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Biodiesel: a renewable and biodegradable fuel

New US specification ensures product identity and quality for biodiesel

M. BOWMAN, D. HILLIGOSS and **S. RASMUSSEN,** PerkinElmer Life and Analytical Sciences, Shelton, Connecticut, and **R. THOMAS,** Scientific Solutions, Washington, DC

> Comments? Write:
> editorial@HydrocarbonProcessing.com

Biodiesel is a renewable and biodegradable fuel refined from vegetable oil (or animal fat). It is rapidly gaining momentum in the US as an alternative fuel source for diesel engines. Currently, the industry is producing approximately 300 million gallons per year (gpy) of biodiesel, but, with the anticipated demand, additional manufacturing plants are being built. This will increase production by another 600 million gpy in the near future.

What is commercially attractive about biodiesel, besides not being refined from crude oil? Compared to petroleum diesel, biodiesel is environmentally friendly and is government mandated. It reduces carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2), hydrocarbons (HC) and other particulate matter emissions that cause respiratory damage. Biodiesel also eliminates the cloud of dense, black smoke normally associated with diesel vehicles. The exhaust fumes from an engine running biodiesel smells like popcorn or french fries. It also has better lubricity than diesel fuel because of its higher viscosity.

Benefits. Some of the advantages that biodiesel has over petroleum-based diesel include:

Requires less energy. The fossil fuel energy required to produce biodiesel from soybean oil is only 30% of the energy contained in one gallon of the fuel. In other words, approximately 3.2 units of fuel energy are generated from biodiesel for every unit of fossil energy used to produce the fuel. That estimate includes the energy used in diesel farm equipment and transportation vehicles (trucks, locomotives); fossil fuels used to produce fertilizers and pesticides; fossil fuels used to produce steam and electricity; and methanol used in the manufacturing process.

Harmful emissions reduction. When biodiesel displaces petroleum, it reduces levels of global warming gases such as CO_2. As plants like soybeans grow, they take CO_2 from the air to make the stems, roots, leaves and seeds. After the oil is extracted from soybeans, it is refined into biodiesel and, when burned, produces CO_2 and other emissions, which are returned to the atmosphere. However, this cycle does not add to the CO_2 level in the air because the next soybean crop will reuse the CO_2 to grow.

Another important environmental factor is that biodiesel reduces tailpipe particulate matter (PM), HC and CO emissions. These benefits occur because biodiesel contains 11% oxygen (O_2) by weight. The presence of O_2 allows the fuel to burn more completely, resulting in fewer emissions from unburned fuel. This same principle also reduces air toxicity, which is associated with the unburned or partially burned HC and PM emissions. Testing has shown that PM, HC and CO reductions are independent of the vegetable oil used to make biodiesel. This has been confirmed by the EPA, which reviewed 80 biodiesel emission tests and concluded that the benefits are real and predictable over a wide range of biodiesel blends.

Biodiesel's environmentally friendly image has captured the attention of one of the US's most famous and controversial celebrities. While Willie Nelson travels from venue to venue in his luxurious touring bus, one of the trucks in his ensemble tows a tank of biodiesel, which refuels the bus, pictured here. Nelson is so enamored by this new fuel that he formed a bioenergy company – Willie Nelson's Biodiesel. The main product, *BioWillie,* is predominantly refined from soybeans and is being marketed directly to US truck stops and gas stations.

Human health. It is well-documented that many PM and HC emissions from petroleum diesel fuel combustion are toxic and suspected of causing cancer and other life-threatening diseases. Using biodiesel can eliminate a significant number of these toxic components. Biodiesels' positive impact on air toxicity is supported by numerous studies, including the Bureau of Mines Center for Diesel Research (BMCDR), The Department of Energy (DOE) and Southwest Research Institute (SRI). The National Biodiesel Board (NBD) also conducted Tier I and Tier II health effect studies under "The Clean Air Act" that also support these claims. Recently, the Department of Labor's Mining Safety Health Administration (MSHA) tested and approved using biodiesel in underground mining equipment where workers are exposed to high levels of diesel exhaust.

Low sulfur content. Currently, the sulfur specification for petroleum-based diesel fuel is less than 500 parts per million (ppm). However, by the end of 2006, all US highway diesel has to contain less than 15-ppm sulfur. Most biodiesel fuels being manufactured today contain less than 15-ppm sulfur and some have levels that are too low to measure.

Improved lubricity. Engine manufacturers depend on good lubrication to keep moving parts, such as fuel pumps, from wearing prematurely. Biodiesel is approximately twice as viscous as petroleum diesel and therefore has better lubricating properties. This is an extremely important property when biodiesel is blended with ultra-low-sulfur diesel, which is known to be a poor lubricant. Even the lubrication properties of dry fuels such as kerosine can be improved by using 2% biodiesel.

Implementation is seamless. Probably the biggest benefit to using biodiesel is that it is easy to use. No new equipment is necessary and conventional diesel engines can seamlessly run up to 20% biodiesel blends. However, minor modifications to the engine are required to run neat, undiluted biodiesel. Biodiesel/ petroleum diesel blends can also be stored in diesel fuel tanks and pumped with diesel equipment.

Production. Biodiesel is refined by transesterfication, where a vegetable oil or animal fat is reacted under heat with an alcohol, in the presence of a catalyst. The chemical reaction products are an alkyl ester, commonly referred to as a biodiesel and glycerol (Fig. 1).

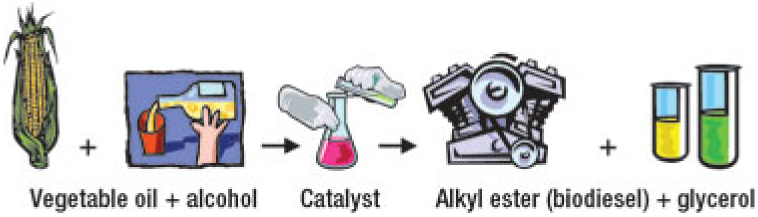

Fig. 1 Simplified transesterfication of vegetable oil into biodiesel (alkyl ester).

The reacting components in vegetable oil are mono-, di- and triglycerides, consisting of long chains of carbon and hydrogen atoms or fatty acids. For example, soybean oil consists of pure triolein, which is a triglyceride where all three fatty acid chains are oleic acid. If triolein is reacted with methanol at 120°F, using potassium hydroxide as a catalyst, the alkyl ester called methyl oleate will be formed together with glycerol ($C_3H_8O_3$) as a by-product (Fig. 2).

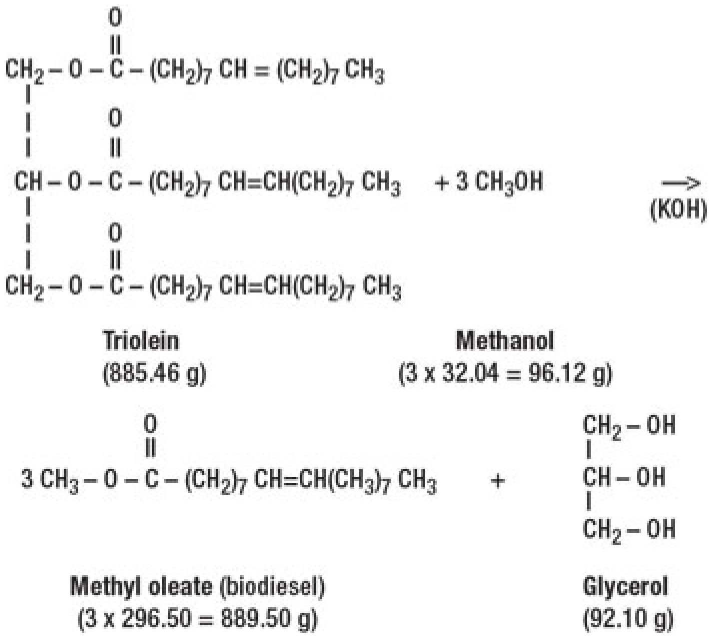

Fig. 2 Methyl oleate (biodiesel) production from soybean oil.

The biodiesel yield from this chemical reaction is in the order of 100%. Thus, a unit weight of vegetable oil will produce the same unit weight of biodiesel. The process is so straight-forward that many people are making biodiesel in their garages at home for only a few thousand dollars investment. Bulk cooking oil can be purchased from a restaurant wholesale supplier; potassium hydroxide can be obtained from a hardware store, while alcohol can be purchased from a racetrack or chemical supplier. Once the chemicals are mixed at the right temperature and allowed to stand for a couple of hours, the mixture will separate into two distinct layers. The biodiesel (alkyl ester) will form at the top while the glycerol will settle to the bottom. Once the alkyl ester is separated from the glycerol and washed with water, it is ready to be used in a diesel engine.

However, it must be emphasized that, even though the transesterfication process is relatively straightforward, homemade biodiesel is not going to generate the highest-quality product. It will most probably contain impurities like residual alcohol, moisture, unreacted vegetable oil (triglycerides), incompletely reacted mono- and diglycerides, free fatty acids and trace metals from the catalyst.

Commercial manufacturers must ensure that the manufacturing process quality is well-controlled in order to produce bulk biodiesel for blending with petroleum products. For that reason, all commercial-grade biodiesel has to conform to the American Society of Testing Materials International's ASTM D6751 specification if it is going to be used in diesel engines.

Although neat, undiluted biodiesel can be used in most diesel engines, the engine has to be modified in order to ensure trouble-free, long-term use. It is therefore more usual for it to be blended in small quantities with petroleum diesel. Biodiesel blends are typically denoted as "BXX" with "XX" representing the percentage of biodiesel contained in the blend. For example, B20 is a 20% biodiesel, 80% petroleum diesel mix. Many states are now passing legislation to mandate that all petroleum diesels for road use contain at least 2% biodiesel.

Standard specification. The National Biodiesel Board has adopted ASTM D-6751 as the standard to produce B100 biodiesel. In fact, a fuel cannot technically be called a biodiesel unless it meets the specifications set down in D-6751. The method covers the analytical methodology and specification for biodiesel grades S15 and S500 (variable sulfur content) that are used as blend components in low- and high-sulfur petroleum diesel fuels. The analytical methodology for each analyte and its specifications limits are summarized in Table 1.

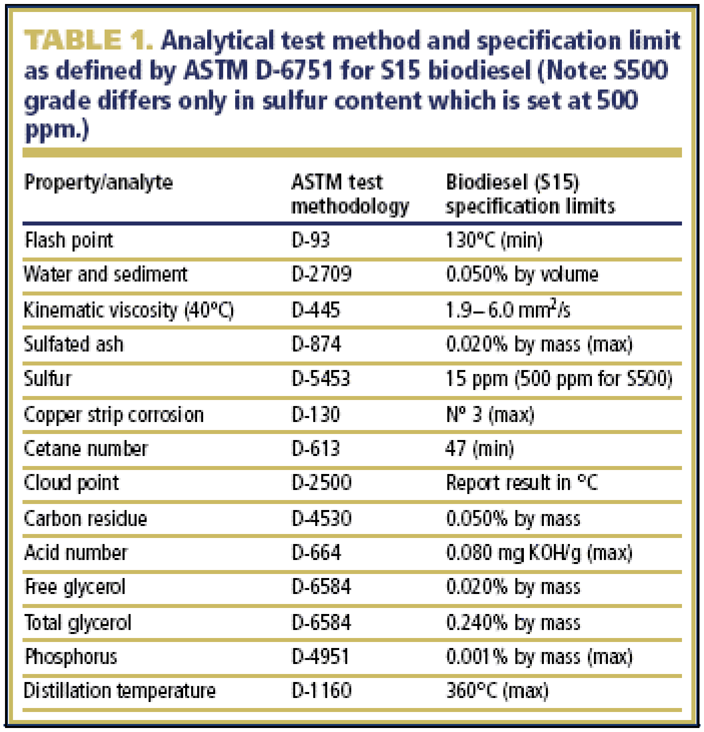

TABLE 1. **Analytical test method and specification limit as defined by ASTM D-6751 for S15 biodiesel (Note: S500 grade differs only in sulfur content which is set at 500 ppm.)**

Property/analyte	ASTM test methodology	Biodiesel (S15) specification limits
Flash point	D-93	130°C (min)
Water and sediment	D-2709	0.050% by volume
Kinematic viscosity (40°C)	D-445	1.9– 6.0 mm^2/s
Sulfated ash	D-874	0.020% by mass (max)
Sulfur	D-5453	15 ppm (500 ppm for S500)
Copper strip corrosion	D-130	Nº 3 (max)
Cetane number	D-613	47 (min)
Cloud point	D-2500	Report result in °C
Carbon residue	D-4530	0.050% by mass
Acid number	D-664	0.080 mg KOH/g (max)
Free glycerol	D-6584	0.020% by mass
Total glycerol	D-6584	0.240% by mass
Phosphorus	D-4951	0.001% by mass (max)
Distillation temperature	D-1160	360°C (max)

This standard, which is comprised of both physical and chemical tests, is meant to guarantee that all biodiesel manufactured for use as a blend for diesel engines conforms to a purity standard. This ensures that the refining process is under control and produces a product that has no adverse effects on the engine, is going to run with no long-term engine components degradation, is contaminate free and is not going to pollute the air with any toxic gases or particulates.

D-6751, which was originally adopted as a standard by the ASTM committee on Petroleum Products and Lubricants in 2003, is actually made up of a compendium of 14 ASTM standard methods, and references an additional 21 other methods. Some of these test methods include:

- **Flash point** using D-93 – A closed-cup test method: This is an indicator of the level of unreacted alcohol remaining in the fuel.

- **Viscosity** using D-445 – A dynamic viscosity test method: Too high or too low a viscosity can result in power loss due to inefficiency in the injection pump.
- **Sulfur** using D-5453 – An ultraviolet (UV) fluorescence method: Sulfur degrades engine wear by leaving deposits on engine components. It also impacts emission-control systems performance.
- **Acid number** using D-664 – A potentiometric titration test method: This is used to indicate the level of free fatty acids or processing acids in biodiesel.
- **Phosphorus** using D-4951 – An inductively coupled plasma atomic emission spectrometry (ICP-AES) test method: High levels of phosphorus have been shown to damage catalytic converters used in emission control systems. Note: Because ICP-AES is a rapid, multi-element technique, many labs are also determining calcium, magnesium, sodium and potassium using this method, to determine if the biodiesel contains any trace metal contamination derived from the catalyst and other material.
- **Free glycerol** using D-6584 – A gas chromatography (GC) test method: Free glycerol, which is a by-product of the transesterfication process, causes injector deposits, which can clog the fuel system. It can also build up in the bottom of storage and fuel tanks.
- **Total glycerol** using D-6584 – A GC test method: This measures the level of free glycerin plus any unreacted oil or fats (mono-, di- or triglycerides) in the biodiesel. These unreacted glycerides can cause injector deposits and may adversely affect cold-weather operation.

Of all the individual ASTM test methods that cover biodiesel analysis and specification, probably the most important with regard to monitoring the actual refining process is ASTM D-6584 – determining free and total glycerin in B-100 biodiesel methyl esters by GC. Measuring the level of free glycerol and any unreacted mono-, di- or triglycerides in biodiesel will indicate how efficient the transesterfication reaction is proceeding. Ideally, all the vegetable oil will react with the methanol and be converted to the methyl ester. Analyzing the sample using this GC method will give an indication if there are any unreacted triglycerides in the final product as well as any traces of free glycerol.

ASTM D-6584. This describes a method for quantitatively determining free and total glycerol in B-100 methyl esters (biodiesel) by GC using flame ionization detection (FID) technology. The detection range for this method is 0.005% – 0.05% for free glycerol and 0.5% – 0.5% for total glycerol. The sample is first derivatized with a silyating agent and then injected into an open tubular GC column packed with a 5% phenylpolydimethylsiloxane.

Calibration is achieved with two internal standards (butanetriol and tricaprin) and four reference materials. Mono-, di- and triglycerides are determined by comparison with mono-olein, di-olein and tri-olein, respectively. Conversion factors are then applied to the results for mono-, di- and triglycerides to calculate the sample's bonded glycerol content. The total glycerol represents the sum of the free and bonded glycerol.

Operating conditions. One microliter (1µL) of sample is injected onto the column, which is then heated to 50°C. Initially, the GC oven is ramped up to 180°C at 15°C/min. It is then increased to 230°C at 7°C/min. Finally, it is ramped to 380°C at 30°C/min and held there for 10 minutes. The resulting chromatographic peaks are driven off the column using hydrogen or helium carrier gas at 3 mL/min and detected using an FID (Table 2).

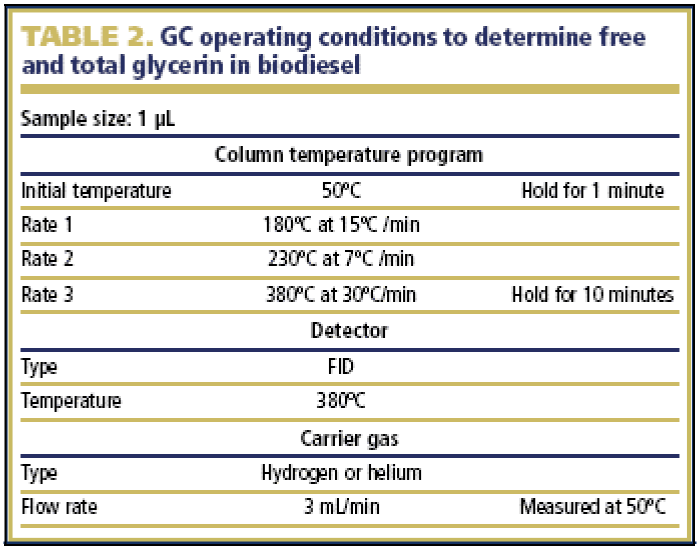

TABLE 2. GC operating conditions to determine free and total glycerin in biodiesel

Sample size: 1 µL		
	Column temperature program	
Initial temperature	50°C	Hold for 1 minute
Rate 1	180°C at 15°C /min	
Rate 2	230°C at 7°C /min	
Rate 3	380°C at 30°C/min	Hold for 10 minutes
	Detector	
Type	FID	
Temperature	380°C	
	Carrier gas	
Type	Hydrogen or helium	
Flow rate	3 mL/min	Measured at 50°C

The eluting peaks are then identified and quantified by comparing retention times and peak areas with the calibration standards, and the relative peak intensities and masses of the internal standards. Typical chromatograms for a calibration standard and two biodiesel samples using ASTM Method D-6584 are shown in Figs. 3, 4 and 5, respectively. Fig. 3 represents a calibration mixture spectral display of glycerol, mono-, di- and triglycerides (as mono-, di- and tri-olein) and the internal standards butanetriol and tricaprin. The x-axis shows retention time, while peak intensity is shown on the y-axis. Concentration values for all six components are summarized in Table 3.

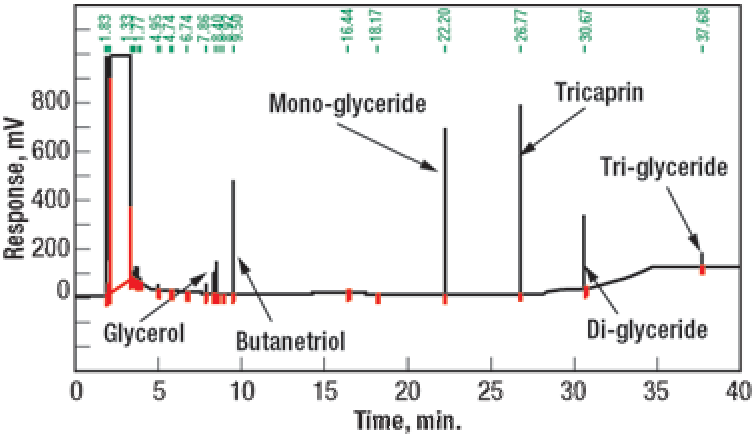

Fig. 3 Chromatographic display of a calibration mixture of glycerol, mono-, di- and triglyceride and the internal standards butanetriol and tricaprin – generated using ASTM Method D-6584 (see Table 3 for concentration levels).

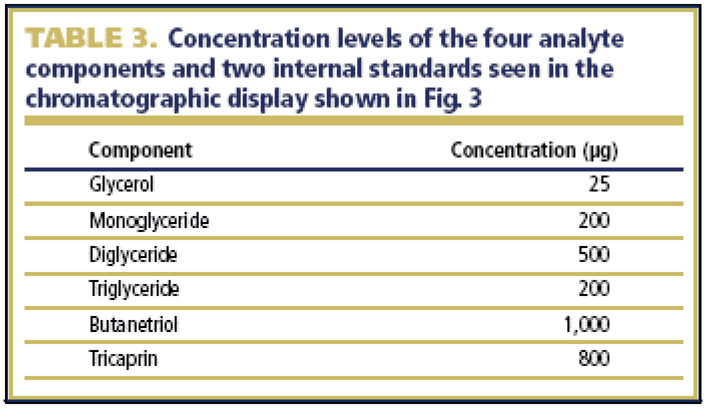

TABLE 3. Concentration levels of the four analyte components and two internal standards seen in the chromatographic display shown in Fig. 3

Component	Concentration (µg)
Glycerol	25
Monoglyceride	200
Diglyceride	500
Triglyceride	200
Butanetriol	1,000
Tricaprin	800

It can be seen that the glycerol retention time is in the order of 8.5 min, while the mono-, di- and triglycerides are seen at 21.8 min, 30.7 min and 37.7 min, respectively. As expected, strong spectral signals are also seen for butanetriol and tricaprin at 9.5 min and 26.8 min, respectively. Fig. 4 identifies a biodiesel sample with low levels of glycerol, mono- and diglycerides, but no triglyceride, whereas Fig. 5 shows that the second sample contains no glycerol or triglyceride, a very small amount of diglyceride and a high level of monoglyceride. Both these biodiesel samples met the free and total glycerol specifications shown in Table 1.

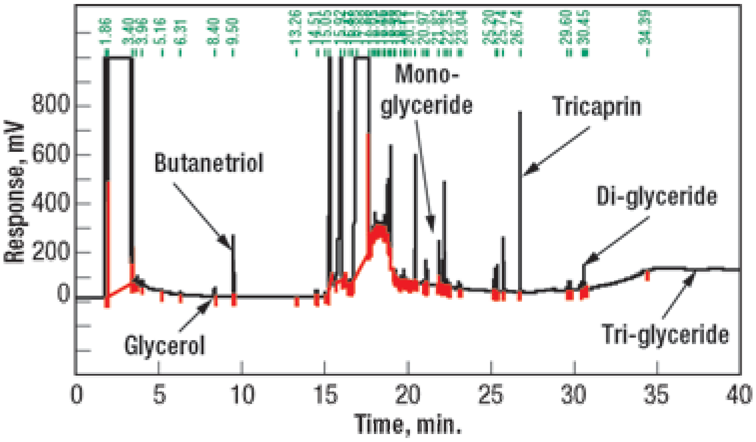

Fig. 4 Chromatogram of a biodiesel sample with low levels of glycerol, mono and diglycerides, but no triglyceride – generated using ASTM Method D-6584.

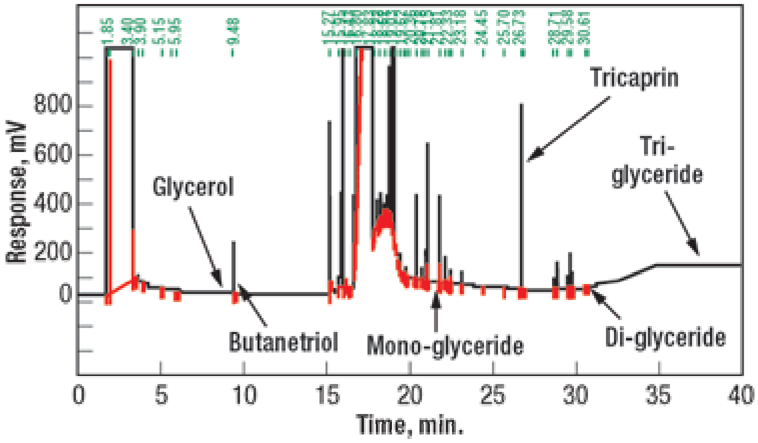

Fig. 5 Chromatogram of a second biodiesel sample showing no glycerol or triglyceride peaks, but very small amounts of diglyceride and a high level of monoglyceride – generated using ASTM Method D-6584.

The final analysis. Biodiesel represents a small but tangible way of breaking total dependence on fossil fuels. It is relatively straight-forward to produce and can be blended with petroleum diesel with no modifications to the engine. It is environmentally friendly because its combustion emission gases are nontoxic to the atmosphere – and it is also extremely biodegradable, posing no long-term health problems.

However, the relatively simple and inexpensive production process could also prove to be a disadvantage, because it will attract many commercial manufacturers. It is therefore absolutely essential that, if biodiesel is going to compete with fossil fuels, it must be manufactured to the highest purity standards. The only way this can be guaranteed is to ensure that the process is well-controlled by manufacturing to strict quality specifications like ASTM D-6751. There is no question that, by using sensitive instrumental techniques like GC, ICP-AES, UV fluorescence spectrometry and other traditional technology to monitor both the physical and chemical properties, it will help to enhance biodiesel's reputation as a high-quality, environmentally safe viable alternative to petroleum-based fuels. **HP**

The authors

Matt Bowman spent 12 years in the industry focused on instrumentation, process optimization and quality improvement. He joined PerkinElmer LAS in 2004 as a business development specialist and was recently promoted to global technical sales development manager. His key responsibilities are working with chemical, petrochemical and refinery customers to find innovative solutions for their toughest problems.

David Hilligoss is the business development manager for new and used oils business at PerkinElmer LAS. He has been with PerkinElmer for 29 years in numerous field application and support positions in the analytical instruments business. Mr. Hilligoss's current responsibilities are working with the lubricants industry in understanding their needs to develop better applications and instrumentation.

Sandra Rasmussen is the business unit manager for the gas chromatography business at PerkinElmer LAS and has over 20 years experience in the analytical instruments and biotechnology industry. She joined PerkinElmer in 1989 and has held senior roles in technology, marketing and business management throughout her career there.

Robert Thomas runs his own scientific writing company, Scientific Solutions. He has written over 50 articles/ papers covering a wide variety of topics including analytical chemistry, spectroscopy, industrial process monitoring, biotechnology and life science subject matter. Mr. Thomas recently published a textbook on trace metals' analysis entitled, *Practical Guide to Inductively Coupled Plasma Mass Spectrometry (ICP-MS)* and he can be contacted on his Website at: www.scientificsolutions1.com.

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