BIOFUEL BOOM: Chromatography Goes to Work on Fuel-Grade Ethanol

Ethanol producers and fuel refiners need procedures and equipment to ensure quality

Editor's Note: As biofuels continue to be pushed to the forefront of the energy market, accurate analytical evaluation is increasing in importance. Analysis speed is becoming a crucial matter in every part of the fuel manufacturing process. The following article examines this important trend and discusses the refinements of methods and equipment aimed at ensuring quality.

By Jim Mott, Ph.D.

As the cost of crude oil on the wholesale market continues to hover near $70 per barrel, biofuels and fuel additives are receiving increasing amounts of attention from commercial refiners. This has been furthered by building public and scientific awareness of so-called "greenhouse gasses" and their potential deleterious effects on the natural environment.

Ethyl alcohol, commonly called ethanol, is a high-octane fuel produced from the fermentation of plant sugars. Ethanol has been added to gasoline since the late 1970s and is currently used in approximately 46 percent of U.S. retail gasoline produced for the transportation market. Until the late 1980s, ethanol's primary role in the fuels market was that of an octane enhancer, and it was viewed as an environmentally sound alternative to lead in gasoline. With its 112.5 blending octane value (R+M)/2, ethanol is one of the most economical octane enhancers available to refiners and fuel blenders.

In the U.S., E-10 (10 percent ethanol/90 percent gasoline) is the most widely available ethanol/gas blend, but auto fuel blends up to E-85 are produced. Operating on E-85 requires a specially manufactured "flexible fuel vehicle" &#151 or FFV. There are 5 million FFVs currently in use.

According to the Renewable Fuels Association's 2005 figures, the U.S. had more than 4.3 billion gallons of combined total annual capacity at 95 ethanol-producing 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.

With this growing market, it's critical that ethanol producers and fuel refiners put in place appropriate procedures and equipment for testing the quality of products throughout the entire manufacturing process. Two of the most efficient, accurate, and cost-effective tools for this are the gas chromatograph (GC) and the high-performance liquid chromatograph (HPLC).

Analysis of Materials

Analytical evaluation using GC or HPLC technology includes raw materials (feedstocks), materials in process, and finished product evaluation for purity and quality. An HPLC is commonly used to analyze materials during the fermentation

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

ASTM D5501-04

Going From Field to Fuel: Fast Facts About Ethanol

Corn is the primary feedstock for ethanol production in the U.S. 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 used. Ethanol can also be produced from wild grasses, wheat straw, and other organic matter currently considered wastes such as rice straw, timbering waste, and plant stover. Corn stover is the most abundant agricultural debris in the Americas.
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 flour 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 then 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.
In wet milling, the grain is soaked in water and dilute sulfuric 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.

Most ethanol production laboratories follow ASTM Method D5501-04 for GC analysis of the finished denatured ethanol. This method is often modified to determine the amount of ethanol, methanol, and total denaturant in the product.

As the guideline for the performance of the GC analysis and the processing of the data, ASTM D5501-04 does not require any exotic analytical instruments. This chromatograph must be capable of providing reproducible flows of all gases and reproducible temperature programmability of the column oven. The gas chromatograph should have a temperature range up to at least 300&#176C for the heated zones and a split/splitless injection system capable of split ratios up to 200:1. Typically, labs will use very long, non-specific, narrow-bore capillary GC columns with moderate phase thickness, flame ionization detection (FID), low carrier gas linear velocity, and a long temperature program &#151 one that runs approximately 40 minutes. Helium is frequently used in the mobile phase, and most systems are equipped with auto-samplers.

The data acquisition system should be capable of performing computer-based control of the chromatographic system, allow for the accurate collection of the chromatographic trace, perform post-collection processing of the chromatogram, and produce an easily understood report of the results. Additionally, it is the primary user interface with the instrument.

The quality of the chromatograph is determined by the consistency of its temperature programming and its ability to control accurately 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). The long GC column ensures that the ethanol peak is well-separated from the other components. Unfortunately, due to the long isothermal segments in the GC temperature program, much of the chromatogram does not contain any discernable peaks. All peaks of interest generally fall between eight and 23 minutes in an analytical method that approaches 40 minutes in total run time.

From the peak areas, it's possible to calculate the mass response corrected area percentage of these components. Applying the appropriate specific gravity and Karl-Fisher water analysis values to the calculation, the lab can provide a certificate of analysis.

But labs often run into challenges in correctly identifying specific peaks because the instrumentation isn't properly configured or because they're not using appropriate technology. Scientists are also looking for ways to shorten the total run time. Peaks from incompletely separated components are frequently mistaken for the methanol peak. So, choosing the right GC and pairing it with the right column is critical. This will also help reduce total run times.

The BAC1 column by Restek, for example, has a well-known record of successful separations of lower alcohols. Initially developed specifically for performing rapid and clean separations for blood-alcohol analysis, the BAC1 is well-suited to ethanol analysis. This column has a high mass capacity due to its thick phase thickness, yet it is capable of operating over a wide temperature range. The standard

configuration, which is a 0.32 mm x 30 m column with a 1.8 micron phase, is a good starting point for most investigations.

Alternative Approaches

Research has shown that alternate column technologies can be used to shorten GC analysis time greatly for product certification. Initial results have indicated that the analysis may be reduced to as little as 10 minutes. However, the ASTM method is still the controlling authority for this analysis, and new column technologies are still under investigation. With additional study and refinement of column technologies, and presentation of the results to the ASTM committee, this time improvement may become an accepted alternate to the current method.
Another option is two-dimensional (2-D) chromatography. Based on a simplified Dean's switch design, 2-D chromatography uses two short columns of different selectivity to analyze the alcohol content in denatured fuel-grade ethanol. This arrangement allows users to complete the analysis in significantly less time than the standard D5501 method, and it can be done without cryogenic oven cooling. This allows for the complete separation of the polar alcohol from the non-polar hydrocarbons.

More ASTM Standards

Also significant for the production of mainstream passenger-car fuels, such as E-10, is ASTM Method D4806-06c, 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 D4815-04, Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol, and C1 to C4 Alcohols in Gasoline by Gas Chromatography, is used to define the ethanol content of gasoline/ethanol blends up to E-10 but specifically excludes high-ethanol-content fuel blends. It allows for the use of either thermal conductivity (TCD) or flame ionization (FID) detection systems.
This method uses a multidimensional configuration to isolate and then separate the oxygenated fraction. These two steps are carried out using two analytical columns featuring different polarities, connected in series through a gas-switching valve.
ASTM also details the method for testing oxygenates in gasoline using oxygen-selective flame ionization detection (O-FID) chromatography in ASTM D5599-00 (2005). This test method allows for the quantitative determination (the mass concentration) of organic oxygenated compounds in gasoline having a final boiling point not greater than 220&#176C and oxygenates having a boiling point limit of 130&#176C. It is applicable when oxygenates are present in the 0.1 percent to 20 percent by mass range. It requires knowledge of the identity of each oxygenate being determined for calibration purposes.
This method converts only the oxygenated compounds into methane so that the system must be configured to provide complete separation of only the oxygen-containing compounds. This can be accomplished with one non-polar capillary column with a film thickness and length appropriate for resolution of the separation.
The first of these two methods, ASTM D4815-04, is a bit more time-consuming to execute and could yield inaccurate results from lost compounds not completely

eluted from a pre-cut column. Also, O-FID analysis is less complex to set up, is quicker, and avoids the secondary effects of column aging such as retention time shifts. However, both methods, when performed correctly, yield similarly accurate results.

Reformulating a spark-ignition fuel to contain ethanol requires benzene in the range of 0.1 and 5 volume percent and toluene between 2 and 20 volume percent. The EPA requires analyzing labs to use a modified ASTM D-3606-06e1 method to prevent the co-elution of ethanol and benzene. This method can be performed using a two-column set on GC-FID using helium as the carrier gas at a flow rate of 25mL/min in constant-flow mode using 2-butanol as an internal standard.

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