Biofuels blend measurements with portable mid-infrared analyzers

Sandra Rintoul

Globally, governments are putting more emphasis on sustainable energy sources and are creating energy policies that promote the production and use of biofuels. With the Renewable Fuels Standard-2 (RFS-2), the United States set biofuels blending volumes to 12.95 billion gallons (49.0 billion liters) for 2010, increasing to 36 billion gallons (136 billion liters) by 2022. With similar mandates or guidelines coming from other countries, the need to easily and accurately measure biofuels blends becomes more important.

BLENDING METHODS

The splash blend method is often used for blending biodiesel. With this method, the petrodiesel fuel and B100 (i.e., 100% biodiesel) are pumped separately into a delivery truck or storage tank, and it is assumed the blend will have been adequately mixed in the tank by the time the truck arrives at the delivery site. However, a demonstration test was recently conducted with the Wilks InfraCal Biodiesel Blend Analyzer (shown in Fig. 1) five minutes after filling the truck for B20. A sample taken from the top measured 11.9% biodiesel, while another from the bottom was 24.1% (c.f. *inform 19*:787–789, 2008). If the first delivery of fuel from a splash blend-loaded truck is only a few miles away on a smooth road, the chance for delivering an accurate blend/mix is far from guaranteed. And subsequent deliveries will also have an incorrect blend.

In-line (injection) blending offers better blend consistency than splash blending and is typically used for ethanol blending at pipeline racks and terminals. It is also becoming more common for biodiesel blending. The biofuel is mixed as it is metered into the pipe with the diesel or gasoline. Additional mixing occurs as the fuels enter the receiving tank or truck. For biodiesel, density and viscosity changes 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 actual data to validate this claimed assumption.

INFRARED ANALYSIS OF BIOFUELS

The approved methods for biodiesel measurement, EN 14078 and the ASTM Method D7371, both specify mid-infrared spectroscopy for the measurement of the biodiesel blend ratio. Infrared analysis works well for FAME (fatty acid methyl esters) because the biodiesel ester has a characteristic infrared absorption due to the carbonyl bond at 5.7 micrometers or 1745 cm^{-1}. In other words, as the concentration of biodiesel goes up, the infrared absorbance at that wavelength increases. The infrared absorbance can be directly calibrated to read out in percent biodiesel. The same is true for ethanol, as it has an infrared absorbance band unique to gasoline at 9.6 micrometers (1042 cm^{-1}). Again, the increase of infrared absorbance correlates with the increase in concentration of ethanol in gasoline.

ADVANTAGES OF FILTER-BASED INFRARED ANALYZERS

An infrared analyzer can be set up with a filter mounted on a detector that is specific to the analysis, in this case either 1745 cm^{-1} for biodiesel or 1042 cm^{-1} for ethanol. The advantages of a filter-based infrared analyzer are many: convenient size, lower cost, ruggedness, decreased power usage. Regulatory agencies often travel to a fuel station and check to ensure what is specified on the pump is correct. For their application, a six inch square box that will fit in their truck, operate off of a 12-volt car battery, function in a wide range of temperature and humidity, and is quite rugged with no moving parts would be ideal. These features are also important to blenders and terminal operators as they would like the advantage of checking a truck, railcar, or tank on-site after it is loaded rather than hold up a delivery while a sample is taken to a laboratory for testing.

Another critical feature is ease of use. In the analyzer pictured in Figure 1, a fuel sample is placed directly on the exposed sample window, and in less than a minute the percent ethanol or biodiesel is displayed. The sample is cleaned with a wipe, and the analyzer is ready for the next measurement.

FIG. 1. *Portable biodiesel blend analyzer.*

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TECHNICAL SERVICES AOCS

Biodiesel Expert Panel Meeting

AOCS Technical Services sponsored a meeting of biodiesel experts on Sunday, May 16, at the AOCS Annual Meeting & Expo in Phoenix, Arizona, USA. The purpose was to discuss the development of analytical methods for biodiesel. Participants introduced themselves and then proceeded with the agenda.

The update on the International Organization for Standardization (ISO)/Technical Committee (TC) Subcommittees (SC) involved with biofuels pointed out that progress on method development has been moving very slowly. This pertains particularly to ISO/TC 28/SC-7 and ISO/TC 334/SC 11 Joint Working Group Activities. Some of the methods in question are the determination of ester content by gas chromatography of mono-, di-, and triglycerides and the development of different methods for oxidative stability and phosphorus content.

Steve Howell, Mark-IV Consulting (Kearney, Missouri, USA) and National Biodiesel Board Technical Director (NBB; Jefferson City, Missouri), gave an update on activities of the NBB. The top technical priorities of NBB for 2010 are the following:

1. The impact of minor components
2. 2007/2010 Engine and after-treatment
3. Biodiesel quality enforcement
4. Boiler and heating oil research
5. Life cycle analysis/greenhouse gases
6. Biodiesel stability
7. Biodiesel transport in pipelines
8. Feedstock development
9. New, faster, and better test methods
10. Lubricating oil effects with biodiesel

Among other comments regarding this list, Howell pointed out that the National Oilheat Research Alliance (Alexandria, Virginia, USA) has a goal of achieving use of B100 (i.e., 100% biodiesel) for oil heating in the United States by 2050; this would represent 7 billion gallons (26.5 billions liters) annually. He also pointed out that different considerations come into play regarding biodiesel for heating vs. powering engines. For example, the fuel is burned in an open flame, not compressed within an engine.

Other comments were related to optimized biodiesel, which would involve development of a specific fatty acid profile; the use of pipelines to transport biodiesel, which could result in a significant savings vs. truck transport ($0.05–$0.25 per gallon); the implementation of the National Renewable Fuel Standard-2, the requirements for which went into effect July 1, 2010; and the development of methods for detecting metals in fats and oils.

Lisa Clement (Cargill Inc., Wayzata, Minnesota, USA) prepared a handout for this meeting on 21 analytical methodologies for sterol glucosides (SG) in biodiesel. The question arose whether there is a need for a method specifically for SG or for a more general method on filter-clogging components.

Other projects brought before the group included the robustness of the acid number test method (as represented by ASTM D664) for biodiesel, the cold soak filtration test method, and methodologies for monoglycerides. ■

Table 1. *Infrared measurements of different biodiesel feedstocks*

Feedstock	Biodiesel (%)	Feedstock	Biodiesel (%)
Coconut	26.3	Palm	20.5
Soybean	20.2	Animal fat	20.5
Yellow grease	20.1	Rapeseed	20.4

MAKING SURE NO BIODIESEL IS PRESENT

ASTM Method D975 currently allows up to 5% biodiesel in diesel without the requirement for biodiesel content labeling, which is a problem for some diesel users such as nuclear power plants. Fuel can be stored for as long as 10 years to power their standby diesel generators in case of an electrical power shut down. Emergency diesel generators (EDG) supply electrical power to safely shut down the nuclear reactor in the event of a loss of normal off-site power, and they supply power to critical items such as cooling pumps for decay heat removal. Biodiesel is a natural food source for microbial growth; and while biocides should prevent the growth of bacteria, fungi, and mold, nuclear power plants cannot risk that microbial growth could clog filters and shut down the EDG. In cold weather areas, there is also concern that the cold-flow properties of biodiesel-blended fuel may cause it to gel in cold temperatures and again clog filters. Therefore, it has become necessary for many standby generator operators to determine whether their fuel delivery contains biodiesel.

Pipeline operators also need to know that the product they deliver to their customer is as specified. If they receive diesel to be shipped on their pipeline and biodiesel is in the fuel, they have the risk of residual biodiesel being present in a fuel delivery to a customer that requires no biodiesel, such as jet fuel users or nuclear power plants. For low level analysis, more than one infrared wavelength is useful to be able to compensate for the variations found in different diesel fuels. The biodiesel detection measurement can also be done with a filter-based analyzer, this time with a spectrometer that uses a linear variable filter that covers a spectral range of 5.4–10.8 µm (1850–925 cm^{-1}) coupled with a 128 pixel detector array. The variable filter array (VFA) spectrometer is also compact and portable with a low power requirement and no moving parts. It is capable of detecting the presence of biodiesel below 500 ppm.

COMPARISON OF DIFFERENT BIODIESEL FEEDSTOCKS

A concern with any biodiesel blend analysis is whether feedstock differences affect the blend ratio measurement. Table 1 shows the analysis of a nominal 20% biodiesel blend from 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.

COMPARISON TO ANALYTICAL METHODS

The most common question is: How do filter-based infrared analyzers compare to other reference methods? In Table 2 the data for

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MASS SPECTROMETRY AND PRIONS (CONTINUED FROM PAGE 520)

of analysis is typically reserved for proteins that bind other proteins. Since prions don't crystallize, it remains an effective means of checking models with experimental reality.

These analytical approaches are not restricted to prions. There are many proteins that are glycosylated and therefore difficult to analyze. The presence of the GPI anchor with its covalently attached lipid tail further complicates analysis, since it is often difficult to ionize such proteins. Modern mass spectrometry allows us to bypass the constraints imposed by the presence of diverse post-translational modifications and pesky lipids.

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these analyzers are compared to those from ASTM D7371 and EN 14078, which are the US and European methods for biodiesel blend analysis. Table 3 shows a comparison of results from an infrared ethanol blend analyzer to those from tests done by oxygenate flame ionization detection (O-FID). Both sets of data show good correlation between analytical methods.

CONCLUSION

With governments around the world striving for independence from imported fuels, the desire to reduce greenhouse gas emissions, and the recent impact of a major fossil fuel spill, biofuels are becoming a more popular fuel source. As higher percentages of biofuels enter the supply chain, knowing the biodiesel/diesel or ethanol/gasoline blend becomes more important for regulators, distributors, blenders, pipeline operators, and end-users. Having a quick analytical method for blend ratio measurements, which portable infrared analyzers provide, can be a valuable asset for the biofuels industry.

Table 3: *Infrared filter based analyzers compared to O-FID*[a]

Ethanol O-FID (vol%)	InfraCal ethanol blend analyzer	Ethanol O-FID (vol%)	InfraCal ethanol blend analyzer
9.87	9.9	9.97	10.1
9.89	9.8	9.7	9.5
9.84	9.8	10.48	10.5

[a]O-FID, oxygenate flame ionization detection.

Sandra Rintoul is president of Wilks Enterprise, Inc. (Norwalk, Connecticut, USA) and has worked with filter-based mid-infrared analyzers for over 25 years. Her experience ranges from assembly, service, technical support, applications support, and product development to business management and marketing. Contact her via email at srintoul@wilksir.com.

Table 2. *Infrared filter-based analyzers compared to EN and ASTM blend measurement methods*[a]

Sample ID	EN 14078 FTIR	ASTM D7371 FTIR	Single wavelength biodiesel analyzer	Variable filter array infrared spectrometer
105-003	0.2	0	0.2	0.22
1.0 STD	1.1	1.15	1.3	1.4
5.02 STD	5	4.99	5	5.12
30.0 STD	30.2	30.07	30	30.11
50.0 STD	50	50.06	50.4	50.6

[a]STD, biodiesel; FTIR, Fourier-transform infrared.

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