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ABSTRACT

When considering middle distillate fuels, biodiesel is a good alternative as a result of its carbon neutral footprint, sustainability, and economic viability. Recently, there has been improvements in biodiesel quality testing, by developing better test methods. Without sufficient testing, biodiesel can create various issues when used as a fuel, such as engine clogging. One of such test methods is ASTM D6751, the Standard Specification for Biodiesel Fuel (B100) Blend Stock and Distillate Fuel. This specification sets requirements for B100 fuels, which must be tested in accordance with various test methods.

ASTM D6751 is an important method for biodiesel fuels since biodiesel production and consumption is growing in the United States, and the test method ensures that the biodiesel meets the consumer's standards. With growing concerns of climate change and an increasing demand for fuel sources, biodiesel will be seen as a more tasteful fuel alternative for years to come. This poster will discuss the current state of biodiesel in the fuel market, and will review the significance requirements and recent changes of the various biodiesel test methods referenced in ASTM D6751.

INTRODUCTION

Biodiesel has become a very popular supplement or substitute for traditional petroleum derived fuels. The synthesis of biodiesel is a transesterification of triglycerides into mono-alkylated, fatty esters and glycerin [1].

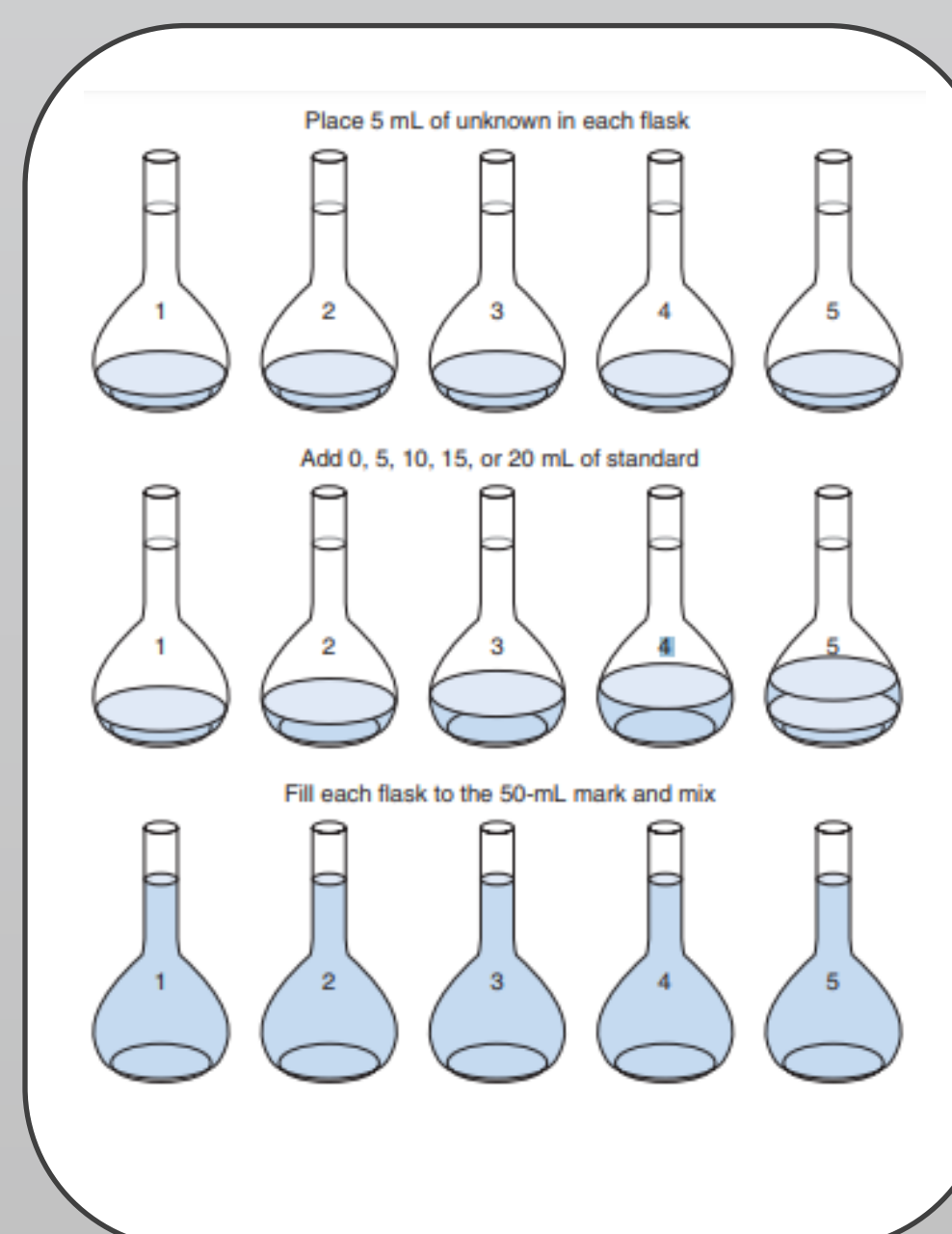
Property	Test Method*	Grade No. 1-B S15	Grade No. 1-B S500	Grade No. 2-B S15	Grade No. 2-B S500
Sulfur, % mass (ppm), max	D5453	0.0015 (15)	0.05 (500)	0.0015 (15)	0.05 (500)
Cold soak filterability, seconds, max	D7501	200	300	300	300
Monoglyceride content, % mass, max	D6584	0.40	0.40	0.40	0.40
Requirements for All Grades					
Calcium and Magnesium, combined, ppm (µg/g), max	EN 14538	5	5	5	5
Flash point (closed cup), °C, min	D93	93	93	93	93
Alcohol content					
One of the following shall be met:					
1. Methanol content, mass %, max	EN 14110	0.2	0.2	0.2	0.2
2. Flash point, °C, min	D93	130	130	130	130
Water and sediment, % volume, max	D2709	0.050	0.050	0.050	0.050
Kinematic viscosity, mm ² /s, 40 °C	D445	1.94-0.0	1.94-0.0	1.94-0.0	1.94-0.0
Sulfated ash, % mass, max	D874	0.020	0.020	0.020	0.020
Copper strip corrosion, max	D130	No. 3	No. 3	No. 3	No. 3
Cetane number, min	D813	47	47	47	47
Cloud point, °C	D2500	Report	Report	Report	Report
Carbon residue, % mass, max	D4530	0.050	0.050	0.050	0.050
Acid number, mg KOH/g, max	D664	0.50	0.50	0.50	0.50
Free glycerin, % mass, max	D6584	0.020	0.020	0.020	0.020
Total glycerin, % mass, max	D6584	0.240	0.240	0.240	0.240
Phosphorus content, % mass, max	D4951	0.001	0.001	0.001	0.001
Distillation temperature, Atmospheric equivalent temperature, 90 % recovered, °C, max	D1160	360	360	360	360
Sodium and Potassium, combined, ppm (µg/g), max	EN 14538	5	5	5	5
Oxidation stability, hours, min	EN 15751	3	3	3	3

Figure 2. Specifications for Biodiesel in ASTM D6751

The EPA has renewed interest in the production of biodiesel through the Energy Independence and Security Act of 2007 setting a goal of 36 billion gallons produced in the United States by 2022 [2]. In order to remain competitive with petroleum products biofuels need to meet a standardized quality. To date there are multiple standards to determine the qualities of biodiesel blend stocks. One of these methods include ASTM D6751: Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. This method lays out the minimum standards and properties for mono-alkyl, fatty acid ester biodiesel in middle distillate fuels, and these specifications are defined in the chart above. The purpose of this poster is to demonstrate the method D6751 and to show the strengths and weaknesses of each individual test.

SULFUR MEASUREMENTS BY XRF USING SAM

Oxygen in biodiesel can reduce the value of X-ray radiation emitted from sulfur in X-ray fluorescence (XRF) testing which can produce a bias leading to inaccurate results. To prevent this it can be beneficial to use the standard addition method (SAM). With gravitational SAM, an increasing amount of standard species matching the analyte should be added to separate containers with equal amounts of the unknown sample. One container is void of the standard. The solutions should then be analyzed and if a linear line is produced then the concentration can be determined. Methyl ester biodiesel contains higher levels of oxygen which can interfere with sulfur emitted x-rays through attenuation. It is useful when there is matrix effects that reduce analytical signals. Gravimetric SAM has also been shown to negate the effects of different C/H ratios [5].



CURRENT BIOFUEL TESTING METHODS

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

The test for flash point can help determine the risk of transporting and storing the product. To determine flash point of a sample of biodiesel it must be placed into a closed container to which an igniter is introduced regularly as the temperature of the sample increases. The minimum flash point for biodiesel in ASTM D6751 is 93°C which coincides with non-hazardous categories set by the NFPA.



Koehler K71000 for ASTM D93



Koehler K60002 for ASTM D2709

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

Water content can cause fouling and corrosion of systems and sediments can collect in containers and filters and cause obstruction to flow. To determine these levels a sample of biofuel must be placed in a centrifuge to separate the water and sediments from the fuel. The maximum percentage by volume of water and sediment is 0.05%.

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

Titration can be used to measure the acid content in a sample of biofuel. To find the acid number the sample is dissolved in a solvent and titrated using alcoholic potassium hydroxide while using either a glass indicating electrode and reference electrode or a combination electrode. This can be used to determine the acid number.



Koehler K90500 for ASTM D664



Koehler K46700 for ASTM D7501

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

There are some substances that are soluble in biodiesel at room temperature however will precipitate out at a lower temperatures. This can lead to problems with filters. To test for these substances a cold soak filtration test can be performed and the time for filtration can be used to predict levels of filter plugging. The maximum allowed time of filtration for No.1-B is 200 seconds and 360 seconds for No.2-B.

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

In most applications, boiling point is more useful than boiling range for a sample of biodiesel. The chains of methyl esters in biodiesel typically have boiling ranges of 330-357°C. A standardized boiling point of 360°C is used to limit the amount of high boiling point contaminants. To perform this test a sample is distilled at pressures between 0.13-6.7 kPa and conditions that would yield a single theoretical plate fraction.



Koehler VDS3000 for ASTM D1160

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

Abrasive solids or soluble metallic soaps composed of sodium, potassium, magnesium, and calcium in biodiesel can collect in vehicle exhausts and lead to increased back pressure, clog filters, and cause excessive wear on engine components. To test for these contaminants an excited state of them is measured by an ICP-OES device which determines the concentration and identity of the atoms found. The limit in biodiesel is 5 ppm.

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

Methanol is a very common precursor for biodiesel however in order to prevent health hazards, environmental impact, and engine wear [4] a limit is set on its' concentration in biodiesel. The method EN 14110 uses gas chromatography to determine alcohol content by percent mass. The maximum amount of alcohol allowed in biodiesel is 0.2%.

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

Compounds in the biofuel can oxidize and form acids and polymers that can cause problems in fuel systems. Because of this it is important to test the oxidation stability of the fuel to see if potentially damaging chemicals can form. To determine this air can be passed through a sample of biodiesel which is heated at 110°C in order to accelerate oxidation. An electrode should be added to this sample to measure the volatile organic acids produced when oxidation occurs. The stability of biodiesel measured by EN15751 is a minimum of 3 hours (D6751).

CURRENT BIOFUEL TESTING METHODS

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

Engines are designed to operate with a set range of fuel viscosities. If the fuel is not in the range set by the manufacturer problems with the engine may arise and lead to degraded performance or engine damage. The kinematic viscosity can be determined by measuring the time it takes for the sample to pass through a glass viscometer. The range for kinematic viscosity is between 1.9 and 6.0 mm²/s.



Koehler KV5000 for ASTM D445



Koehler K25330 for ASTM D130

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

Biodiesel may contain corrosive impurities that can cause complications with distribution, storage, and operation of the fuel. In order to test for these impurities a polished strip is placed into a container with the sample, then held at 50°C for 3 hours. After the time has elapsed the copper strip is compared to a standardized plaque. The limit of corrosion is a No.3 grade on the plaque.

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

It is necessary to analyze the concentration of metals such as barium, calcium, magnesium, sodium, potassium, zinc, and tin in a sample of biofuel or different applications. Sulfated ash can be utilized to determine the concentrations of these metals if they are in the biofuel. This is done by burning the biofuel and analyzing the remaining ash. The maximum ash content is 0.02%.



Koehler K24410 for ASTM D874

ASTM D4530: Standard Test Method for Determination of Carbon Residue



Koehler K41000 for ASTM D4530

Carbon residue number is a way of measuring the tendency for a sample to form carbonaceous residue due to certain degradation conditions. To determine carbon residue number a sample is placed in an inert atmosphere heated to 500°C. The residue left after the end of the test is weighed and a mass percent of the residue is calculated. This mass percent has a maximum of 0.05%.

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

Sulfur can lead to degraded engine performance and increased sulfur emissions which can cause environmental damage. The test to determine sulfur content is outlined in ASTM D5453 by combusting the sample in an oxygen rich vessel, then fluorescence is measured after UV light exposure. There are 4 established grades of biodiesel with varying sulfur contents: No.1-B 15 ppm Sulfur, No.1-B 500 ppm Sulfur, No.2-B 15 ppm Sulfur, and No.2-B 500 ppm Sulfur.

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 can lead to biodiesel of lesser quality. Free and unbounded glycerin content can negatively affect the fuel storage and degraded fuel system performance. High total glycerin content can lead to filter clogging and fuel injectors which negatively impact engine function. Gas chromatography is an effective method to determine glyceride content. The maximum free glycerin and total glycerin is 0.02% and 0.240% by mass respectively.

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ACKNOWLEDGEMENTS

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