Biodiesel Analysis with Mid Infrared - From Feedstock to Fuel

Authors: Joe Boyd, Imperial Western Products
Sandy Rintoul, Wilks Enterprise, Inc. srintoul@wilksir.com

Introduction

The biofuels industry is growing rapidly and so is the need for analysis to ensure quality product. The parameters for quality biodiesel require different types of instruments and measurement systems, such as gas chromatographs (GC), titrators, centrifuges, infrared spectrometers... Although claims are out there for the analyzer that will do it all, unfortunately there is no one instrument, or even type of instrument, that can make all the measurements to ensure product quality.

The bottom line is bad product can cause problems in a diesel engine such as filter plugging and injector coking. These problems have made engine manufacturers wary of extending warrantees to high ratios of biofuels. Product quality begins at the production facility and extends to the final burn in the engine. Some of these analyses are for process control or quality verification and can be done with quick and simple verification tests while others require a more complete test according to the ASTM or EN approved methods. Many crucial measurements can be performed by mid-infrared (mid-IR) analysis. These measurements include free fatty acids and water in the incoming feedstock, total glycerin during transesterification in production, to measuring blend ratios (biodiesel in diesel or ethanol in gasoline) and contamination of the finished fuel on the distribution end.

The Production Facility

There are three areas where analysis is useful or necessary in the production of biodiesel; testing incoming feed stock, monitoring the reaction process and verifying the quality of the finished product.

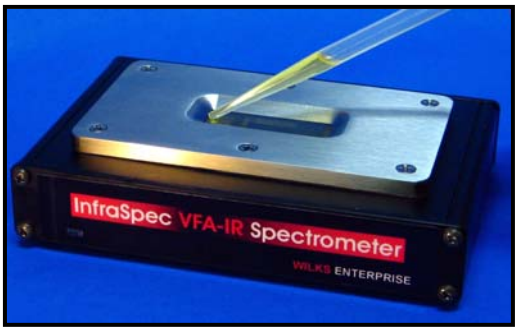
Incoming Feed Stock

Biodiesel is typically made from animal fats or vegetable oils that are chemically reacted with an alcohol (methanol or ethanol) and a catalyst (sodium or potassium hydroxide) to produce an ester or biodiesel. The process is called transesterification. Knowing the amount of Free Fatty Acid (FFA) and water in the incoming feedstock helps the producer to adjust the amount of alcohol and catalyst for a complete reaction. FFA's in oil react with the alkaline catalyst to form soap and can cause a reduction in yield. Water deactivates the catalyst.

FFA and water measurements are for the producer and do not need to be approved methods. The approved method is a non-aqueous potentiometric acid-base titration to determine the acid number. Moisture is typically measured by Karl Fischer Titration. Both of these analyses can also be done with infrared spectroscopy. Water can be extracted from the biodiesel with acetonitrile and measured in the 6 micron region. Measuring FFA involves adding a weak base to form a salt whose carbonyl absorption band is shifted away from that of the biodiesel ester. Even with sample preparation, either measurement takes under 5 minutes and does not require a skilled technician.

During the Reaction Process

Imperial Western Products (IWP) is a manufacturer of alkyl methyl esters, better known as biodiesel. IWP utilizes multiple feedstocks, including yellow grease, soybean oil and corn oil. IWP has been producing biodiesel for over 5 years and is a BQ-9000 accredited manufacturer.



They recently pioneered using a small portable mid infrared analyzer with a variable filter array, the Wilks InfraSpec VFA-IR Spectrometer (shown in the picture to the left), for measuring bound glycerin during the transesterification reaction. The InfraSpec incorporates a patented design consisting of an Attenuated Total Reflection (ATR) sample plate with an electronically modulated source on one end and a linear variable filter (LVF) coupled with a linear variable array on the other. The result is a compact spectrometer with no moving parts and no optical path exposed to air that is portable and rugged.

There are several reactors used in a batch process in which the feedstock oil is transesterified into biodiesel. The transesterification reaction in their process takes 3-4 hours. To determine when the reaction is complete, a sample must be taken from the reactor and the mass % of bound glycerin (mono-, di- and triglycerides) determined on the sample. The ASTM standard D 6751, specifies that the total glycerin, which is the sum of free and bound glycerin, must be below 0.240 mass %. Since virtually all of the free glycerin is removed downstream they are concerned only with the bound glycerin. Therefore, if bound glycerin is below 0.240 mass % the reaction is considered to be complete. If greater than 0.240 mass % the reaction is allowed to continue possibly with the addition of more reactant or catalyst.

Before testing the sample, the excess methanol and sodium hydroxide catalyst are removed by washing the sample several times with water and then drying on a hotplate. After the sample has been washed and dried it is ready for testing by either gas chromatography or the InfraSpec VFA-IR Spectrometer. Running a gas chromatogram takes approximately 45 minutes. The sample can be run on the InfraSpec Spectrometer in less than 5 minutes.

IWP found that the use of the InfraSpec Spectrometer for making pass/fail determinations can significantly reduce analysis time, by about 40 minutes, and thereby decreasing wait time and increasing throughput. It is estimated that use of the InfraSpec increased reactor throughput by 15 -20 %. Although the InfraSpec instrument can not achieve the performance of a gas chromatograph, it can be useful for quickly giving a pass/fail determination for biodiesel while in-process. Testing by gas chromatography per ASTM specifications is still necessary for finished lots of biodiesel.

Distribution Center

Ensuring Product Quality at the Buyers End

A buyer should insist on a complete Certificate of Analysis that guarantees that the fuel meets ASTM D6751 requirements or buy from a BQ-9000 certified producer. Listed in the table below are the primary concerns for engine performance and the associated official test method. For their own peace of mind they may want to verify the most important parameters for engine performance. The last column lists potential test options, some of which are different from the ASTM method and may be quicker or simpler.

Parameter	***Testing for***	***Engine problem***	***Official test method***	***Test Options***
Residual Glycerin	Free and total glycerin	Injector coking, filter plugging, shortened shelf life, sediment formation,	ASTM D6584 (GC)	GC or IR
Residual Catalyst	Sulfated ash	Injector plugging, filter plugging, ring wear	ASTM D874 (gravimetric)	Gravimetric

		issues with lubricant		
Residual alcohol	Flash point or % methanol (GC)	Degrades some plastics and elastomers, corrosive, can lower flashpoint (fire safety)	ASTM D93 (Pensky-Martens Closed Cup Tester)	Pensky-Martens Closed Cup Tester, GC or IR
FFA	Acid number	Poor cold flow properties, deposits on injectors and in cylinders	ASTM D664 potentiometric titration	Titration or IR
Water and Sediment	Water and sediment	Accelerated oxidation, filter plugging	ASTM D2709 (centrifuge)	Centrifuge
Cloud point		Reduced fuel flow in cold climates	ASTM D2500 (visual test)	Cooling system, visual test
Bacterial growth (in storage tanks)		Clogs filters, deteriorates fuel	ASTM D6974-04 (membrane filter)	Membrane filter procedure

Storage

The main concerns for storage are water, sediments, bacterial growth and old fuel contamination. Water and sediments can be tested with a centrifuge while bacterial growth requires a membrane filter procedure.

Biodiesel/diesel Blend Ratio

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 warrantee terms. The Volumetric "Blend" Tax Credit at the blender level makes the IRS concerned about the percent blend. Many regulatory Weights and Measures agencies are also required to know the blend ratio. In the mid infrared region, the biofuel ester has characteristic absorption due to the carbonyl band (5.8 um) and therefore is a quick and accurate way to measure the blend ratio. Inexpensive filter based analyzers that select the 5.8 micron wavelength, such as the InfraCal Filtometer (shown on right), allow for portable and easy analysis, ideal for onsite measurements. EN 14078 and the ASTM method currently in progress, both specify mid infrared for the biodiesel blend ratio.

Conclusion

No one method can satisfy all the measurement criteria to ensure that biodiesel meets the required standard. Mid infrared analysis is often a quicker method that can be used for production monitoring, to verify product quality on the buyers end, and to determine biodiesel blend. Filter based mid infrared analyzers offer the ease of use, portability and ruggedness that is required for in plant or field analysis. More time consuming methods such as GC and titration are sometimes required to meet ASTM or EN standard requirements. Determining whether your analysis has regulatory requirements or time, cost and labor requirements will help you decide what equipment you need for your specific analyses.