

## Biodiesel Standards and Quality Testing: A Review

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**Abstract**—As biodiesel expands to be a viable alternative fuel to traditional petroleum-based fuels, many forward-looking companies are starting to produce and distribute it. Biodiesel produced from different feedstocks such as rapeseed and soybean waste vegetable oils have different properties. Quality and consistency of the finished product is of major concern because of the variety of production techniques and feedstocks. Standards are of high significance for producers, suppliers and users of biodiesel for the assessment of safety, risks and environmental pollution. Standardization of biodiesel is important so that engine manufacturers have reference fuels for engine systems development. Furthermore, standards play a vital role in warranty issues and regulatory compliance. International ASTM D6751 and National SANS 342 standards specify the minimum biodiesel quality requirements and the National Biodiesel Accreditation Committee (USA) has a BQ-9000 certification programme for manufacturers who maintain ASTM D6751 standards. Meeting quality control standards for biodiesel products supports their use, storage, blending and marketing of products, ensuring their acceptance and success in the marketplace. This paper examines standards for biodiesel, biodiesel specifications, physical and chemical properties.

**Key words:** Biodiesel, standards, specifications, vegetable oils, fatty acid methyl esters, feedstock, quality.

### 1. Introduction

Biodiesel is a clean-burning alternative to petroleum diesel made from domestic, renewable resources such as vegetable oils, used cooking oil and animal fats. Biodiesel can be used in virtually any diesel engine without modification in its pure form (B100) or as a blend with diesel fuel at any ratio.

At present, biodiesel production is relatively low compared to other types of fuel production. Feedstock supply lines are therefore quite limited, either being sourced from widely distributed waste products of other industries, or from niche crops like rapeseed (canola), soybeans and mustard. This may create problems for both major and minor biodiesel producers, who have the daunting task of producing homogeneous, high-quality fuel sourced from feedstock of varying and ultimately unknown purity and content.

The quality of biodiesel is critical to performance and acceptance in the market. Standards are of high significance for producers, suppliers and users of biodiesel for reasons of safety, risk and environmental pollution. Standardization of biodiesel is important so that engine manufacturers have reference fuels for engine

systems development, and standards play a vital role in warranty issues and regulatory compliance. The most widely used standard is ASTM D 6751. This is the American Society for Testing & Materials standard that defines pure biodiesel (B100). BQ-9000 is a quality management system endorsed by the National Biodiesel Board (USA) and the Canadian Renewable Fuels Association. It combines the standard for biodiesel, ASTM D 6751, and a quality systems program that includes storage, sampling, testing, blending, shipping, distribution, and fuel management practices. BQ-9000 is open to any manufacturer, marketer or distributor of biodiesel and biodiesel blends in the United States and Canada. In South Africa the standard for automotive fuel for diesel engines is SANS 342. The standard specifies the requirements and test methods for marketed and delivered biodiesel.

Worldwide, researchers and the scientific community has focused on the development of biodiesel and the optimization of the processes to meet the standards and specifications needed for the fuel to be used commercially.

To meet the standards, the fuel must meet quality testing specifications such as: cetane number,

kinematic viscosity, free glycerin, carbon residue, distillation temperature, total glycerin, acid number, cloud point etc., which are examined in this paper.

**2. Biodiesel Standards And Specifications**

Table 1 illustrates biodiesel specifications and test methods according to ASTM D6751 and EN 14214

are compared with those of petroleum diesel (EN 590:2004). Both ASTM D6751 and EN 14214 establish specifications for key fuel properties for biodiesel—the former for the biodiesel blend component, the latter for both blend stock and neat biodiesel automotive fuel.

**Table 1. US and EU biodiesel specifications.**

Property	ASTM D975-08a		ASTM D6751-12			EN 590:2004		EN 14214:2012	
			2-B	1-B	Test				
Flash point, min	No 1D 38 °C No 2D 52 °C	D93	<b>93 °C</b>		D93	55 °C	EN 22719	<b>101 °C</b>	EN ISO 2719
Water & sediment, max	0.05 % vol	D2709	<b>0.050 % vol</b>		D2709				
Water, max						200 mg/kg	EN ISO 12937	<b>500 mg/kg</b>	EN ISO 12937
Total contamination, max						24 mg/kg	EN 12662	<b>24 mg/kg</b>	EN 12662
Distillation temperature (% vol recovered)	90%: 1D 288 °C max 2D 282-338 °C	D86	<b>90%: 360 °C max</b>		D1160	65%: 250 °C min 85%: 350 °C max	EN ISO 3405		
Kinematic viscosity	1D 1.3 mm <sup>2</sup> /s to 2.4 mm <sup>2</sup> /s 2D 1.9-4.1 mm <sup>2</sup> /s	D445	<b>1.9 mm<sup>2</sup>/s to 6.0 mm<sup>2</sup>/s</b>		D445	2.0 mm <sup>2</sup> /s to 4.5 mm <sup>2</sup> /s	EN ISO 3104	<b>3.5 mm<sup>2</sup>/s to 5.0 mm<sup>2</sup>/s</b>	EN ISO 3104
Density						820 kg/m <sup>3</sup> to 845 kg/m <sup>3</sup>	EN ISO 3675 EN ISO 12185	<b>860 kg/m<sup>3</sup> to 900 kg/m<sup>3</sup></b>	EN ISO 3675 EN ISO 12185
Ester content	5 % vol. max	EN 14078				5 % vol. max FAME	EN 14078	<b>96.5 % min</b>	EN 14103
Ash, max	0.01 % wt	D482				0.01 %wt	EN ISO 6245		

Property	ASTM D975-08a		ASTM D6751-12			EN 590:2004		EN 14214:2012	
			2-B	1-B	Test				
Sulfated Ash, max			<b>0.020% mass</b>		D874			<b>0.02% mass</b>	ISO 3987
Sulfur, max (by mass)	1D and 2D: S15 15 mg/kg S500 0.05% S5000 0.50%	D5453 D2622 D129 <sup>2</sup>	<b>Two grades: S15 15 ppm S500 0.05%</b>		D5453	Two grades: 50 mg/kg 10 mg/kg	EN ISO 14596 EN ISO 8754 EN ISO 24269	<b>10.0 mg/kg</b>	EN ISO 20846 EN ISO 20884 EN ISO 13032
Copper strip corrosion, max	No 3	D130	<b>No 3</b>	D130	class 1	EN ISO 2160	<b>class 1</b>	EN ISO 2160	
Cetane number, min	40	D613	<b>47</b>	D613	51.0	EN ISO 5165	<b>51.0</b>	EN ISO 5165	
Cetane index, min					46.0	EN ISO 4264			
One of: - cetane index - aromaticity	40 min 35 % vol max	D976-80 D1319							
PAH, max					11 %wt	IP 391 EN 12916			
Operability, one of: - cloud point - LTFT/CFPP	Report	D2500 D4539 D6371							
Cloud point			<b>Report</b>	D2500	Location & season dependant	EN 23015	<b>Location &amp; season dependant</b>	EN 23015	
CFPP					Location & season dependant	EN 116	<b>Location &amp; season dependant</b>	EN 116	
Carbon residue on 10% distillation residue, max	1D: 0.15 %wt 2D: 0.35 %wt	D524	<b>0.050 %wt<sup>5</sup></b>	D4530	0.30 %wt	EN ISO 10370			
Acid number, max			<b>0.50 mg KOH/g</b>	D664			<b>0.50 mg KOH/g</b>	EN 14104	

Property	ASTM D975-08a		ASTM D6751-12			EN 590:2004		EN 14214:2012	
			2-B	1-B	Test				
Oxidation stability			3 hrs min		EN 14112	25 g/m <sup>3</sup> max	EN ISO 12205	8 hrs min	EN 14112
Iodine value, max								120 <sup>1</sup> g iod/100g	EN 14111 EN 16300
Linolenic acid methyl ester, max								12.0 %wt	EN 14103
Polyunsaturated methyl esters, max								1.00 %wt	EN 15779
Alcohol control			0.2 %wt methanol max, or		EN14110			0.20 %wt methanol max	EN 14110
			130 °C flash point min		D93				
Monoglycerides, diglycerides & triglycerides, max				MG 0.40 %wt	D6584			MG 0.70 %wt DG 0.20 %wt TG 0.20 %wt	EN 14105
Group I metal (Na + K), max			5 mg/kg		EN 14538			5.0 mg/kg	EN 14108 EN 14109 EN 14538
Group II metals (Ca + Mg), max			5 mg/kg		EN 14538			5.0 mg/kg	EN 14538
Free glycerin, max			0.020 %wt		D6584			0.02 %wt	EN 14105 EN 14106
Total glycerin, max			0.240 %wt		D6584			0.25 %wt	EN 14105
Phosphorous, max			0.001 %wt		D4951			4.0 mg/kg	EN 14107 prEN

Property	ASTM D975-08a		ASTM D6751-12			EN 590:2004		EN 14214:2012	
			2-B	1-B	Test				
									16294
Lubricity, max	520 μm	D6079				460 μm	ISO 12156-1		
Conductivity, min	25 pS/m	D2624 D4308							
Cold soak filtration time (CSFT), max			360 s <sup>4</sup>	200 s	D7501				
(1) Spain's Royal Decree 1700/2003 sets the maximum iodine value at 140 to facilitate the use of soybean oil as a feedstock. (2) D129 is only applicable to S5000 grades. (3) Limits only apply to S15 and S500 grades. (4) 200 s if fuel temperature ≤ -12°C. (5) Tested on 100% sample but reported using 10% residual calculation.									

The US specification, ASTM D6751, defines biodiesel as a mono-alkyl ester of long chain fatty acids derived from vegetable oils and animal fats. The type of alcohol used is not specified. Thus mono-alkyl esters could be produced with any alcohol (methanol, ethanol, etc.) so long as it meets the detailed requirements outlined in the fuel specification. By requiring that the fuel be mono-alkyl esters of long chain fatty acids, other components, apart from additives, would automatically be excluded.

There are some significant differences among the regional standards. Table 2 shows a list of the world biodiesel quality standards. The biodiesel standards in Brazil and the U.S. are applicable for both fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE), whereas the current European biodiesel standard is only applicable for fatty acid

methyl esters (FAME). Also, the standards for biodiesel in Australia, Brazil, India, Japan, South Africa and the U.S.A. are used to describe a product that represents a blending component in conventional hydrocarbon-based diesel fuel, while the European biodiesel standard describes a product that can be used either as a stand-alone fuel for diesel engines or as a blending component in conventional diesel fuel. Some specifications for biodiesel are feedstock neutral and some have been formulated around the locally available feedstock. The diversity in these technical specifications is primarily related to the origin of the feedstock and the characteristics of the local markets.

**Table 2. World biodiesel quality standards.**

Country/Area	Specifications	Title
India	IS 15607	Biodiesel (B 100) blend stock for diesel fuel - Specification
South Africa	SANS 1935	Automotive biodiesel fuel
EU	EN 14213	Heating fuels - Fatty acid methyl esters (FAME) - Requirements and test methods
EU	EN 14214	EN 14214 Automotive fuels - Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods
U.S.	ASTM D 6751	ASTM D6751 - 11a Standard Specification for Biodiesel Fuel Blend Stock

		(B100) for Middle Distillate Fuels
Australia		Fuel Standard (Biodiesel) Determination 2003
Brazil	ANP 42	Brazilian Biodiesel Standard (Agência Nacional do Petróleo)
Japan	JASO M360	Automotive fuel - Fatty acid methyl ester (FAME) as blend stock

Table 3 shows the biodiesel standards and specifications of the imposed limits for the main properties of biodiesel and the required test methods for India. Properties of biodiesel—defined as a fatty acid alkyl (methyl or ethyl) ester

for use as blending component in diesel—are specified in the Indian Standard 15607:2005. The standard is based mainly on the European specification EN 14214, with some specifications taken from the ASTM D 6751 standard.

**Table 3. Biodiesel standard in India.**

Property	Test method	Limits min	Limits max	Units
Density at 15 °C	ISO 3675 /P 32	860	900	kg/m <sup>3</sup>
Kinematic viscosity at 40 °C	ISO 3104 / P25	2.5	6.0	mm <sup>2</sup> /s
Flash point (closed cup)	P21	120	—	°C
Sulphur	D5443/P83	—	50	mg/kg
Carbon residue (Ramsbottom)	D4530	—	0.05	% (m/m)
Sulphated ash	ISO 6245/P4	—	0.02	% (m/m)
Water content	D2709 / P40	—	500	mg/kg
Total contamination	EN 12662	—	24	mg/kg
Copper corrosion 3 hr at 50 °C	ISO 2160 / P15	—	1	—
Cetane number	ISO 5156/ P9	51	—	—
Acid value	P1	—	0.50	mg KOH/g
Methanol	EN 14110	—	0.20	% (m/m)
Ethanol		—	0.20	% (m/m)
Ester content	EN 14103	—	96.5	% (m/m)
Free glycerol, max	D6584	—	0.02	% (m/m)
Total glycerol, max	D6584	—	0.25	% (m/m)m
Phosphorous, max	D 4951	—	10.0	mg/kg
Sodium and potassium	EN 14108	To report	To report	mg/kg
Calcium and magnesium	—	To report	To report	mg/kg
Iodine value	EN 14104	To report	To report	—
Oxidation stability at 110 °C	EN 14112	6	—	hours

Table 4 shows the biodiesel standards and specifications for South Africa. Biodiesel specifications (IS15404) have been adopted with the view that only non-edible feedstocks will be used. It is based on ASTM and European standards. The term ‘biodiesel’ refers to mono-alkyl (methyl or ethyl) esters of vegetable oils like rapeseed, soya bean, sunflower, *Jatropha curcas*, *Karanja*, etc, and other fats.

This standard specifies requirements and test methods for marketed and delivered biodiesel to be used either as automotive fuel for diesel engines at 100 % concentration, or as an extender for automotive fuel for diesel engines in accordance with the requirements of SANS 342. At 100 % concentration it is applicable to fuel for used in diesel engine vehicles designed or subsequently adapted to run on 100 % biodiesel.

**Table 4. South African biodiesel standard.**

Property	Test method	Limits min	Limits max	Units
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Ester content	EN 14103	96.5	–	% (m/m)
Density, at 15 °C	ISO 3675, ISO 12185	860	900	kg/m <sup>3</sup>
Kinematic viscosity at 40 °C	ISO 3104	3.5	5.0	mm <sup>2</sup> /s
Flash point	ISO 3679	120	–	°C
Sulphur content	ISO 20846, ISO 20884	–	10.0	mg/kg
Carbon residue (on 10 % distillation residue)	ISO 10370	–	0.3	% (m/m)
Cetane number	ISO 5165	51.0	–	–
Sulphated ash content	ISO 3987	–	0.02	% (m/m)
Water content	ISO 12937	–	0.05	% (m/m)
Total contamination	EN 12662	–	24	mg/kg
Copper strip corrosion (3 hours at 50°C)	ISO 2160	–	No.1	rating
Oxidation stability, at 110 °C	EN 14112	6	–	hours
Acid value	EN 14104	–	0.5	mg KOH
Iodine value	EN 14111	–	140	g I/100 g
Linolenic acid methyl ester	EN 14103	–	12	% (m/m)
Content of FAME with ≥ 4 double bonds		–	1	% (m/m)
Methanol content	EN 14110	–	0.2	% (m/m)
Monoglyceride content	EN 14105	–	0.8	% (m/m)
Diglyceride content	EN 14105	–	0.2	% (m/m)
Triglyceride content	EN 14105	–	0.2	% (m/m)
Free glycerol	EN 14105; EN 14106	–	0.02	% (m/m)
Total glycerol	EN 14105	–	0.25	% (m/m)
Group I metals (Na + K)	EN 14108; EN 14109	–	5.0	% (m/m)
Group II metals (Ca + Mg)	EN 14538	–	5.0	% (m/m)
Phosphorus content	EN 14107	–	10.0	mg/kg
Cold Filter Plugging Point (CFPP) Winter/Summer	EN 116	–	–4/+3	°C

### 3. Properties Of Biodiesel

Biodiesel fuel quality depends upon composition of feedstock, production process, storage and handling. Biodiesel quality is evaluated through the determination of chemical composition and physical properties of the fuel. Contaminants and other minor components due to incomplete reaction are the major issues in the quality of biodiesel i.e., glycerol, mono-, di-, triglycerides, alcohol, catalysts and free fatty acids present in the biodiesel. Moreover, biodiesel composition can change during storage and handling. Biodiesel can absorb water or undergo oxidation during storage. The significance of these parameters and their analytical or engine test methods are addressed in standards. Each country has its own

fuel quality testing methods and standards to specify the properties of the fuel.

Fuel properties can be grouped conveniently into:

- (i) Physical,
- (ii) Chemical and
- (iii) Thermal properties.

The important properties of vegetable oils are classified into three groups:

- (i) Physical properties - viscosity, cloud point, pour point, flash point etc.
- (ii) Chemical properties - chemical structure, acid value, saponification value, sulphur content, copper corrosion, oxidation resistance and thermal degradation etc.

(iii) Thermal properties - distillation temperature, thermal conductivity, carbon residue and calorific value etc.

The physiochemical properties of fuel are important in design of fuel systems for compression ignition engines that run on diesel, biodiesel or biodiesel blends. Biodiesel (B100) standards specify the limit values of these properties for blending with diesel. There are variations in the properties of biodiesel. The properties of biodiesel vary depending on the feedstock, vegetable oil processing, production methods and degree of purification.

### 3.1 Acid Number

The acid number is used to determine the level of free fatty acids or processing acids that may be present in biodiesel under the conditions specified by this standard (ASTM D664). The acid number is directly related to the free fatty acid content. The higher the free fatty acid content, the higher is the acid number (Scherpenzeel, 1999; Schumacher, 1996). These acids emanate from two sources: (i)

acids utilized in the production of the biodiesel that are not completely removed in the production process; and (ii) degradation by oxidation. For biodiesel, the standard calls for a maximum acid number of 0.80 mgKOH/g. For biodiesel blends the acid number will change because of the normal oxidation process over time. Once purchased, biodiesel fuel blends that will not be utilized immediately should be monitored for changes in acid number as an indicator of fuel degradation.

Soybean oil experience: A test carried out by Fernando et al. (2007), hereafter called the soybean experience, indicated that the entire sample's acid numbers were well below the specified limits.

The acid number increased with the increase in soybean oil (Figure 1). This increase is mainly due to the increase in the amount of free fatty acids that are present in soybean oil. The acid number can become a serious issue when feedstocks with high free fatty acids are used to produce biodiesel.

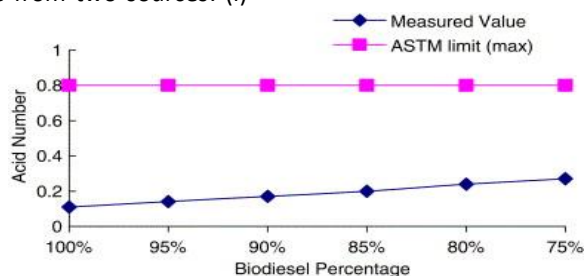


Figure 1. Effect of raw oil presence in biodiesel on acid number.

Biodiesel with a high acid number has been shown to increase fueling system deposits and may increase the likelihood of corrosion. Increased recycle temperatures in new fuel system designs may accelerate fuel degradation which can result in high acid values and increased filter plugging potential. For producers/blenders: High acid values on the feedstock indicates unrefined or poorly refined product. Typical problems would be poor process control, such as methanol carryover, when converting the oils and fats to FAME fuel. For distributors/end users: High acid number fuel can have a strong solvency effect on rubber seals and hoses in the engine, thereby causing premature failure. It may also leave deposits, which can clog the fuel filter or drop fuel pressure.

### 3.2 Ash

Ash is a measure of the volume of metals contained in a fuel. Ash forming materials may be present in three forms: (i) abrasive solids, (ii) soluble metallic soaps, and (iii) residual biodiesel catalysts. Abrasive solids and biodiesel catalyst materials result in wear of fuel systems and internal engine components exposed to fuel after injection which contributes to injector, fuel pump, piston and ring wear, and also to engine deposits. Metallic soaps can contribute to deposits in the fuel system engine and have little effect on wear. All ash forming compounds can contribute to the accumulation of materials on diesel particulate filters, requiring filter maintenance. The levels specified are considered acceptable for engine performance; however, more stringent requirements may be necessary for optimal

particulate filter maintenance intervals (ASTM D482).

### 3.3 Calcium and Magnesium Combined

Calcium and magnesium may be present in biodiesel as abrasive solids or soluble metallic soaps. Abrasive solids can contribute to injector, fuel pump, piston, and ring wear, as well as to engine deposits. Soluble metallic soaps have little effect on wear, but they may contribute to filter plugging and engine deposits. High levels of calcium and magnesium compounds may also be collected in exhaust particulate removal devices, are not typically removed during passive or active regeneration, and can create increased back pressure and reduced time to service maintenance (EN 14538).

### 3.4 Carbon Residue

While not directly correlating with engine deposits, this property is considered an approximation. Although biodiesel is in the distillate boiling range, most biodiesels boil at approximately the same temperature and it is difficult to leave a 10 % residual upon distillation. Thus, a 100% sample is used to replace the 10 % residual sample, with the calculation executed as if

it were the 10 % residual. Parameter E (final weight flask charge/original weight flask charge) of Test Method D 4530-93 is a constant 20/200. ASTM D4530 is the standard test method for determination of carbon residue. Carbon residue testing is intended to provide some indication of the extent of carbon residue that results from the combustion of a fuel and therefore gives a measure of the carbon depositing tendencies of a fuel oil. In fuels, carbon residue is the part remaining after a sample has been subjected to thermal decomposition. This test provides some indication of the coking tendencies of a fuel. It is performed via heating a weighed sample of a fuel to 500 °C under a nitrogen atmosphere for a specified length of time. At these conditions, the sample experiences coking reactions and any volatiles that are formed are purged by the nitrogen. The residue that remains is the carbon residue. The maximum limit for carbon residue in biodiesel is 0.050 % by mass. We can see in Figure 2 that the average carbon residues of three samples (100 %, 95 % and 90 %) have carbon residues less than 0.05 %. The other three samples (85 %, 80 % and 75 %) failed to meet the ASTM standards.

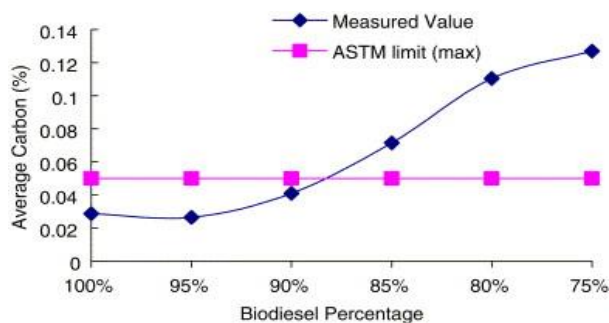


Figure 2. Effect of raw oil presence in biodiesel on carbon residue.

The authors found that the carbon residue increased as the amount of soybean oil in the samples increased. The only exception to this was at 100% biodiesel which, when burnt, gave 0.028667 % carbon whereas a 95 % biodiesel and 5 % soybean oil combination gave 0.026444 % carbon. The most common cause of excess carbon residues in B100 is an excessive level of total glycerin (Gerpen et al., 2004).

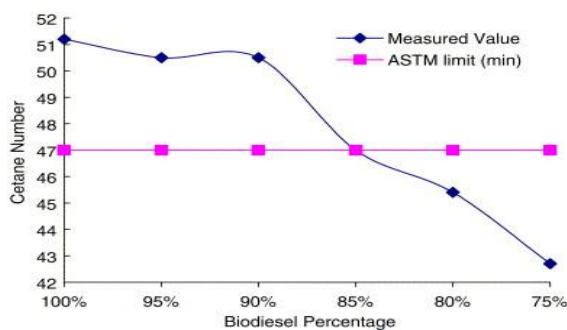
### 3.5 Cetane Number

The cetane number requirements depend on engine design, size, nature of speed and load variations, and on starting and atmospheric

conditions. The calculated cetane index, test methods D976 or D4737, may not be used to approximate the cetane number with biodiesel or its blends. There is no substantiating data to support the calculation of cetane index with biodiesel or biodiesel blends. [ASTM D613]. The cetane number of biodiesels is determined by

ASTM D613 (ASTM International, 2002). The cetane number can be defined as a measurement of the ignition performance of a diesel fuel oil obtained by comparing it to reference fuels in a standardized engine test. Cetane number is a measure of the ignition quality of the fuel and influences white smoke and combustion roughness. The cetane number for biodiesel should be a minimum of 47. A cetane number that

is too high can lead to engine problems. Fuels with low cetane numbers will cause hard starting, rough operation, noise and increased smoke opacity. Biodiesel cetane number depends on the feedstock used for its production. Test reports from Southwest Research Institute suggests that samples with biodiesel with percentages below 85 % failed to meet the ASTM standard as can be seen in Figure 3 .



**Figure 3. Effect of raw oil presence in biodiesel on cetane number.**

As expected, the cetane number decreased as the soybean oil content increased in the samples. This was due to the reduced combustion properties in soybean oil when compared to biodiesel. Biodiesel contains 10 % to 11 % oxygen by weight, which may encourage more complete combustion than hydrocarbon-based diesel fuels in an engine. A high cetane number reduces ignition delay of the fuel (Department of the Environment and Heritage, 2004; Midwest Biofuels, 1994).

### 3.6 Cloud Point

Cloud point is a test used to characterize the low temperature operability of diesel fuel. The cloud point is defined as the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under the conditions prescribed in ASTM D2500, which generally relates to the temperature at which crystals begin to precipitate from the fuel in use. Biodiesel and biodiesel blends generally have a higher cloud point than petroleum-based diesel fuels. The cloud point depends upon the feedstock used and must be taken into consideration if the fuel is to be used in cold environments (Gerpen et al., 2004). The standard ASTM D2500 does not specify any limit on the cloud point but the cloud point should be reported to the customer (Dunn and Bagby, 1997). In all cases the biodiesel samples showed higher

cloud point than regular diesel, making the fuel gel/freeze easily in cold climates. This is due to the presence of saturated esters in biodiesel. For Producers/Blenders: B100 has a cloud and pour point of 32°F and 25°F respectively. High values may indicate additives are not present to lower the cloud point and pour point or are not present in the desirable concentrations. For the user: The cloud point of biodiesel and its impact on the cold flow properties of the resulting blend should be monitored by the user to ensure trouble-free operation in cold climates. To avoid component precipitation in vehicle fuel tanks and blockage of fuel filters, the traditional blending practices for D1 and D2 for a given ambient temperature should be modified prior to blending with biodiesel. Alternative low temperature operability test methods such as Cold Filter Plugging Point (CFPP) and Low Temperature Flow Test may be agreed to between the supplier and the purchaser of the fuel.

### 3.7 Pour Point

Pour point is the temperature at which the fuel ceases to flow, i.e., the lowest temperature at which there is movement of the fuel when the container is tipped.

### 3.8 Copper Strip Corrosion

This test serves as a measure of possible difficulties with copper and brass or bronze parts of the fuel system. The presence of acids or sulfur-containing compounds can tarnish the copper strip, thus indicating the possibility for corrosion. ASTM D130 is used to measure the level of copper corrosion that would occur if biodiesel were used in any application where metals such as copper are present (Gerpen et al., 2004). This test monitors the presence of acids in the fuel. The test is accomplished by using a copper strip tarnish test. A polished copper strip is immersed in a sample of biodiesel and heated for a specified length of time at a specified temperature. The copper strip is removed, washed, and then compared to the ASTM certified Corrosion Standards.

### 3.9 Distillation Temperature

This is a method for determining the full range of volatility characteristics of a hydrocarbon liquid by progressively boiling off a sample under controlled heating. Different methods are available for distillation: atmospheric,

vacuum, and simulated. Biodiesel exhibits a boiling point rather than a distillation curve. The fatty acid chains in the raw oils and fats from which biodiesel is produced are mainly comprised of straight chain hydrocarbons with 16 carbons to 18 carbons that have similar boiling temperatures. The atmospheric boiling point of biodiesel generally ranges from 330 C to 357 °C, thus the specification value of 360 °C is not problematic. This specification has been incorporated as an added precaution to ensure the fuel has not been adulterated with high boiling contaminants. According to the standard ASTM D1160, the distillation temperature of biodiesel fuel should not be more than 360 °C. The test results indicated that all the samples passed the ASTM D 1160. As can be seen from Figure 4, distillation temperatures of all biodiesel fuel formulations were well below the ASTM limit.

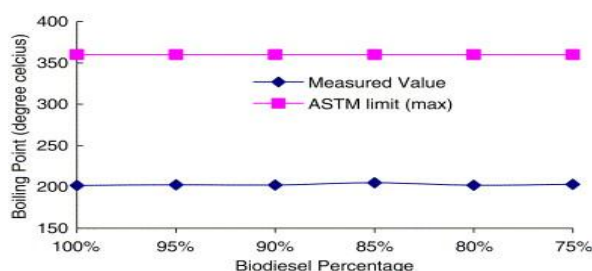


Figure 4. Effect of raw oil presence in biodiesel on boiling point.

There were no significant differences in the distillation temperatures between the samples tested. B100 generally exhibits a boiling point rather than a distillation curve. The fatty acids from which biodiesel are produced, are mainly straight chain hydrocarbons with 16 carbons to 18 carbons having close boiling points. Hence, changing the amount of soybean oil in biodiesel does not have much effect on distillation point. Also, we can observe from Figure 4 that there is a wide gap between the observed value and ASTM standard limits. For producers: High distillation values may indicate the conversion reaction has not gone to completion (flash point may also be high). Low values indicate methanol carryover. For users: High distillation values lead to poor starting,

especially in cold weather; low values can lead to poor timing and seal material failure.

### 3.10 Electrical Conductivity at Delivery to Purchaser

The ability of a fuel to dissipate electric charge that has been generated during pumping and filtering operations is controlled by its conductivity. If a fuel's conductivity is sufficiently high, the static electric charge dissipates fast enough to prevent its accumulation and dangerously high electrical potentials are avoided (ASTM D2624).

### 3.11 Flash Point

The flash point temperature is the minimum temperature at which a fuel will ignite (flash) on application of an ignition source under specified conditions. Flash point varies inversely with the fuel's volatility. The flash point is important in

connection with legal requirements and safety precautions involved in fuel handling and storage that are normally specified to meet insurance and fire regulations. The flash point for biodiesel has been set at 93 °C minimum, so biodiesel falls under the non-hazardous category. Soybean experience (Fernando et al., 2007): A Pensky-Martens closed-cup tester of fuel oils was used in

this method. The flash point of biodiesel should be at least 130 °C. Since biodiesel has a higher flash point than diesels, it is a safer fuel than diesel. The flash point of biodiesel with different proportions of soybean oil is reported in Figure 5. It was found that the flash point of biodiesel increased as the percentage of triglyceride content increased.

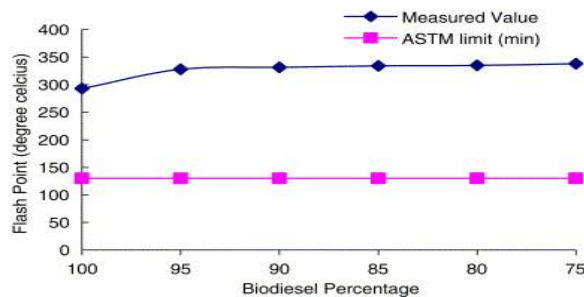


Figure 5. Effect of raw oil presence in biodiesel on flash point.

The reason for rise in flash point is that as the soybean oil content increases the amount of high molecular weight triglycerides increase, decreasing the volatility. This leads to more deposit formation, carbonization of injector tips, ring sticking and lubricating oil dilution and degradation (Petersen et al., 1995). Also in Figure 5 we can observe that the flash points of biodiesel formulations are higher than that of the ASTM requirements. Thus, there is every possibility that a substantial amount of methanol can remain in biodiesel without affecting the ASTM standard. Therefore, there is a requirement of chromatographic analysis of methyl esters or to test the presence of alcohols to ensure that these remain within acceptable limits.

Note that the biodiesel component must meet a flash point criteria, prior to blending, for the purpose of assuring that the biodiesel component does not contain methanol.

For producers/blenders: A low flash point can indicate residual methanol remaining from the conversion process. A high flash point can mean the reaction has not proceeded to completion. For distributors/end users: A low flashpoint in biodiesel can result in premature ignition, causing irregular timing, excessive fuel blow by into the crankcase oil, and excessive emissions. A high flash point can lead to poor ignition, resulting in inconsistent firing, and variable engine performance. It can also indicate potential

clogging of fuel lines, filters and injector clogging in cold climates.

### 3.12 Free Glycerin and Total Glycerin

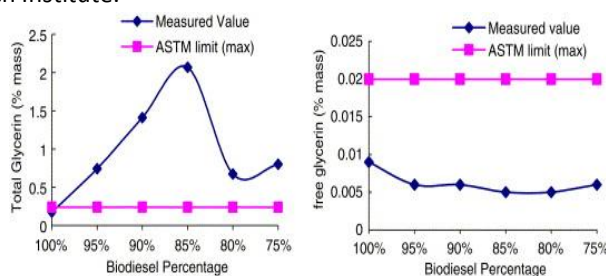
The free glycerin method is used to determine the level of glycerin in the fuel. The key reaction in biodiesel production, transesterification, involves converting oils and fats to fatty acid methyl esters (FAME). Glycerin is the major byproduct and is higher in density and more polar than FAME. Glycerin may be present in free form, and bonded (mono-, di- and triglycerides). Measurement of both is necessary to determine how the conversion reaction will proceed. High levels of free glycerin can cause injector deposits, engine deposits (engine durability concerns) as well as clog fueling systems, and result in a buildup of free glycerin in the bottom of storage and fueling systems.

The total glycerin method is used to determine the level of glycerin in the fuel and includes the free glycerin and the glycerin portion of any unreacted or partially reacted oil or fat. Low levels of total glycerin ensure that high conversion of the oil or fat into its mono-alkyl esters has taken place. High levels of mono-, di-, and triglycerides can cause injector deposits and may adversely affect cold weather operation and fuel filter plugging.

ASTM D6584 is used to measure free glycerol and total glycerol in biodiesel (ASTM International, 2002). One of the products of the transesterification reaction is glycerol (or glycerin).

Glycerol can be free or bonded. Free glycerol is the amount of glycerol not in glyceride bonds, and bonded glycerol is the amount of glycerol in mono-, di- and triglyceride bonds. Total glycerol is the sum of free and bonded glycerol. The free glycerol content of biodiesel should not exceed 0.020 % by mass. For biodiesel, the maximum amount of total glycerol should be 0.240 % by mass.

Soybean experience (Fernando et al., 2007): Tests for determination of free and total glycerin were done at Southwest Research Institute.



**Figure 6. Effect of raw oil presence in biodiesel on total and free glycerol content.**

There was not much change in the free glycerol content throughout the sample population. This is due to the fact that crude soybean oil is usually free from free-glycerin and the biodiesel used was ASTM D6751 compliant with significantly lower free glycerol content than what the standard specifies. Accordingly, addition of crude triglycerides did not affect the free glycerol content. Fuel with excessive free glycerol will usually have problems with glycerol settling in storage tanks, creating a very viscous mixture that can plug fuel filters and cause combustion problems in engines (Mittelbach et al., 1983). Indirect hints of high glyceride content in biodiesel samples correspond to increased values of viscosity and carbon residue (Mittelbach et al., 1992). For producers: high glycerol content indicates the reaction has not proceeded to completion, or your driver and /or catalyst is weak (wrong concentrations). For distributors/end users: high glycerol may separate out in storage, plugging pumps and filters. It can also contribute to dirty injectors, thus causing poor combustion conditions.

### 3.13 Kinematic Viscosity

Viscosity is an important property of any fuel as it is an indication of the ability of a material to flow or the resistance of a fluid to flow. Fuels must have suitable flow characteristics to ensure that an

adequate supply reaches injectors, at different operating temperatures. ASTM D445 provides a method for obtaining the kinematic viscosity and the calculation method to determine the dynamic viscosity (Gerben et al., 2004). For biodiesel, the kinematic viscosity at 40 °C should be between 1.9 mm<sup>2</sup>/s and 6.0 mm<sup>2</sup>/s. Kinematic viscosity affects injector lubrication and fuel atomization. Biodiesel fuel blends generally have improved lubricity; however, their higher viscosity levels tend to form larger droplets on injection which can cause poor combustion and increased exhaust smoke. The limits established provide an acceptable level of fuel system performance.

For some engines it may be advantageous to specify a minimum viscosity because of power loss due to injection pump and injector leakage. Maximum allowable viscosity, on the other hand, is limited by considerations involved in engine design and size, and the characteristics of the injection system. The upper limit for the viscosity of biodiesel (6.0 at mm<sup>2</sup>/s at 40 °C is higher than the maximum allowable viscosity in specification D975 Grade 2-D and 2-D low sulfur (4.1 mm<sup>2</sup>/s at 40 °C). Blending biodiesel with diesel fuel close to its upper limit could result in a biodiesel blend with viscosity above the upper limits contained in Specification D 975.

It can be seen in Figure 6 that only 100 % biodiesel had lower total glycerol content than the limits specified by the standards. There was an increase in the amount of total glycerides with the increase of soybean oil content in the fuel blends. This is mainly due to the addition of bonded glycerol from soybean oil to the samples. But the reason for the sudden fall in total glyceride content for 80 % biodiesel is not clear.

adequate supply reaches injectors, at different operating temperatures. ASTM D445 provides a method for obtaining the kinematic viscosity and the calculation method to determine the dynamic viscosity (Gerben et al., 2004). For biodiesel, the kinematic viscosity at 40 °C should be between 1.9 mm<sup>2</sup>/s and 6.0 mm<sup>2</sup>/s. Kinematic viscosity affects injector lubrication and fuel atomization. Biodiesel fuel blends generally have improved lubricity; however, their higher viscosity levels tend to form larger droplets on injection which can cause poor combustion and increased exhaust smoke. The limits established provide an acceptable level of fuel system performance.

Soybean experience (Fernando et al. 2007). A Cannon Fenske Routine type viscometer was used for determination of viscosity of biodiesel mixed with soybean oil. From Figure 7, it can be observed

that all the samples except 75 % biodiesel met the requirements.

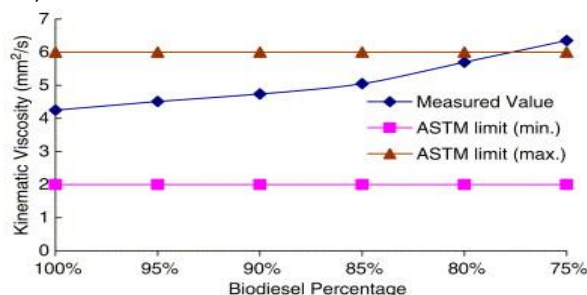


Figure 7. Effect of raw oil presence in biodiesel on kinematic viscosity.

The viscosity of samples increased as the soybean oil content increased. High viscosity of soybean oil is due to high molecular mass and large chemical structure. The viscosity of pure vegetable oils is 10 to 15 times greater than the viscosity of diesel. Transesterification of vegetable oils produces esters with a viscosity of approximately twice that of diesel. Vegetable oils have high molecular weights in the range 600 to 900, which are three or more times higher than diesel fuels (Department of the Environment and Heritage, 2004; Stavinoha and Howell, 1999). Free fatty acids or compounds with hydroxy groups possess significantly higher viscosity (Knothe and Steidley, 2005). For producers/blenders: Verify that the transesterification reaction has proceeded properly. The glycerin content may be elevated and flash point high. Reprocess the batch. For distributors/end users: High viscosity can cause fuel flow problems, and lead to stall out, or fuel pump failure.

### 3.14 Low Temperature Flow

The low temperature flow test was developed in order to predict low-temperature operability of fuels to which a wax modifier has been added to improve said quality. The low-temperature operability of low-level biodiesel fuels blends can be a limiting factor in some applications. That is, biodiesel ester components typically have relatively high cloud points (-15 °C to 10 °C reported for different biodiesel methyl esters.) Thus, the addition of up to 5 % biodiesel ester to a diesel fuel can degrade the low-temperature operability of the low-level biodiesel fuel blend (ASTM D4539).

### 3.15 Lubricity

Lubricity is a measure of the fuel's ability to provide adequate lubrication of the components of the fuel system, including fuel pumps and injectors. The precision required in the manufacturing of these components and the significant influence of abnormal wear require that they be adequately protected from scuffing, scratching, wearing, etc. that may affect their fuel delivery characteristics. The level specified is consistent with that recommended by suppliers of fuel injection equipment for modern diesel engines (ASTM D6079).

### 3.16 Oxidation Stability

Products of oxidation in biodiesel can take the form of various acids or polymers, which, if in high enough concentration, can cause fuel system deposits and lead to filter clogging and fuel system malfunctions. Additives designed to retard the formation of acids and polymers can significantly improve the oxidation stability performance of biodiesel (ASTM EN14112).

### 3.17 Phosphorus Content

The spectrometric analysis technique can be used for detecting and quantifying metallic elements in a fuel resulting from contamination, soap formation or additives. The fuel sample is energized to make elements emit or absorb a quantifiable amount of energy, which indicates the element's concentration in the fuel. Phosphorus can damage catalytic converters used in emissions control systems and its level must be kept low. Catalytic converters are becoming more common on diesel-powered equipment as emissions standards are tightened, so low phosphorus levels

will be of increasing importance. Biodiesel produced from U.S. sources has been shown to have low phosphorus content (below 1 ppm) and the specification value of 10 ppm maximum is not problematic. Biodiesel from other sources may or may not contain higher levels of phosphorus and this specification was added to ensure that all biodiesel, regardless of the source, has low phosphorus content (ASTM D 4951).

Phosphorus has been shown to damage the ability of aftertreatment systems to reduce exhaust emissions as intended. The influence of phosphorus is cumulative; therefore, very low levels of contamination over time and the significant amount of fuel consumed by an engine may lead to unexpected deterioration of the aftertreatment system. For distributors/end users: Phosphorus can poison catalytic converters, rendering them ineffective. It can also create hard deposits on piston crowns, valves and injectors, affecting the engine performance and reliability.

### **3.18 Relative Gravity (ASTM D1298)**

Relative Gravity testing is required to determine biodiesel production lot and storage tank homogeneity before other testing is carried-out. The need to test for homogeneity is based upon the type of storage tank used, as follows:

**Non-Mechanically Mixed or Agitated Tanks** For each production lot, testing should be performed to insure the product in the tank is homogeneous. Tank homogeneity is established by obtaining tank samples at the upper, middle and lower regions of the tank. All three samples must conform to the tank homogeneity requirements. If homogeneity requirements are met then the upper, middle and lower samples can be combined to form a composite sample for testing purposes.

### **3.19 Mechanically Mixed or Agitated Tanks**

In cases where mechanical tank mixing methods are used, tank homogeneity is established after five consecutive production lots meet the tank homogeneity requirements. Once established, the producer will identify the method by which production lot samples will be acquired for testing. If homogeneity cannot be established, then a composite or all levels sample can be used.

### **3.20 Sodium and Potassium Combined**

Sodium and potassium may be present in biodiesel as abrasive solids or soluble metallic soaps. Abrasive solids can contribute to injector, fuel pump, piston and ring wear, filter plugging, and to engine deposits. Soluble metallic soaps have little effect on wear, but they may contribute to filter plugging and engine deposits. High levels of sodium or potassium compounds may also be collected in exhaust particulate removal devices which are not typically removed during passive or active regeneration, and they can create increased back pressure and reduced period to service maintenance (EN 14538).

### **3.21 Calcium and Magnesium**

Calcium and magnesium metals clog particulate traps which are used with ULSD (spectrometric analysis).

### **3.22 Sulfated Ash**

Ash-forming materials may be present in diesel fuels in three forms: (1) abrasive solids and (2) soluble metallic soaps, and (3) un-removed catalysts. ASTM D 874 is the standard test method for determining sulfated ash from lubricating oils and additives (ASTM International, 2002). Ash content describes the number of inorganic contaminants, such as abrasive solids and catalyst residues, and the concentration of soluble metal soaps contained in a fuel sample. The ASTM D874 standard mentions that the samples can have a maximum 0.02 % sulfated ash. All the samples had the sulfated ash of less than 0.001 % by weight. The reason for no increase in the sulfated ash content can be because the oil mixed into the biodiesel did not have any inorganic contaminants. Abrasive solids and un-removed catalysts contribute to injector, fuel pump, piston and ring wear, and also to engine deposits. Soluble metallic soaps have little effect on wear but can contribute to filter plugging and engine deposits.

### **3.23 Sulfur**

Sulfur is a common contaminant in fuel. Sulfur in fuel leads to sulfur oxides being produced as exhaust gases, which can harm the environment, and as acids in the engine crankcase, which will attack the lubricant. Biodiesel has little to no sulfur present, making it a great emissions reduction fuel. Some sulfur is desirable in refined petroleum-based diesel as it provides lubricity for the fuel

pump. Biodiesel fulfills that function with the free fatty acids present.

The effect of sulfur content on engine wear and deposits appears to vary considerably in importance and depends largely on operating conditions. Fuel sulfur can also affect emissions control systems performance and various limits on sulfur have been imposed for environmental reasons. B100 is essentially sulfur-free. The amount of total sulfur in motor fuels is determined by ASTM D 5453 (ASTM International, 2002). This standard specifies a limit of 0.0015 (max) % of mass of sulfur content in biodiesel. Sulfur levels in fuel are regulated by various governmental agencies to assure compatibility with emission standard requirements.

Tests performed at Southwest Research Institute concluded that all the samples had less sulfur content than the standard specifies. The sulfur content in B100 was observed to be less than 1 ppm, which is one of the major advantages of biodiesel. Low sulfur helps both environment and engine life (Williams Alaska Petroleum, n.d.). The tests showed an increase in sulfur content as the soybean oil content increased. This can be attributed to the presence of sulfur in soybean oil and increasing soybean oil content in the fuel mixture causing an increase of sulfur content in the fuel blends. For producers: If sulfur is present, check the source of the feedstock to make sure it is not hydrocarbon based. For distributors/end users: High sulfur leads to emissions problems.

### **3.24 Visual Appearance Inspection**

Visual inspection indicates successful biodiesel reaction in two distinct layers. Top layer: if 80 % to 90 % of the product is lighter in color than the bottom layer, it is biodiesel. Bottom Layer: 10 % to 20 % of the reaction, darker color, a mixture of glycerin, catalyst/lye, alcohol and possibly food particles. A milky middle layer in the test batch indicates the production of soap (due to water in vegetable oil or too much lye). Biodiesel with this middle layer should undergo a water wash. Unsuccessful reactions results in no layering or one solid batch of soap (ASTM D4176).

### **3.25 Water in Oil**

Moisture is considered a chemical contaminant when suspended or mixed with lubricating oils. It presents a combination of chemical and physical

problems for the lubricant and machinery, respectively. The effects of water are insidious. Failure due to water contamination may be catastrophic, but it may not be immediate. Many failures blamed on lubricants are actually caused by excess water. The following are some of the effects of water on equipment:

- Shorter component life due to rust and corrosion;
- Water etching/erosion and vaporous cavitation;
- Hydrogen embrittlement;
- Oxidation of bearing Babbitt; and
- Wear caused by loss of oil film or hard water deposits (ASTM D6304).

### **3.26 Water and Sediment**

Fuel should be clear in appearance and free of water and sediment. The presence of these materials generally indicates poor fuel handling practices. Large amounts of water and sediment in a fuel such as biodiesel tend to disrupt fuel handling and also cause fouling in the fuel system of an engine. Water and sediment can shorten filter life or plug fuel filters, which can lead to engine fuel starvation. In addition, water can promote fuel corrosion and microbial growth. The level of water specified is within the solubility level of water in fuel and, as such, does not represent free water. Limits are established to allow measured results to be compared to a maximum level acceptable for proper engine operation.

Biodiesel can contain as much as 1500 ppm of dissolved water (Gerpen et al., 1997). ASTM D2709 is the standard test method for determining water and sediment in fuels (ASTM International, 2002). At the most, biodiesel should contain only 0.050 % by volume water and sediment.

It was evident that the entire sample's water and sediment content was well within limits specified by the standard. The water and sediment content did not change in most cases with increased triglyceride content. The reason for this is that water is insoluble in soybean oil and generally water does not encounter soybean during its preparation. However, in preparation of biodiesel, water is used during washing which increases the risk of biodiesel having dispersed water. High water content may cause poor combustion,

plugging and smoking. For distributors/end users: Improper storage may be the reason, and poor ignition, filter clogging, fuel pump problems can be the result. If sediment is present, replace the fuel filter cartridges.

#### 4. Conclusions

This paper examined selected biodiesel standards, specifications and test methods, and discussed the underlying issues. From the study, the following conclusions have been made:

- The US and EU standards have international significance; they are usually the starting point for biodiesel specifications developed in other countries.
- An adequate and constant quality of biodiesels can only be assured by respecting the biodiesel quality standards. To achieve this goal it is necessary to monitor the quality throughout the biodiesel manufacturing process, from the feedstock to the distribution stations. The physicochemical properties of biodiesels are strongly influenced by the nature and the composition of the feedstocks used in their production.
- The main criterion of biodiesel quality is the inclusion of its physical and chemical properties into the requirements of the adequate standard. Quality standards for biodiesel are continuously updated due to the evolution of compression ignition engines, ever stricter emission standards, reevaluation of the eligibility of feedstocks used for the production of biodiesel, etc. The current standards for regulating the quality of biodiesel on the market are based on a variety of factors which vary from region to region.

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