OVERVIEW OF BIOFUELS AND THE ANALYTICAL PROCESSES USED IN THEIR MANUFACTURE

As the cost of crude oil on the wholesale market continues to hover near $70 per barrel, and the United States and Western Europe remain dependent on petroleum imports from the politically unstable Middle East, biofuels and fuel additives are receiving an ever-increasing amount of attention from both commercial refiners and the general public. This has been furthered along by building public and scientific awareness of so-called “greenhouse gasses” and their potential deleterious effects on the natural environment.

These alternative products are manufactured from biomass, which is organic matter such as wood, plants, and organic wastes. Unlike other renewable energy sources, biomass can be converted directly into liquid fuels for transportation purposes. These biofuels are being researched and developed as direct replacements for petroleum-based fuels and as additive partial replacements (admix) to “stretch” existing petroleum reserves and reduce overall dependence on fossil fuels. For example, every one barrel of ethanol produced displaces 1.2 barrels of petroleum.

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The secondary goal is to reduce air pollution caused by combustion of petroleum-based fuels, where the additive serves as an oxygenate. At this time the leading biofuels/additives are ethanol (for gasoline and diesel) and biodiesel (for diesel).

This white paper will provide an overview of biofuel development for the transportation sector, the biofuels market, and laboratory testing processes used in quality control and general research.

Ethanol’s Rapid Market Expansion

Brazil is the world’s largest ethanol producer and exporter, generating 4 billion gallons in 2004 representing 37 percent of the world’s total. The United States is second, and is also the second largest ethanol importer.

In August 2005, President Bush signed the Energy Policy Act of 2005 (EPAct 2005), which included the Renewable Fuels Standard (RFS) that established the first nationwide baseline for the use of fuels derived from renewable sources. RFS required petroleum refiners to use at least 4 billion gallons of renewable fuel beginning in 2006, increasing incrementally to 7.5 billion gallons per year by 2012. Then, in his January 2006 State of the Union Address, President Bush informally furthered this goal, calling for the country to reduce dependence on imported fossil fuels 75 percent by the year 2025 through the use of biofuels.

Today, ethanol is blended into approximately 46 percent of the nation's gasoline in an admix called E-10 (10 percent ethanol/90 percent standard petroleum-based gasoline). The U.S. Department of Energy (DOE) reported that in 2005 U.S. ethanol plants produced 3.9 billion gallons, up 15 percent from 2004, and DOE forecasts an additional increase of at least 18 percent for 2006 to a total of 4.6 billion gallons. As one would expect, U.S. manufacturing capacity also continues to increase. According to the Renewable Fuels Association's 2005 figures, the United States had more than 4.3 billion gallons of combined total annual capacity at 95 facilities. The DOE reported 770 million gallons of capacity added in 2005 from 14 new facilities. The Federal Trade Commission estimates that "110 firms will operate ethanol plants by the end of 2007."

From Feedstocks to Freeways: Ethanol Manufacturing

Ethanol, or ethyl alcohol, is a high-octane fuel produced from the fermentation of plant sugars. In the United States, E-10 (10 percent ethanol/90 percent gasoline) is the most widely available ethanol/gas blend available for retail purchase for transportation, but auto fuel blends up to E-85 are produced. (Operating on E-85 requires a specially manufactured "flexible fuel vehicle" (FFV), five million of which are currently in use.) While ethanol can and is used as an oxygenate for traditional diesel, most research and marketing is centered on its use in gasoline blends.

Corn is the primary feedstock for ethanol production in the United States. Ethanol is also produced from other organic sources such as barley, wheat, rice, sorghum, sunflower, potatoes, cassava and molasses. Outside North America, sugar cane and sugar beets are the most common feedstocks. It can also be produced from wild grasses, wheat straw and other organic matter currently considered wastes, such as rice straw, timbering waste, and plant leaves and stalks (called "stover"). Corn stover (including cobs) is the most abundant agricultural debris in the Americas.

Corn feedstocks-based production results in a net energy gain, producing 67 percent more energy than it takes to grow and process the corn into ethanol.

According to the National Corn Growers Association, about 13 percent of the nation's corn crop —some 1.43 billion bushels — went into ethanol in 2005. One bushel of corn yields about 2.8 gallons of ethanol. Corn feedstocks-based production results in a net energy gain, producing 67 percent more energy than it takes to grow and process the corn into ethanol.

Wet milling and dry milling are the two production processes for generating ethanol from corn. In dry milling, the entire corn kernel is first ground into flour (also called meal). The powder is made into a slurry with water, to which enzymes are added to convert the starch to dextrose. Ammonia is added for pH control and as a nutrient for the yeast. The mash is processed in a high-temperature cooker to reduce bacteria levels ahead of fermentation. The mash is cooled and yeast is added.

The fermentation process generally takes about 40 to 50 hours, after which the ethanol is separated from the remaining stillage. The ethanol is concentrated to 190 proof using conventional distillation and then is dehydrated to 200-proof anhydrous ethanol. It is then blended with a denaturant, such as gasoline or other petroleum distillates (about 5 percent).

In wet milling, the grain is soaked in water and dilute sulfurous acid for up to 48 hours to facilitate the separation of the grain into its component parts. After steeping, the corn slurry is ground to separate the corn germ. The starch and any remaining water from the mash are then fermented in a process similar to the dry method.

Alcohol Analysis (Not Done With a Breathalyzer)

Quality control testing via laboratory analysis is typically conducted on feedstocks, in-process materials, and end products. High-performance liquid chromatography (HPLC) is commonly used to analyze materials during the fermentation process to monitor the breakdown of starch molecules in glucose, then the conversion to ethanol following typical Krebs cycle dynamics. Excessive fermentation will cause the ethanol to convert into acetic acid.

Typical column technology for fermentation analysis uses ion exchange, ion exclusion, and size-exclusion technologies. The components normally include:

- The mobile phase, a dilute solution of sulfuric acid (0.002-0.005N);
- An isocratic pumping system;
- An autosampler;
- The capillary column (such as Phenomenex Rezex ROA, 300 mm x 7.8 mm);
- A refractive index detector;
- A data acquisition system.

Most systems also include a mobile phase degasser to maintain a bubble-free mobile phase delivery, a column heater, and a sample cooler.

Calibration of the HPLC system by use of a standard solution of the components of interest allows the users to obtain results as weight percent for the analytes of the broth samples. This data can then be used to maximize production.

The primary method for certifying the quality of fuel ethanol is ASTM D5501-04. According to ASTM, “this test method covers the determination of the ethanol content of denatured fuel ethanol by gas chromatography. Ethanol is determined from 93 to 97 mass percent and methanol is determined from 0.1 to 0.6 mass percent…. This test method does identify and quantify methanol but does not purport to identify all individual components that make up the denaturant. Water cannot be determined by this test method and shall be measured by a procedure such as Test Method D 1364 and the result used to correct the chromatographic values. This test method is inappropriate for impurities that boil at temperatures higher than 225°C or for impurities that cause poor or no response in a flame ionization detector, such as water.”

This certification method uses the following GC components:

- A temperature-programmable gas chromatograph;
- The mobile phase, helium;
- An autosampler;
- An analytical capillary column (a typical column is the Restek RTX-1 PONA, 100m x 0.25 mm i.d., 0.5 µm film);
- A flame ionization detector (FID);
- A data-acquisition system.

The quality of the chromatograph is determined by the consistency of its temperature programming and its ability to accurately control the carrier gas flow. The data determines three critical values: the methanol peak, the ethanol peak and the sum of all other peak areas (the denaturant). From these areas it is possible to calculate the mass response corrected area percentage of these components. Applying the appropriate specific gravity and Karl-Fisher water analysis values into the calculation, the lab can provide a certificate of analysis.

“The real key to getting the accuracy desired in biofuel production is proper instrument configuration,” said Jim Mott, Ph.D., a Senior Field Technical Support Specialist with Shimadzu Scientific Instruments’ (SSI) Midwest Regional Office, “as well as the training and support for the personnel who will use it. The best-designed, most rugged instrument in the world is not going to give long-term adequate results if the end-users do not understand how to use and maintain it – timely service and technical support are critical.”

Also, significant for the production of mainstream passenger car fuels, such as E-10, is ASTM method D4806-06b, Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuels. “This specification covers nominally anhydrous denatured fuel ethanol intended to be blended with unleaded or leaded gasolines at 1 to 10 volume percent for use as a spark-ignition automotive engine fuel.”

ASTM D4806 for ethanol used for fuel

Property	Limits	Units
Ethanol	92.1 min.	% v/v
Methanol	0.5 max. (5,000 ppm)	% v/v
Water	1.0 max. (10,000 ppm)	% v/v
Solvent-washed gum	5 max. (50 ppm)	mg/100 mL
Chloride ion	40 max. (40 ppm)	mg/L
Copper content	0.1 max. (0.1 ppm)	mg/kg
Acidity as acetic acid	0.007 max. (70 ppm)	% w/w
Appearance	Visibly free of suspended or precipitated contaminants	
Denaturant	Minimum 1.96% v/v and maximum 4.76% v/v natural gasoline, gasoline components or unleaded gasoline.	

Another ASTM method frequently employed is ASTM D6423-99(2004): Standard Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75-Ed85). “This test method covers a procedure to determine a measure of the acid strength of high-ethanol content fuels. These include ethanol, denatured fuel ethanol, and fuel ethanol (Ed75-Ed85). The test method is applicable to fuels containing nominally 70 volume percent ethanol or higher. Acid strength as measured in this test method is defined as pHe. A pHe value for alcohol solutions is not directly comparable to pH values of water solutions. The value of pHe will depend somewhat on the fuel blend, the stirring rate, and the time the electrode is in the fuel.”

Biodiesel Is Booming — Market Overview

According to a report by researchers SRI Consulting, “The global biodiesel industry is among the fastest-growing markets the chemical industry has ever seen…. The market potential for biodiesel is defined by the size of the existing fossil diesel fuel market. There is no major technical limitation on replacing fossil diesel with biodiesel.”

The report further explains that from 2000 to 2005, global capacity, production, and consumption of biodiesel grew by 32 percent per year on average. SRI projects 115 percent capacity and 101 percent demand growth per year through 2008 and beyond. Despite reaching a peak in consumption in 2006-07, SRI projects excess capacity worldwide.

The National Biodiesel Board reports that there are currently 86 biodiesel manufacturing plants operating in the United States with a total combined capacity of 580 million gallons per year. Currently known plans call for the addition of 820 million gallons before the middle of 2008.

In 2005, Germany accounted for 61 percent of biodiesel consumption. Other significant markets included France, the United States, Italy and Brazil. By 2010, the United States is expected to become the largest single market, accounting for roughly 18 percent of world biodiesel consumption.

Produced by transesterification, biodiesel comprises mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats. It thus differs structurally from the alkanes and aromatic hydrocarbons found in petroleum-derived diesel. But because it is miscible with traditional diesel in all proportions, biodiesel is compatible with all existing fuel infrastructures without major modifications. In the retail consumer market it is typically blended at levels from 2 to 30 percent and named for that percentage (B5, for example, is 5 percent biodiesel/95 percent conventional diesel.) It can also be used in its pure form, referred to as B100. Like petroleum-based diesel fuel, biodiesel needs additives to keep it from coagulating in cold weather. Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the 1990 Clean Air Act Amendments.

While fossil-based diesel already produces about 70 percent less greenhouse gasses than gasoline, adding biodiesel will further reduce these emissions. Interest in biodiesel as a admix got another huge push when, in the fall of 2006, new guidelines from the

Environmental Protection Agency (EPA) went into effect requiring petrochemical manufacturers to produce and sell only ultra-low sulfur diesel (ULSD) for all diesel fuel, diesel fuel additives and distillate fuels blended with diesel for on-road use. ULSD contains 15ppm sulfur compared to 500ppm in low-sulfur diesel, which was the previous U.S. standard. The same rule goes into effect for off-road, locomotive, and marine (NRLM) diesel fuel on June 1, 2007. The processing required to meet the new standard also removes naturally occurring lubricity agents in the fuel. Adding biodiesel re-establishes normal lubricity levels to the fuel mix.

Oily Options: Feedstocks, Manufacture and Analysis

The choice of feedstocks for biodiesel manufacture depends on local availability and affordability. It can be produced from waste vegetable oils, such as those used in cooking, but most commercial refiners currently consume unused oils. Refined soybean oil is the most commonly used material in the United States. Oddly, Brazil, the world's second-largest producer of soybeans in the world, uses castor oil as its main raw material. Rapeseed oil is preferred in Western Europe, while countries in Southeast Asia utilize abundant palm kernel and palm seed oils. India and China are developing jatropha (physic nut) plantations, and the use of cottonseed oil is rapidly increasing.

In the United States fuel-grade biodiesel must be produced to ASTM Method D6751. In Europe the standard is CEN 14214. Parameters under these guidelines include viscosity, flash point and cetane number.

GC analysis of glycerin concentration yields an effective measure of fuel quality.

The transesterification reaction of triacylglycerols (TAGs) in oils is most commonly done by reacting TAGs with methanol in the presence of a catalyst yielding the fatty acid methyl ester (FAME). During the process, monoacylglycerols (MAGs), diacylglycerols (DAGs) and other intermediate glycerols are formed. These, along with unreacted TAGs, can remain in and contaminate the final product, and potentially cause severe engine problems.

ASTM Standard D6751-06a Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels covers "biodiesel (B100) Grades S15 and S500 for use as a blend component with diesel fuel oils defined by Specification D 975 Grades 1-D, 2-D, and low sulfur 1-D and 2-D. Biodiesel may be blended with fuel oils whose sulfur, aromatic, cetane, or lubricity levels are outside Specification D 975 Grades 1-D, 2-D, and low sulfur 1-D and 2-D, provided the finished mixture meets pertinent national and local specifications and requirements for these properties. This specification, unless otherwise provided by agreement between the purchaser and the supplier, prescribes the required properties of biodiesel fuel at the time and place of delivery."

ASTM Standard D6751 criteria for biodiesel

Property	ASTM Test Method	Limit	Units
Flash point (closed cup)	D93	130.0 min.	°C
Water and sediment	D2709	0.050 max.	% volume
Kinematic viscosity, 40°C	D445	1.9-6.0	mm2/s
Sulfated ash	D874	0.020 max.	% mass
Sulfur, grade s15	D5453	0.0015 max (15)	% mass (ppm)
Sulfur, grade s500	D5453	0.05 (500) max	% mass (ppm)
Copper strip corrosion	D130	No. 3 max.	
Cetane number	D613	47 min.	
Cloud point	D2500	Report	
Carbon residue	D4530	0.050 max.	% mass
Acid number	D664	0.50	mg KOH/g
Free glycerin	D6584	0.020	% mass
Total glycerin	D6584	0.240	% mass
Phosphorous content	D4951	0.001	% mass
Distillation temperature, atmospheric equivalent temperature, 90% recovered	D1160	360	°C

Analytical parameters, typically detected by GC — but today more frequently by HPLC and LC[1] for their faster analysis times — include sulfur, phosphorus and glycerin content. Total glycerin content over the specified limit of 0.24 mass percent will cause filter clogging and poor cold flow, critical in cooler climates.

Free glycerin, along with water, is a byproduct of fatty acid methyl ester production. GC analysis of glycerin concentration yields an effective measure of fuel quality. ASTM method D6584-00e1, Standard Test Method for Determination of Free and Total Glycerin in B-100 Biodiesel Methyl Esters By Gas Chromatography, "provides for the quantitative determination of free and total glycerin in B-100 methyl esters by gas chromatography. The range of detection for free glycerin is 0.005 to 0.05 mass percent, and total glycerin from 0.05 to 0.5 mass percent. This procedure is not applicable to vegetable oil methyl esters obtained from lauric oils, such as coconut oil and palm kernel oil."

"The results of biofuels analyses must be available in an easy-to-interpret format," said Mark Taylor, GC/GCMS Product Manager for SSI. "This is not the time to fill a page

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[1] Other instruments and processes can be used by production laboratories for elemental analysis, including Atomic Absorption (AA), Inductively Coupled Plasma (ICP), Fourier Transform Infrared (FTIR) and Fluorescence spectroscopy, and Energy Dispersive X-Ray (EDX) Fluorescence Spectrometry. This report, however, focuses only on GC and HPLC.

with numbers. The intention of the biofuels methodologies is to produce a report that is as 'to the point" as possible. The methodology should provide reliable analysis with the type of data processing that the end-user can pick out the result they need without having to sift through a long list of other numbers.”

ASTM D-6584 calls for flame ionization detection (FID) technology. The sample is first derivatized with a silyating agent and then injected into an open tubular GC column packed with a 5 percent 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 glycerin content. The total glycerin represents the sum of the free and bonded glycerin.

Biodiesel components cover a huge range of boiling points. When conducting a GC analysis, injection must be done on column. Columns must be rated for a maximum temperature above 380°C because of the presence of triglycerols. Further, operators should choose a fused silica column with a small ID (<= 0.32mm) and with a film thickness <=0.25µm. Either a retention gap or, alternatively, an on-column liner should be used.

Summary

As biofuels continue to be pushed to the forefront of the energy market and the public’s consciousness, there will be a growing need for accurate analytical evaluation of every part of the fuel manufacturing process. Continued refinements in methods and equipment will help insure quality products in the marketplace, which will, in turn, eliminate any potential stigmas or objections that remain in consumers’ minds about these alternatives.

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