Assessment of biodiesel quality test methods for use in middle distillate fuels

Dr. Raj Shah, Koehler Instrument Company
Aristidis Mihalos, Stony Brook University

KOEHLER INSTRUMENT COMPANY, INC.

Abstract

In recent years, biodiesel has proven to be a good alternative fuel option on the basis of its low carbon intensity relative to petroleum diesel and is a cleaner burning alternative. Over the past 15 years there have been many changes in the fuels industry as well as in vehicle design. The introduction of ULSD (Ultra Low Sulphur Diesel) in 2007 was required for new engine after treatment systems. Correspondingly, the biodiesel standard has required improvement and new tests over that period. Thus, producing high quality biodiesel is paramount to the success of a petroleum-based fuel alternative. Seeing the need in the marketplace, ASTM Subcommittee E with help from the National Biodiesel Board collaborated with the Vehicle Technologies Office to improve the specifications for B100 biodiesel blend stocks that are to be mixed with middle distillate fuels in ASTM D6751: Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels.

Introduction

Biodiesel is an attractive fuel supplement and alternative to standard petroleum-based fuel. The industrial process of synthesizing biodiesel is transesterification of triglycerides found in nature to produce mono-alkylated, fatty esters and glycerin [1].

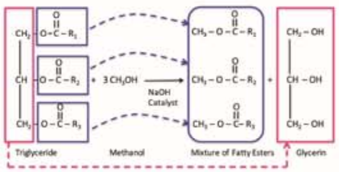

Figure 1. Chemistry of biodiesel production [1]

The EPA has set a priority on the production of biodiesel in the Energy Independence and Security Act of 2007. By 2022, 36 billion gallons of renewable fuels must be produced by the United States [2]. The billions of gallons of renewable fuel available must be of a certain quality in order to remain commercially viable. Parameters of varying standard biodiesel blend stocks are located in ASTM D6751: Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. D6751 dictates the minimum standards for the contents and properties of mono-alkyl, fatty acid ester biodiesel used in middle distillate fuels. This poster serves to introduce the biodiesel testing methods in D6751 and to elucidate the significance and limitations of each test. Additionally, this poster discusses a method that would be a useful addition to test sulfur concentrations in biodiesel.

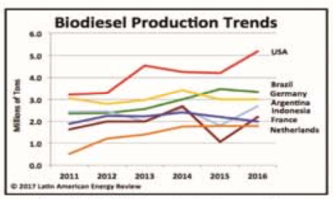

Figure 2. The USA is increasing biodiesel production [3]

Current biodiesel test methods

Figure 3. Automatic Pensky-Martens Closed Cup Flash Point Tester

ASTM D93: Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester.

The flash point can be indicative of hazardous elements concerning the risk of fire in transit and in storage. In this method, a sample of biodiesel is placed into a closed container and then periodically subjected to an ignition source as the temperature of the container increases. In ASTM D6751, the minimum flash point for biodiesel has been set to 93°C to coincide with non-hazardous categories with the NFPA.

EN 14110: Fat and oil derivatives - Fatty acid methyl esters (FAME) - Determination of methanol content.

Methanol is widely used precursor for biodiesel. As such, a limitation on the amount that is present in biodiesel after manufacturing is crucial to avoid health hazards, environmental concerns, and engine degradation [4]. EN 14110 utilizes gas chromatography to measure the alcohol content by mass percent. The maximum allowed alcohol content in biodiesel is 0.2% by mass. ASTM D93 is also utilized for methanol content and sets a maximum flash point at 130 °C

ASTM D5453: Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence.

Varying amounts of Sulfur can negatively impact engine performance and sulfur emissions is of concern to the environment. In this method, a sample of biodiesel is combusted in an oxygen rich environment, which oxidizes the sulfur into sulfur dioxide. The sulfur dioxide is then subjected to UV light, the excited sulfur dioxide emits fluorescent light. A photomultiplier tube detects the emitted radiation and the information is analyzed to determine the sulfur in the sample. 4 grades of biodiesel are established: No.1-B 15 ppm Sulfur, No.1-B 500 ppm Sulfur, No.2-B 15 ppm Sulfur, No.2-B 500 ppm Sulfur.

Figure 4. Automatic Heated Oil Test Centrifuge

EN 14538: Fat and oil derivatives - Fatty acid methyl ester (FAME) - Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES).

Sodium, potassium, magnesium, and calcium present as abrasive solids or soluble metallic soaps in biodiesel can collect in the exhaust devices and increase back pressure, clog filters, and cause wear on injectors and pistons. In this test, a photon emitted from the excited state of an atom is analyzed by a ICP OES device, the concentration and identity of the atom is found. The limit for these elements is 5 ppm in biodiesel.

ASTM D2709: Standard Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge.

Fouling and corrosion are more likely to occur in systems that contain appreciable amounts of water. Sediment deposits inside of a container, or a filter screen, have the ability to obstruct flow. To combat these issues, it is imperative to test and maintain a minimum level of water and sediment present in biodiesel. In this method, water and sediment are separated from biodiesel using a centrifuge. The max allowed volume percent of water and sediment is 0.05%.

Figure 5. Programmable Ashing Furnace

ASTM D874: Standard Test Method of Sulfated Ash from Lubricating Oils and Additives

It is useful to know the concentrations of metals, such as barium, calcium, magnesium, sodium, potassium, zinc, and tin, present in the biodiesel for different applications. Sulfated ash can be used to deduce the concentrations of these metals if they are known to be in the biodiesel. In this test, a sample of biodiesel is burned and the ash that remains is analyzed. 0.02 % is the maximum ash content allowed.

ASTM D7501:Standard Test Method for Determination of Fuel Filter Blocking Potential of Biodiesel (B100) Blend Stock by Cold Soak Filtration Test (CSFT).

Some substances remain soluble at room temperature in biodiesel but will precipitate when the temperature falls. The precipitation can cause problems with filters. In this test, filtration time after cold soaking of biodiesel is measured to assess levels of filter plugging. For grade No.1-B the max allowed time is 200 seconds, for No.2-B its 360 seconds

Figure 6. Digital Copper Strip Bath

ASTM D130: Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test.

Biodiesel can contain impurities that may cause corrosion. The severity of biodiesel corrosion is important for appropriately distributing, storing, and operating with biodiesel. This test consists of a polished strip of copper, a vessel that can withstand large pressures, and a sample of biodiesel. The copper strip is put inside the vessel and immersed in the biodiesel sample. The vessel is then submerged in a heating bath at 50°C for 3 hours. After 3 hours have passed, the corrosion is analyzed visually by comparing the copper strip to a standardized plaque. The requirement is no higher than a No.3 grade on a standardized plaque.

EN 15751: Automotive fuels - Fatty acid methyl ester (FAME) fuel and blends with diesel fuel - Determination of oxidation stability by accelerated oxidation method

Products of oxidations can form various acids and polymers that can hinder the fuel system of an engine. Performing test to ensure the oxidation stability of biodiesel is important to see if these chemicals will form. In this test, air is passed through a sample of biodiesel heated to 110C to accelerate degradation of the biodiesel esters. An electrode in the vapor/air after the sample measures volatile organic acids indicating degradation has occurred.The stability of the Biodiesel as measured by EN15751 should be a minimum of 3 hours (D6751).

ASTM D445: Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity).

Engine systems are designed to tolerate a certain range of fuel viscosities. Problems with pumps and injection devices could develop if the viscosity of biodiesel is not within the range of the manufacturer: the engine could underperform or malfunction. The kinematic viscosity of the biodiesel is evaluated by measuring the time it takes for the fluid to travel through a glass viscometer at a certain temperature. The range for the kinematic viscosity is 1.9-6.0 mm^2/s.

Figure 7. Kinematic Viscosity Bath with Optical Flow Detection System

ASTM D664: Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration.

The acid number is a measurement of the acid content in biodiesel. The quantity of acid inside of biodiesel could be useful knowledge for certain applications. The acid number is not reflective of the relative corrosiveness of biodiesel with metals. In this method, a sample of biodiesel is dissolved in solvent and then titrated with alcoholic potassium hydroxide using a glass indicating electrode and a reference electrode, or a combination electrode. A titration graph is plotted with meter readings and volume of titrating solution added. Calculations from the results will yield the acid number of the sample biodiesel.

ASTM D6584: Standard Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography.

High free and total glycerin content are detrimental to the quality of biodiesel. Free and unbounded glycerin can negatively impact fueling systems and storage. High total glycerin content can affect fuel filters and injections systems by fouling and clogging filters and fouling fuel injectors. In this test method, a sample of biodiesel is tested via gas chromatography for monoglycerides, diglycerides, triglycerides, and free and total glycerin. An important note is that this method is not applicable for lauric oils, an example of which would be coconut oil and palm kernel oil. The allowed free glycerin and total glycerin is up to 0.02% or 0.240% by mass, respectively.

Figure 8. VDS3000 Manual Vacuum Distillation System

ASTM D4530: Standard Test Method for Determination of Carbon Residue.

The carbon residue number is a rating of the tendency for a sample of biodiesel to form carbonaceous residue under certain degradation conditions. In this method, a sample of biodiesel is heated to 500°C in an inert atmosphere. The sample undergoes coking reactions and the non-volatile residue is collected and recorded as a percentage of the original sample by weight. The percentage is the Carbon residue. The maximum allowed carbonaceous material by mass percent should be 0.05% by mass.

ASTM D1160: Standard Test Method for Distillation of Petroleum Products at Reduced Pressure.

A boiling point is more applicable than a boiling range for biodiesel. The carbon chains on methylated esters that comprise biodiesel are primarily composed of 16-18 carbons, which have general boiling ranges of 330- 357°C. A boiling point of 360°C standard was incorporated to ensure that the biodiesel does not contain any high boiling point contaminants. In this method, a sample of biodiesel is distilled at pressures between 0.13-6.7 kPa under conditions that yield one theoretical plate fractionation.

Sulfur measurements by X-ray fluorescence using gravimetric standard addition method (SAM)

Oxygen in biodiesel attenuates X-ray radiation emitted from sulfur in XRF testing that produces bias which makes the results inaccurate. SAM is a useful tool to prevent this case [5]. In gravimetric SAM, an increasing amount of a standard, species of which matches the analyte, is added to separate vessels containing an equal amount of unknown. One vessel is void of the standard. The solutions are analyzed, and if a linear line is produced, the concentration of the sample can be concluded [6].

Advantages

Methyl ester biodiesel contains sizable quantities of oxygen, which interferes with sulfur emitted x-rays via attenuation. Useful when there are matrix effects that reduce analytical signals, gravimetric S.A.M. has been shown to negate the affects of different C/H ratios [5].

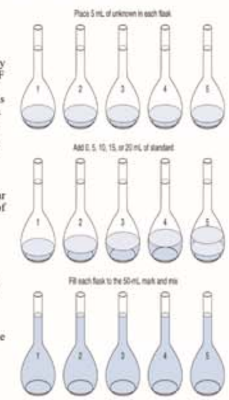

Figure 9. Illustration for standard addition method [2]

References

[1] Clifford, Caroline Burgess. "9.2 The Reaction of Biodiesel: Transesterification." PennState College of Earth and Mineral Sciences. www.e-education.psu.edu/egee439/node/684.Web. July 24, 2018.

[2] "Economics of Biofuels." United States Environmental Protection Agency. https://www.epa.gov/environmental-economics/economics-biofuels. February 2, 2018. Web. August 26, 2018.

[3] St.James, Carlos, " Biodiesel production becoming a zero-sum game." Latin American Energy Review 2017. April 3, 2017. Web. July 24, 2018.

[4]Kirtania, Kawnish." Excess Methanol Recovery in Biodiesel Production Process Using a Distillation Column: A Simulation Study." Chemical Engineering Research Bulletin. Bangladesh Journals Online. Web. July 12, 2018.

[5] Harris DC. Quantitative Chemical Analysis. 7th ed. W. H. Freeman and Company; 2007. Standard Addition Method on page 87-90.

[6] Barker LR, Kelly WR, Guthrie WF. "Determination of Sulfur in Biodiesel and Petroleum Diesel by X-ray Fluorescence (XRF) Using the Gravimetric Standard Addition Method–II." Energy & Fuels. 2008;22(4):2488–2490.

information from the " Current Biodiesel Test Methods" section was sourced from the various methods, unless otherwise specified from another reference.