The Cutting Edge Advances in Worldwide Biodiesel Testing Specifications and Standardisation

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The search for alternatives to replace fossil fuel based energy sources has contributed to the development of fuels from various sources which include renewable feedstock such as fats and oils. Several types of fuels can be derived from this triglyceride-containing feedstock. Biodiesel is one of the most sought after forms of alternative fuel in the industry. This fuel can be made from various resources including agricultural oils, recycled cooking oil and animal fat; the diversity of this mix is increasing every day. Due to the increasing prices of petroleum, biofuels are gradually becoming more prevalent worldwide. Accordingly, biodiesel standards have been established and continue to be developed in regions like the United States, Europe, Brazil, South Africa and elsewhere. This article cites the specifications and standards pertaining to testing biodiesel in particular regions around the world.

The primary motivation behind biofuels as an alternative source of energy stems from the world's increasing demand for energy. With depleting fossil fuel sources, fears of global warming and for many, the intent to decrease the dependence on fuel imports, biodiesel is becoming more and more prelevant in the fuel industry as an alternative. Petroleum caught on early as the primary source of energy because it was plentiful and relatively inexpensive to refine. Currently, biodiesel is one of the most sought after fuel alternatives due to its biodegradability and low emission profile. The ultimate goal is to one day replace petro fuels with bio-based fuels. These days however, biodiesel is primarily used as a blend with petrodiesel.

The concept of bio-based fuels is not as new as one may think. A bio-based fuel was first used in 1895 by the German engineer Rudolf Diesel who invented the first engine that ran on vegetable oil. Due to the lack of interest in this alternative fuel in his days, the idea did not flourish. Nowadays, Biodiesel can be blended and used in many different concentrations1, these include: B100 (pure biodiesel), B20 (20% biodiesel, 80% petrodiesel), B5 (5% biodiesel, 95% petrodiesel) and B2 (2% biodiesel, 98% petrodiesel). The most common blend currently used in the United States is B20.

As we consider B100 to one day fully replace petrodiesel, some key differences are to be cited. Diesel is obtained through distillation of crude oil to separate lighter and heavier components, whereas biodiesel is obtained by chemically reacting lipids with an alcohol. Biodiesel is made up of a combination of esters of different fatty acids whereas diesel contains a broad range of hydrocarbons. Their different compositions pose a number of issues; biodiesel may contain heavy materials which would thermally decompose when exposed to heat in a working engine. A large number of unsaturated carbons are found in biodiesel whereas crude oil contains few olefins which would not cause instability and contribute to degradations. The presence of oxygen in biodiesel is an advantage because it allows for a more complete combustion which results in lower emissions, but it also negatively affects the performance of the engine by slightly reducing its peak power.

Biodiesel is obtained by reacting lipids with an alcohol to produce fatty acid esters through a process known as transesterification of vegetable fats and oils with glycerin as a co-product (figure 1). This fuel has steadily been gaining interest in the industry due the increasing price of petroleum. With the increasing interest and use, the successful commercialisation and market acceptance of biodiesel has become a major focus of the market.

Accordingly, biodiesel standards have been established or are being developed in various countries and regions around the world, which include the United States, Europe, Brazil, South Africa and elsewhere. This article cites the specifications for testing in the biodiesel industry. Due to the different emerging biofuel economies, one of the main issues facing the alternative fuels industry is the international compatibility of testing standards.

ASTM International has recently published new specifications for a broader range of Biodiesel Blends. Advancements in other bio- or alternative energy technology have widened the scope of what we see as feasible solutions to our energy problems. These developments and advances are a positive sign for the alternative fuels industry.

Standardisation is however not the only issue which is to be dealt with as this fuel's usage becomes more common. Issues dealing with the use of vegetable oil as feedstock and its relatively high costs are also to be considered. This is primarily due to the availability of vegetable oil in that it will always have uses, such as food rather than to be used as an energy source. Only a fraction of vegetable oil production is available for non-food use. It is unlikely that this problem should be solved by merely producing more vegetable oil to use for fuel due to the lack of land and other natural limitations.

ASTM D6751, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, was first developed in 1999 as Provisional Specification, PS121-99 by the American Society for Testing and Materials (ASTM). It was adopted as a standard in 2002 as D6751-02; since then several revisions have been made and its latest form stands as ASTM D6751-11a. This test method is used as a basis for several other standards for biodiesel. Another standard prevalently used as a reference to other methods is the European method, EN14214.

The European standard EN14214 (table 2) is broadly based on DIN 51606. This standard outlines the requirements and test methods for fatty acid methy esters (FAME) to be used as automotive fuel for diesel engines at concentrations of up to 100% or as an "extender" for these engines as specified by EN 590.

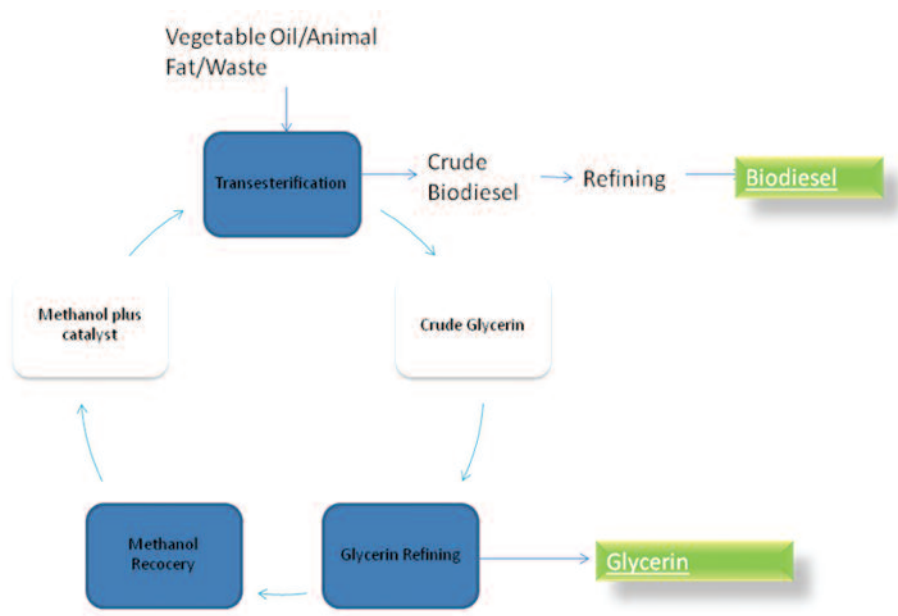

Figure 1: Transesterification Process[2]

ASTM D6751 highlights specifications dealing with the physical and chemical characteristics that ensure safe and adequate operation of diesel engines. It does not consider the feedstock or refining process used in the production of the fuel. The fuel's final blend stock simply must meet these required conditions (Table 1). The content of Magnesium (Mg) and Calcium Combined in biodiesel is limited because these metals can form harmful deposits that damage emission control equipment. One of the most vital physical properties to be measured is the Flash Point of the product. The standard minimum set for pure biodiesel is 93°C; this is to make certain that it is classified as "nonhazardous under the National Fire Protection Association"(2).

There are two specifications stated under alcohol content in the fuel of which only one has to be met. The first pertains to the flash point to ensure that it isn't affected by the methanol presence from the manufacturing process; this minimum is set to a value of 130 °C. The other is based on the amount of methanol present which shall be reduced to a maximum of 0.2 vol %. During the manufacturing process, both Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) can be used for analysis of ester content. Their presence can lead to operational problems such as engine deposits, filter clogging or fuel deterioration5.

Property	Test Method	Grade S15 Limits	Grade S500 Limits	units
Calcium and Magnesium combined	EN 14538	5 max	5 max	ppm (_g/g)
Flash point (closed cup)	D93	93 min	93 min	°C
Alcohol control				
One of the following must be met:				
1. Methanol content	EN 14110	0.2 max	0.2 max	mass %
2. Flash point	D93	130 min	130 min	°C
Water and sediment	D2709	0.050 max	0.050 max	% vol.
Kinematic viscosity, 40°C	D445	1.9-6.0	1.9–6.0	mm^2/s
Sulfated ash	D874	0.020 max	0.020 max	% mass
Sulfur	D5453	0.0015 max (15)	0.05 max (500)	% mass (ppm)
Copper strip corrosion	D130	No. 3 max	No. 3 max	
Cetane number	D613	47 min	47 min	
Cloud point	D2500	ReportD	ReportD	°C
Carbon residue	D4530	0.050 max	0.050 max	% mass
Acid number	D664	0.50 max	0.50 max	mg KOH/g
Cold soak filterability	Annex A1	360 max F	360 max F	seconds
Free glycerin	D6584	0.020 max	0.020 max	% mass
Total glycerin	D6584	0.240 max	0.240 max	% mass
Phosphorus content	D4951	0.001 max	0.001 max	% mass
Distillation temperature, Atmospheric equivalent temperature, 90 % recovered	D1160	360 max	360 max	°C
Sodium and Potassium combined	EN 14538	5 max	5 max	ppm (_g/g)
Oxidation stability	EN 15751	3 minimum	3 minimum	hours

Table 1: ASTM D6751 Specification for Biodiesel (B100)2

Glycerol esters are examined by GC using flame ionisation detector (FID). Specifications for the use of GC's are both addressed in EN14124 and ASTM D6751. The latter references the use of ASTM D6584 for analysis whereas EN14214 uses EN 14103.

Water and Sediment content in the fuel raises several concerns that encourage manufacturers to remove this component before moving forward in the production process. If it isn't properly addressed, water can promote microbial growth and also will lead to corrosion in tanks during storage in the presence of oxygen. Water content also causes phase separation to create emulsion as well as hydrolytic oxidation. The European standard suggests the use of titration to determine the amount of water present in a fuel sample as opposed to the centrifugal method of ASTM D2709 (referenced in D6751). Fuel oxidation can also cause an increase in the amount of sediment present in the biofuel stock.

One of the most commonly used feedstock in Europe for biodiesel production is high-oleic rapeseed oil. EN14214 restricts the presence of any methyl linolenate in its biodiesel fuel because of its tendency to oxidise. EN14103 is the test method used to determine ester and linoleic acid methyl ester content in biodiesel fuel. Oxidation Stability is one of the primary issues to be dealt with in biodiesel. EN14112 AOCS Oil Stability Index method Cd12b-92 outlines a method for testing the oxidation stability of the fuel. Oxidation stability is measured by heating the fuel sample to a specified temperature and bubbling air through it which takes up any volatile components into water. Conductivity of the water with the components in it is measured.

Injection pumps in some engines cause power loss which could adversely affect the performance of an engine. For this reason, the kinematic viscosity is measured and used to monitor the fuel during storage; the more viscous the fuel the poorer the quality. The minimum viscosity of the fuel being pumped that is required for proper operation is 1.9 mm2/s. ASTM D6751 refers to ASTM D445 and EN14214 refers to ISO3104/ISO3105 to test the viscosity of the fuel.

The Sulfated ash test (ASTM D874) is performed to measure any compounds prone to forming ash that would later contribute to fouling in the fuel system. ASTM D6751 references D874 while EN14124 refers to ISO3987; the test is designed to determine the sulphated ash from lubricating oils containing various metals. It covers Ba, Ca, Mg, Na, K and Sn. The most applicable to biodiesel is to determine the residual sodium and potassium from the catalyst.

ASTM D4951 is typically used to determine the sulphur content of a product. For biodiesel, it is determined by D5453 by analysing the sample with ultraviolet fluorescence during combustion. The presence of this element in the fuel would cause pollutant emissions in diesel engine; biodiesel typically contains less than 15 ppm. The common test used (D4951) for sulphur analysis is not used because it often results in falsely high sulphur contents due to the presence of oxygen in biodiesel. Similarly, EN14214 uses ISO20846 to determine this component via UV fluorescence.

One of the critical aspects of biodiesel production is the separation of free fatty acids. An acid number level of 0.50 has been associated with shortened lifespan of fuel pumps and filters and deposits in the fuel system over time. High levels of acid will lead to stability and compatibility issues with fuels system's metals. This high content would fail the Copper Strip Corrosion Test. The requirements for diesel and biodiesel are the same. For pure biodiesel meeting all D6751 specification, the copper strip corrosion test is usually passed. This test is performed to predict impending difficulties with copper and bronze components of fuel systems. Prolonged

EN 14214 - Property	Units	Lower Limit	Upper Limit	Test - Method
Ester content	% (m/m)	96.5	-	EN 14103
Density at 15°C	kg/m_	860	900	EN ISO 3675 / EN ISO 12185
Viscosity at 40°C	mm_/s	3.5	5	EN ISO 3104
Flash point	°C	> 101	-	ISO 3679
Sulfur content	mg/kg	-	10	-
Tar remnant (at 10% distillation remnant)	% (m/m)	-	0.3	EN ISO 10370
Cetane number	-	51	-	EN ISO 5165
Sulfated ash content	% (m/m)	-	0.02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper band corrosion (3 hours at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Thermal Stability	-	-	-	-
Oxidation stability, 110°C	hours	6	-	EN 14112
Acid value	mg KOH/g	-	0.5	EN 14104
Iodine value	-	-	120	EN 14111
Linolic Acid Methylester	% (m/m)	-	12	EN 14103
Polyunsaturated (>= 4 Double bonds) Methylester	% (m/m)	-	1	-
Methanol content	% (m/m)	-	0.2	EN 14110
Monoglyceride content	% (m/m)	-	0.8	EN 14105
Diglyceride content	% (m/m)	-	0.2	EN 14105
Triglyceride content	% (m/m)	-	0.2	EN 14105
Free Glycerine	% (m/m)	-	0.02	EN 14105 / EN 14106
Total Glycerine	% (m/m)	-	0.25	EN 14105
Alkali Metals (Na+K)	mg/kg	-	5	EN 14108 / EN 14109
Phosphorus content	mg/kg	-	10	EN 14107

Table 2: EN14214 General Requirements and Test Method

contact with copper and bronze may serve as catalyst that would degrade the biodiesel over time.

The most common number used to evaluate a diesel's quality is its Cetane Number. A minimum cetane number is required for an engine to operate satisfactorily. Typical diesel is required to meet a cetane number of at least 40 in the United States; typically it is found to be between 40 and 52. Good low temperature start properties are associated with high cetane numbers. The minimum cetane number allowable in biodiesel by ASTM D6751 and EN14214 surpass the number tolerable for petrodiesel.

Cloud point is the most commonly used measure of low-temperature operability; fuels are generally expected to operate at temperatures as low as their cloud point. Cloud point of B100 fuel is commonly greater than that of petrodiesel. Carbon residue indicates the tendency of fuel to accumulate carbon in an engine over time. It is measured on the entire biodiesel sample rather than on 10 percent distillate that is measured on conventional diesel. Free and total glycerin values is a direct indication of the amount of left over unconverted fats and glycerin byproduct in the final product. The presence of glycerin and fats in a fuel can lead to plugging in fuel system filters. Determining this number can be very difficult because ASTM D6584 references that GC be used for this. The user may find difficulty because simply the type of column used can yield incorrect results. D6584 calls for the use of an open tubular column with a 5% phenylpolydimethylsiloxane bonded and cross linked phase internal coating.

With the use of biodiesel, catalytic converters are often susceptible to damage due to the presence of Phosphorous compounds. A maximum of 10 ppm is allowed for its content in biodiesel. The United States produces biodiesel containing a level of around 1ppm.

The test methods cited in this paper have become the back bone of the biodiesel industry for long term biodiesel storage, usage and blending. Standardisation societies are working towards making more advancement in methodology to improve the quality of biodiesel. As biodiesel continues to develop toward commercialisation as a fuel on its own and as a blend, the need for worldwide uniformity in the standards is essential.

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