Application Note: 51258

Biodiesel (FAME) Analysis by FT-IR

Mike Bradley, Ph.D., Thermo Fisher Scientific, Madison, WI, USA

Key Words

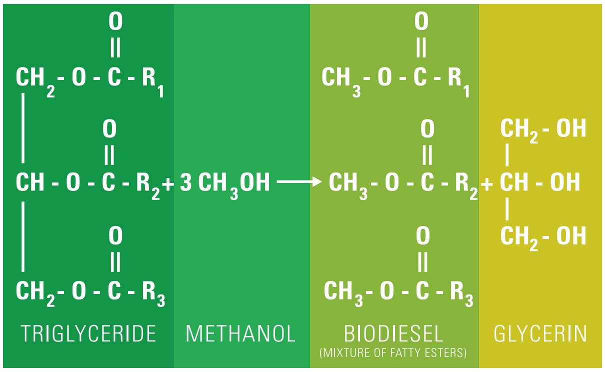
- **Attenuated Total Reflectance (ATR)**
- **Biodiesel**
- **Biofuel**
- **Chemometrics**
- **Diesel Blend**
- **FAME**
- **Fatty Acid of Methyl Ester**
- **FT-IR**
- **Palm**
- **Rapeseed**
- **Soy**

Introduction

The compression-ignition engine patented by Rudolf Diesel used large injectors to prevent clogging by the viscous, heavy fuels, which were unrefined petroleum and vegetable oils. Because of the size of the engines, large warships, like the *HMS Queen Elizabeth* class battleships, were among the first mobile users of Diesel's technology. In the 1920's, technological changes made possible much smaller diesel engines, which required lower viscosity fuels. The petroleum industry began producing inexpensive medium-weight diesel fuels, essentially shutting down the biofuel market.

Several developments spurred new interest in biofuels. While the increase in petroleum costs has been the big motivator, pollution concerns and political pressure to decrease dependence on foreign fuel stocks have also risen. The interest is worldwide. Countries that have no domestic petroleum reservoirs are intensely investigating biodiesel opportunities.

Vegetable and animal fats consist of triglycerides, three-carbon backbones with long chain fatty acids hanging off. In their native form, these materials have poor characteristics as fuels. Transesterification is a chemical process whereby the triglyceride is reacted with an alcohol, as shown in Figure 1. Methanol is commonly used, so the process makes glycerol and fatty acid methyl esters, or FAME. Once separated from the glycerol and washed, FAME, which is also called biodiesel, has flow properties and ignition properties (cetane values) compatible with most diesel engines.



$$\begin{matrix} CH_2-O-\overset{O}{\overset{\|}{C}}-R_1 \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-R_2 \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R_3 \end{matrix} + 3\,CH_3OH \longrightarrow \begin{matrix} CH_3-O-\overset{O}{\overset{\|}{C}}-R_1 \\ CH_3-O-\overset{O}{\overset{\|}{C}}-R_2 \\ CH_3-O-\overset{O}{\overset{\|}{C}}-R_3 \end{matrix} + \begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix}$$

Figure 1: The chemistry of transesterification

Biodiesels are often blended with petroleum diesel to make biodiesel blends. These are denoted as B#, where the number refers to the percent biodiesel. B100 would be pure FAME; B20 and B2 are fairly common blend levels. B100 fuel has a desirable pollution profile (no sulfur, no aromatics, particulates down by 70%, and slightly elevated NO_X emission) relative to petroleum diesel.

Diesel engines depend upon the fuel for lubrication. Regulations lowering the allowed sulfur content in fuels have considerably reduced the lubricity of petroleum diesel. FAME restores the lubricity even at the B2 level, making biodiesel extremely attractive as an additive. Additionally, several legislative acts provide benefits for users of biodiesel, including alternative fuel credits and tax breaks.

The analytical issues with biodiesels have two sources. The production facilities and terminal services need to ensure quality (completion of transesterification, glycerol removal, etc.) while testing labs and regulatory agents must ensure the labeled blend levels are present. The former are generally concerned with high FAME content materials (B100), while the latter may be exposed to a wide range of FAME content, from B2 and B20 up to B100. Infrared provides a rapid, precise and accurate tool for this analysis when these needs are taken into account.

Experimental

A Nicolet™ 380 Fourier transform infrared spectrometer equipped with standard KBr beam splitter and DTGS detector was used. The Smart ARK™ attenuated total reflection accessory was used to collect the data, with tremendous advantages as noted below. Spectra were collected in 40 seconds (32 scans and 4 cm^{-1} resolution). The Smart ARK made sample introduction and cleaning extremely simple, and required no more than 0.4 ml of the sample. The crystal was cleaned either with a mixture of acetone-toluene-methanol, or with the next sample. The tri-solvent cleaning method was used before background collection.

The data were collected using OMNIC™ spectroscopy software, and the chemometrics were performed using TQ Analyst™. The procedures for the analysis followed, in general, the guidelines being developed by the ASTM Committee on biodiesel analysis using PLS.

Biodiesel and biodiesel blend samples came from the Missouri Department of Agriculture Alternative Fuels Office, the National Renewable Energy Laboratory in Colorado and South Korea. Additional samples from an oil terminal in Madison, Wisconsin and from a home producer were also examined. This covered a wide range of petroleum and biodiesel sources.

Results and Discussion

The infrared spectra of a No. 1 Diesel and FAME (from soybean oil) are shown in Figure 2. The strong ester peaks at 1750 (the C=O vibration) and around 1170 – 1200 cm^{-1} (C-O vibrations) are clear, and are the basis for the quant procedure. There is no interference in the 1750 cm^{-1} region, but the petroleum signals do interfere with the 1170 – 1200 cm^{-1} region. There can be considerable variation in petroleum stocks, which can affect the quant method as discussed below.

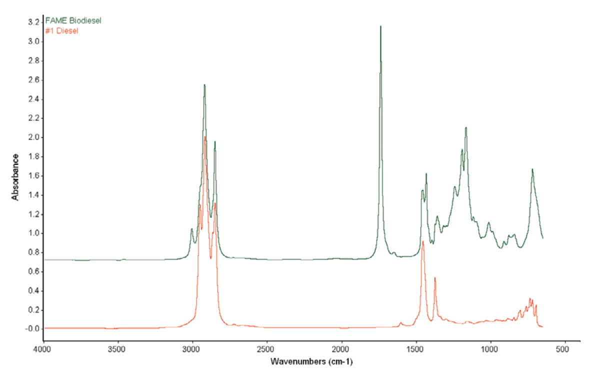


Figure 2: Spectrum of a #1 Diesel and FAME

The intensity of absorbance is related to the cell path length, the sample's absorptivity, and its concentration (Beer-Lambert Law). Accurate quantitative work requires that the absorbance stay within the linear range for the instrument. For infrared, this generally means the absorbance should not exceed 1.2 Au, with path length being the only variable for a user. The Smart ARK uses interchangeable top plates, with fixed crystals, to alter the path length in an ATR experiment. The affect of this is seen in Figure 3. The 45° ZnSe plate shows FAME absorptions exceeding the 1.2 Au limit from B30 and higher. The 60° ZnSe plate gives a signal of around 0.8 Au for FAME, well below the 1.2 Au limit. The 45° plate is more suited for the lower concentration samples, as the ester peaks are more intense. The plate interchange is reproducible since the plates snap in – no adjustments – so there is no need for recalibration.

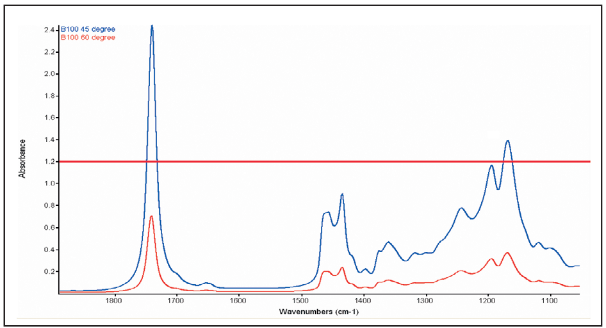


Figure 3: Spectrum of FAME collected on the 45° and 60° ARK plates

The ASTM method recommends PLS be used for the analysis of biodiesels. Essentially, PLS models the variation in sample and matrix, so a well-defined set of standards is required to cover the range of matrix effects. Calibrations for the two plates are shown in Figures 4 and 5. Clearly, the process is very well modeled even with a low number of PLS factors. Prediction of a series of unknown samples gave answers within ± 0.07 or better over the low range (45° plate), and ± 0.1 or better over the high range (60° plate).

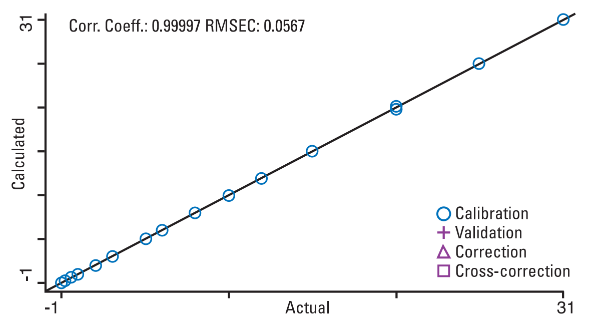


Figure 4: Calibration result for a 45° ARK ATR biodiesel blend

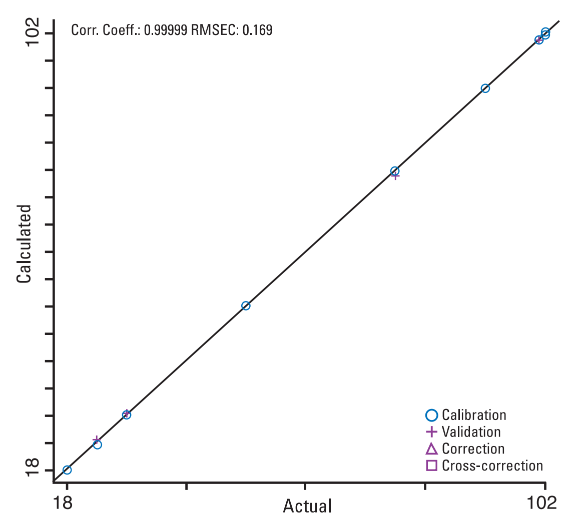


Figure 5: Calibration result for a 60° ARK ATR biodiesel blend

The key concern for testing labs is that the variability in petroleum diesels from region to region must be modeled for the analysis to be useful. Initial predictions (using a calibration based on one petroleum stock) of a set of biodiesel blends made with a different petroleum base gave poor results, as shown in Table 1, due to the un-modeled behavior of the petroleum base. Incorporation of only three samples with the different petroleum base improved these predictions dramatically, as seen in column three of the table. None of the biodiesel stocks examined thus far shows extreme variation.

Actual B%	Initial Prediction	Inoculated Method
18.00	15.95	17.92
20.00	14.36	20.01
2.00	1.21	2.03

Table 1: Data showing effect of training a PLS method with standards covering petroleum base variability.

Transfer of the calibration between spectrometers can be addressed with the Thermo Scientific ACLS algorithm, developed by Sandia National Laboratories. Figure 6 shows data taken from two spectrometers, one being used to predict the other. A small offset is visible. The ACLS algorithm removes this offset cleanly. Thus, once a calibration is built on one spectrometer, methods can be transferred to another spectrometer by “inoculating” the method with data from the second unit, as is frequently done in FT-NIR applications.

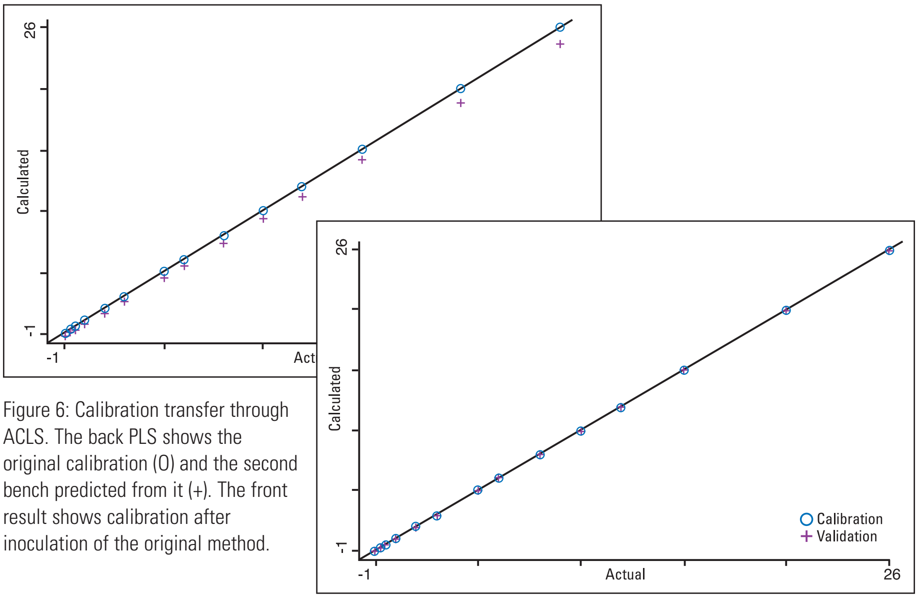


Figure 6: Calibration transfer through ACLS. The back PLS shows the original calibration (O) and the second bench predicted from it (+). The front result shows calibration after inoculation of the original method.

The methods developed thus far have focused only on the FAME content, in keeping with the work being outlined by the ASTM D02 committee. However, FT-IR can be used to analyze for many other components, including free fatty acids or glycerol, with proper calibration. A generalized method could be developed given a proper set of standards.

Conclusions

Biodiesel is appearing more commonly in the media, and is evoking interest at many levels. The need for a rapid and simple analysis tool for FAME is filled very effectively by the Nicolet FT-IR spectrometer family coupled with the unique Smart ARK ATR accessory. Our product offering includes a booklet that covers the analysis of biodiesel, including a step-by-step procedure for data collection. With the addition of the OMNIC and TQ Analyst software packages, Thermo Scientific’s biodiesel analysis package provides the scientific knowledge and instrumental capabilities needed for this analysis.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Australia	+61 2 8844 9500
Austria	+43 1 333 50340
Belgium	+32 2 482 30 30
Canada	+1 800 532 4752
China	+86 10 5850 3588
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