another demonstration test, 5 minutes after filling the truck for B20, a sample taken from the top was 11.9% and another from the bottom was 24.1%. Efforts at convincing a driver to draw a sample at each delivery to check whether the blend has mixed have not yet been successful.


*Figure 1: InfraCal Biodiesel Blend Analyzer by Wilks Enterprise, Inc*

Ambient temperature is also an issue. Blending fuels in cold weather with non-heated biodiesel further reduces the chance of an adequate blend prior to delivery. Each feedstock has a different temperate at which it will begin to solidify, this is called the cloud point. To account for cold flow properties of each feedstock, B100 should ideally be kept at least 10° above the cloud point for blending and storage. If unheated biodiesel is loaded first into an empty delivery truck on a very cold day, there will be little or no mixing. These mixing challenges verify the need for on-site blend measurements.

## Pre-blending

Biodiesel and diesel fuel are also pre-blended in bulk storage tanks by a distribution company before loading into a delivery truck. Without the help of mixing that occurs in a delivery truck while traveling a bumpy road, there should be some form of mixer in the storage tank to help ensure a proper blend. Pre-blending has the same challenges facing splash blending with the addition of stratification of different concentrations in the tank due to different densities. This blending method also needs a simple measurement technique to ensure an accurate blend.

## In-Line (Injection) Blending

While not new to pipeline terminals and racks, relatively few fuel biodiesel distributors are using in-line blending. With in-line blending, the biodiesel is metered into the diesel fuel as it travels through a pipe. There are different blending system configurations and equipment. Sequential blending loads the biodiesel and diesel through the same meter sequentially.

Ratio blending loads the individual products through separate meters simultaneously. They are then blended at the downstream connection. Because the biodiesel and diesel are pumped in at the same time, they tend to mix better than they do with sequential blending. In side-stream blending, the B100 is metered into the diesel line upstream of the delivery meter prior to loading the truck. Passing through the delivery meter gives the blend an additional mechanical mix.

Additional mixing for all of these systems occurs as the fuels enter the receiving tank. These methods offer better blend consistency than splash or pre-blending. Density and viscosity changes in the biodiesel require adjustments to the meters for an accurate blend. Although manufacturers of in-line blending systems claim indisputable accuracy, a quick check for the correct blend gives real data to validate this claimed assumption.

| 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 |

*Table 1: Comparison of the EN Method 14078 and a Fixed Filter Infrared Analyzer*

| Feedstock | % Biodiesel |
|---|---|
| Coconut | 26.3 |
| Soybean | 20.4 |
| Yellow Grease | 20.1 |
| Palm | 20.5 |
| Animal fat | 20.5 |
| Rapeseed | 20.4 |

*Table 2: Comparison of different feedstocks using a fixed filter infrared analyzer calibrated for soy biodiesel*

| Feedstock | Approximate Percent FFA |
|---|---|
| Soy oil | 1 |
| Rapeseed | 3 |
| Sunflower | 3.5 |
| Palm oil | 4.5 |
| Corn oil | 9 |
| Yellow grease | 1-15 |
| Inedible tallow | 2-35 |
| Brown grease | 50-100 |
| Animal fats | 5-50 |
| Coconut | 5 |

*Table 3: Free Fatty Acid contend in Feedstock*

## Feedstock, Climate and Blending

As mentioned earlier, the choice of feedstock will affect the cold weather performance. In a study done by NERL[1], a variety of biodiesel/diesel blends were tested for a number of parameters including cloud point and Cold Filter Plugging Point (CFPP). The CFPP is the temperature at which crystals begin to form in a vehicle's fuel tank and can then plug the fuel filter. Depending on the blend this can occur well above freezing.

The feedstocks that start out with a lower free fatty acid (FFA) level operated better at low temperatures. As *Table 3* shows, vegetable feedstock sources have lower FFA levels and it increases with animal sources. Yellow grease had some of the same properties as animal biodiesels even though they were originally vegetable oils. The cold flow properties varied according to blend ratio and the feedstock used. Up to a 5% blend of biodiesel in diesel, the changes were minimal. Blends in the 10 – 20% range show significant increases in the temperature at which the crystals will form for filter plugging, especially with animal fats and brown grease. With this information, a reliable distributor may want to change blend ratios according to climate conditions to ensure that customers will have a reliable fuel.

## Infrared Measurement of Biodiesel/Diesel Blend Ratios

In the mid-infrared region, the biodiesel ester has an absorption unique to diesel due to the carbonyl band (5.7 micrometer, 1745 $cm^{-1}$) and therefore offers a quick and accurate way to measure the blend ratio. Inexpensive filter based analyzers that select the 5.7 micrometer wavelength, (*Figure 1*), allow for portable and easy analysis needed by regulatory agencies, blenders and fleet managers.

EN 14078 and the recently-passed ASTM Method D 7371, both specify mid-infrared for the biodiesel blend ratio. The data in *Table 1* shows a comparison of volumetrically mixed standards tested using a fixed filter infrared analyzer and with a Fourier Transform Infrared spectrometer (FTIR) using the EN Method 14078. The filter based infrared method was comparable in accuracy and precision to EN 14078.

A concern with any blend analysis is whether feedstock differences effect the blend ratio measurement. *Table 2* shows different feedstocks referenced to a soy biodiesel blend calibration. Most feedstock types do not require a separate analyzer calibration. Of the feedstocks tested, only the coco methyl esters require a separate calibration in order to accurately determine the blend ratio.

*Figure 2: InfraSpec VFA-IR Spectrometer by Wilks Enterprise, Inc.*

## Testing for Fuel Adulteration

With the escalating fuel prices and the lure of tax incentives, there is a temptation for the scrupulous to extend fuels with non-biodiesel additives. A common additive is pure vegetable oil that has not been transesterified to produce biodiesel. Because vegetable oil also has a carbonyl band, the measurement at the 5.7 micrometer wavelength does not distinguish biodiesel from vegetable oil. A multi-wavelength analyzer such as an FTIR or a portable Variable Filter Array (VFA) spectrometer (pictured in *Figure 2*) can scan different wavelengths and detect whether the blend contains vegetable oil. On-site testing can alert state and federal tax enforcement agencies to possible fraud.

## Conclusion

Knowing the biodiesel/diesel blend is important to distributors, engine manufacturers, fleet operators, and regulatory agencies. Many engine warrantees are not valid above a specified biodiesel percentage and fleet operators need to know the blend to ensure compliance with the warranty terms. As more states and countries are requiring diesel fuel to contain biodiesel, state Weights and Measures and other regulatory agencies need to be able to test the biodiesel blend ratio at fuel stations. The U.S. EPA also has programs promoting the reduction of emissions for existing diesel engines through the use of cleaner fuels such as biodiesel. Fleet operators need to verify that they are using a B20 blend in order to reap the financial incentives. Having a quick analytical method and portable analyzers to assess the blend ratio can be a valuable asset for fuel distributors, engine manufacturers, fleet operators, and regulatory agencies. The same instruments can also be used to quickly and easily measure the percent ethanol in gasoline.

## References

1 Production of Biodiesels from Multiple Feedstocks and Properties of Biodiesels and Biodiesel/Diesel Blends, J. A Kinast, March 2003, NREL/SR-510-31466