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# Biodiesel Quality, Standards and Properties

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## 1. Introduction

Quality is a prerequisite for the long-term success (successful use, without technical problems) of a biofuel. Biodiesel quality depends on several factors that reflect its chemical and physical characteristics. The quality of biodiesel can be influenced by a number of factors: the quality of the feedstock; the fatty acid composition of the parent vegetable oil or animal fat; the production process and the other materials used in this process; the post-production parameters; and the handling and storage. Given the fact that most current diesel engines are designed to be powered by diesel fuel, the physicochemical properties of biodiesel should be similar to those of diesel oil.

This chapter presents the main standards on commercial biodiesel quality adopted in different regions of the world and the importance and significance of the main properties that are regulated (cetane number, density, viscosity, low-temperature performances, flash point, water content, etc.) and unregulated (elemental composition, fatty acid methyl and ethyl esters composition, heating value, lubricity, etc.). Properties of fatty acid methyl and ethyl esters obtained from different feedstocks<sup>1</sup> are presented based mainly on data published in the specialized literature, but also on personal research.

## 2. Biodiesel standardization world-wide

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, including

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<sup>1</sup> ALME – algae methyl ester; CCEE – coconut oil ethyl ester; CCME – coconut oil methyl ester; CME – canola oil methyl ester; COME – corn oil methyl ester; CSOME – cottonseed oil methyl ester; FOEE – fish oil ethyl ester; FOME – fish oil methyl ester; JME – jatropha oil methyl ester; OEE – olive oil ethyl ester; OME – olive oil methyl ester; PEE – palm oil ethyl ester; PEEE – peanut oil ethyl ester; PEME – peanut oil methyl ester; PME – palm oil methyl ester; REE – rapeseed oil ethyl ester; RME – rapeseed oil methyl ester; SAFEE – safflower oil ethyl ester; SAFME – safflower oil methyl ester; SEE – soybean oil ethyl ester; SFEE – sunflower oil ethyl ester; SFME – sunflower oil methyl ester; SME – soybean oil methyl ester; TEE – tallow ethyl ester; TME – tallow methyl ester; WCOEE – waste cooking oil ethyl ester; WCOME – waste cooking oil methyl ester; YGME – yellow grease methyl ester; YMEE – yellow mustard oil ethyl ester; YMME – yellow mustard oil methyl ester.

characteristics of the existing diesel fuel standards, the predominance of the types of diesel engines most common in the region, the emissions regulations governing those engines, the development stage and the climatic properties of the region/country where it is produced and/or used, and not least, the purpose and motivation for the use of biodiesel (European Commission, 2007).

In Europe the fleet of cars equipped with diesel engines is considerable, while in the United States of America and Brazil diesel engines are specifically used in trucks. The most common feedstocks used are rapeseed and sunflower oil in Europe, soybean oil and waste vegetable oil in the USA and Canada, soybean oil in South America, palm, jatropha and coconut oil in Asia, palm oil and soybean oil in Australia and waste vegetable oil and animal fat in New Zealand. It is therefore not surprising that there are some significant differences among the regional standards, a universal quality specification of biodiesel is, and will be impossible. Table 1 presents a list of the most important biodiesel quality standards in the world, while in Tables 2-9 specifications of the imposed limits for the main properties of biodiesel and the required test methods are presented.

Country/ Area	Specifications	Title
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)
India	IS 15607	Bio-diesel (B 100) blend stock for diesel fuel - Specification
Japan	JASO M360	Automotive fuel - Fatty acid methyl ester (FAME) as blend stock
South Africa	SANS 1935	Automotive biodiesel fuel

Table 1. Biodiesel 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. 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 (European Commission, 2007; NREL, 2009; Prankl, et al., 2004).

The European standard EN 14214 is adopted by all 31 member states of the European Committee for Standardization (CEN): Austria, Belgium, Bulgaria, Croatia, Cyprus, the Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, the Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, and the United

Kingdom. Thus, there are no national regulations concerning biodiesel quality, but there is a separate section (not presented in the table), which provides cold flow property regulations. The national standards organizations provide the specific requirements for some regulations of CFPP (cold-filter plugging point, method EN 116), viscosity, density and distillation characteristics depending on the climate (6 stages for moderate climate and 5 for arctic climate). The regular diesel quality standard EN 590 specifies that commercial diesel fuel can contain 7% v/v biodiesel, compliant with the standard EN 14214. The standard ASTM D6751 describes the quality requirements and the methods of analysis used for biodiesel blended with diesel oil, applying to methyl esters as well as for ethyl esters. As the requirements for low-temperature properties can vary greatly, the standard foresees the indication of the cloud point. The standard ASTM D975 allows mixing commercial diesel oil with 5% biodiesel that meets the requirements of ASTM D6751, and ASTM D7467 specifies the quality requirements of mixtures with 5-20% of biodiesel.

Property	Test method	Limits		Units
		min	max	
Ester content	EN 14103	96.5	-	% (m/m)
Density at 15°C	EN ISO 3675, EN ISO 12185	860	900	kg/m³
Viscosity at 40°C	EN ISO 3104, ISO 3105	3.5	5.0	mm²/s
Flash point	EN ISO 3679	120	-	°C
Sulfur content	EN ISO 20846, EN ISO 20884	-	10.0	mg/kg
Carbon residue (in 10% dist. residue)	EN ISO 10370	-	0.30	% (m/m)
Sulfated ash content	ISO 3987	-	0.02	% (m/m)
Water content	EN ISO 12937	-	500	mg/kg
Total contamination	EN 12662	-	24	mg/kg
Oxidative stability, 110°C	EN 14112	4.0	-	hours
Acid value	EN 14104	-	0.50	mg KOH/g
Iodine value	EN 14111	-	130	g I/100 g
Polyunsaturated methyl esters (>= 4 double bonds)		-	1	% (m/m)
Monoglyceride content	EN 14105	-	0.80	% (m/m)
Diglyceride content	EN 14105	-	0.20	% (m/m)
Triglyceride content	EN 14105	-	0.20	% (m/m)
Free glycerine	EN 14105, EN 14106	-	0.02	% (m/m)
Cold-filter plugging point	EN 116	-	-	°C
Pour point	ISO 3016	-	0	°C
Net calorific value (calculated)	DIN 51900, -1, -2, -3	35	-	MJ/kg

Table 2. European standard EN 14213 for biodiesel as heating oil

Property	Test method	Limits		Unit
		min	max	
Ester content	EN 14103	96.5	-	% (m/m)
Density at 15°C	EN ISO 3675, EN ISO 12185	860	900	kg/m <sup>3</sup>
Viscosity at 40°C	EN ISO 3104, ISO 3105	3.5	5.0	mm <sup>2</sup> /s
Flash point	EN ISO 3679	120	-	°C
Sulfur content	EN ISO 20846, EN ISO 20884	-	10.0	mg/kg
Carbon residue (in 10% dist. residue)	EN ISO 10370	-	0.30	% (m/m)
Cetane number	EN ISO 5165	51	-	-
Sulfated ash	ISO 3987	-	0.02	% (m/m)
Water content	EN ISO 12937	-	500	mg/kg
Total contamination	EN 12662	-	24	mg/kg
Copper strip corrosion (3 hours, 50°C)	EN ISO 2160	-	1	class
Oxidative stability, 110°C	EN 14112	6.0	-	hours
Acid value	EN 14104	-	0.50	mg KOH/g
Iodine value	EN 14111	-	120	g I/100 g
Linolenic acid content	EN 14103	-	12	% (m/m)
Content of FAME with ≥4 double bonds		-	1	% (m/m)
Methanol content	EN 14110	-	0.20	% (m/m)
Monoglyceride content	EN 14105	-	0.80	% (m/m)
Diglyceride content	EN 14105	-	0.20	% (m/m)
Triglyceride content	EN 14105	-	0.20	% (m/m)
Free glycerine	EN 14105; EN 14106	-	0.02	% (m/m)
Total glycerine	EN 14105	-	0.25	% (m/m)
Alkali metals (Na + K)	EN 14108; EN 14109	-	5.0	mg/kg
Earth alkali metals (Ca + Mg)	EN 14538	-	5.0	mg/kg
Phosphorus content	EN 14107	-	10.0	mg/kg

Table 3. European biodiesel standard (EN 14214)

Property	Test Method	Limits		Units
		min	max	
Calcium & Magnesium, combined	EN 14538	-	5	ppm (µg/g)
Flash Point (closed cup)	D 93	93	-	°C
Alcohol Control (one to be met):				
1. Methanol Content	EN 14110	-	0.2	% (m/m)
2. Flash Point	D93	130	-	°C
Water & Sediment	D 2709	-	0.05	% (v/v)
Kinematic Viscosity, at 40 °C	D 445	1.9	6.0	mm <sup>2</sup> /sec.
Sulfated Ash	D 874	-	0.02	% (m/m)
Sulfur: S 15 Grade S 500 Grade	D 5453	-	0.0015	% (m/m)
	D 5453	-	0.05	% (m/m)
Copper Strip Corrosion	D 130	-	3	No.
Cetane	D 613	47	-	-
Cloud Point	D 2500	report		°C
Carbon Residue, 100% sample	D 4530	-	0.05	% (m/m)
Acid Number	D 664	-	0.05	mg KOH/g
Free Glycerin	D 6584	-	0.020	% (m/m)
Total Glycerin	D 6584	-	0.240	% (m/m)
Phosphorus Content	D 4951	-	0.001	% (m/m)
Distillation-Atmospheric equivalent temperature 90% recovery	D 1160	-	360	°C
Sodium/Potassium, combined	EN 14538	-	5	ppm (µg/g)
Oxidation Stability	EN 15751	-	3	hours
Cold Soak Filtration For use in temperatures below -12 °C	D7501	-	360	seconds
	D7501		200	seconds

Table 4. Biodiesel standard ASTM D6751 (United States)

Property	Test method	Limits		Unit
		min	max	
Sulfur	ASTM D5453	-	50 10	mg/kg
Density at 15 °C	ASTM D1298, EN ISO 3675	860	890	kg/m³
Distillation T90	ASTM D1160	-	360	°C
Sulfated ash	ASTM D 874	-	0.20	% (m/m)
Viscosity at 40 °C	ASTM D445	3.5	5.0	mm²/s
Flash point	ASTM D93	120	-	°C
Carbon residue		-	-	-
- 10% dist. residue	EN ISO 10370	-	0.30	% (m/m)
- 100% dist. sample	ASTM D4530	-	0.05	% (m/m)
Water and sediment	ASTM D2709	-	0.050	% (v/v)
Copper strip corrosion (3 hours at 50°C)				
< 10 mg/kg of sulfur	EN ISO 2160		Class 1	
> 10 mg/kg of sulfur	ASTM D130	-	No. 3	-
Ester content	EN 14103	96.5		% (m/m)
Phosphorus	ASTM D4951	-	10	mg/kg
Acid value	ASTM D664	-	0.80	mg KOH/g
Total contamination	EN 12662, ASTM D5452	-	24	mg/kg
Free glycerol	ASTM D6584	-	0.02	% (m/m)
Total glycerol	ASTM D6584	-	0.25	% (m/m)
Cetane number	EN ISO 5165, ASTM D613 ASTM D6890, IP 498/03	51	-	-
Cold-filter plugging point		report	-	°C
Oxidation stability 6 hours at 110°C	EN 14112, ASTM D2274 (as relevant for biodiesel)	-	-	hours
Metals: Group I (Na, K)	EN 14108, EN 14109 (Group I)	-	5	mg/kg
Metals: Group II (Ca, Mg)	EN 14538 (Group II)	-	5	mg/kg

Table 5. Australian biodiesel standard



Property	Test method	Limits		Units
		min	max	
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 resiue (Ramsbottom)	D4530	-	0.05	% (m/ m)
Sulfated 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		mg/kg
Calcium and magnesium	-	To report		mg/kg
Iodine value	EN 14104	To report		-
Oxidation stability at 110°C	EN 14112	6	-	hours

Table 6. Biodiesel standard in India



Property	Test method	Limits		Units
		min	max	
Ester content	EN 14103	96.5	-	% (m/ m)
Density	JIS K 2249	0.86	0.90	g/ml
Kinematic Viscosity	JIS K 2283	3.5	5.0	mm <sup>2</sup> /s
Flash Point	JIS K 2265	120	-	°C
Sulfur	JIS K 2541-1, -2, -6, -7	-	10	ppm
10% Carbon Residue	JIS K 2270	-	0.3	% (m/ m)
Cetane number	JIS K 2280	51	-	-
Sulfated Ash	JIS K 2272	-	0.02	% (m/ m)
Water	JIS K 2275	-	500	ppm
Total contamination	EN 12662	-	24	ppm
Copper strip corrosion (3 hours at 50 °C)	JIS K 2513	-	Class 1	rating
Total acid number	JIS K 2501, JIS K0070	-	0.5	mgKOH/g
Iodine Number	JIS K 0070	-	120	gI/100g
Methyl linolenate	EN 14103	-	12.0	% (m/ m)
Methanol	JIS K 2536, EN 14110	-	0.20	% (m/ m)
Monoglyceride	EN 14105	-	0.80	% (m/ m)
Diglyceride	EN 14105	-	0.20	% (m/ m)
Triglyceride	EN 14105	-	0.20	% (m/ m)
Free glycerol	EN 14105, EN 14106	-	0.02	% (m/ m)
Total glycerol	EN 14105	-	0.25	% (m/ m)
Metals (Na + K)	EN 14108, EN 14109	-	5	ppm
Metals (Ca + Mg)	EN 14538	-	5	ppm
Phosphorous	EN 14107	-	10	ppm

Table 7. Japanese Biodiesel Specification

Property	Test method	Limits		Units
		min	max	
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
Sulfur 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	–	–
Sulfated 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	mg/kg
Group II metals (Ca + Mg)	EN 14538	–	5.0	mg/kg
Phosphorus content	EN 14107	–	10.0	mg/kg
Cold Filter Plugging Point (CFPP) Winter/Summer	EN 116	–	–4/+3	°C

Table 8. South African Biodiesel Standard

Property	Test method	Limits		Units
		min	max	
Flash point	ABNT NBR 14598, ASTM D93, EN ISO 3679	100	-	°C
Water and sediments	ASTM D2709	-	0.05	% (v/v)
Kinematic viscosity at 40 °C	ABNT NBR 10441, EN ISO 3104, ASTM D445	report		mm <sup>2</sup> /s
Sulfated ash	ABNT NBR 9842, ASTM D874; ISO 3987	-	0.02	% (m/m)
Sulfur	ASTM D5453; EN/ISO 14596	-	0.001	% (m/m)
Copper corrosion 3 hours at 50 °C	ABNT NBR 14359, ASTM D130; EN/ISO 2160	-	No. 1	-
Ester content	EN 14103	report		% (m/m)
Distillation – atmospheric equivalent temperature 90% Recovery	D 1160	-	360	°C
Cetane number	ASTM D613; EN/ISO 5165	45	-	-
Cloud point	ASTM D6371	-	-	°C
Carbon Residue, 100% sample	ASTM D4530; EN/ISO 10370	-	0.05	% (m/m)
Acid number	ASTM D664; EN 14104	-	0.80	mg KOH/g
Total contamination	EN 12662	report		mg/kg
Free glycerin	ASTM D6854; EN 14105-6	-	0.02	% (m/m)
Total glycerin	ASTM D6854; EN 14105	-	0.38	% (m/m)
Distillation recovery 95%	ASTM D1160	-	360	°C
Phosphorus	ASTM D4951; EN 14107	-	10	mg/kg
Specific gravity	ABNT NBR 7148, 14065 ASTM D1298/4052	report		-
Alcohol	EN 14110	-	0.50	% (m/m)
Iodine number	EN 14111	report		gI/100g
Monoglycerides	ASTM D6584; EN 14105	-	1.00	% (m/m)
Diglycerides	ASTM D6584; EN 14105	-	0.25	% (m/m)
Triglycerides	ASTM D6584; EN 14105	-	0.25	% (m/m)
Metals: Group I (Na, K)	EN 14108, EN 14109	-	10	mg/kg
Metals: Group II (Ca, Mg)	EN 14538	report		mg/kg
Aspect	—	clear		-
Oxidation stability at 110°C	EN 14112	6	-	hours

Table 9. Brazilian biodiesel standard

3. Biodiesel fuel properties

The properties of biodiesel can be grouped by multiple criteria. The most important are those that influence the processes taking place in the engine (ignition qualities, ease of starting, formation and burning of the fuel-air mixture, exhaust gas formation and quality

and the heating value, etc.), cold weather properties (cloud point, pour point and cold filter plugging point), transport and depositing (oxidative and hydrolytic stability, flash point, induction period, microbial contamination, filterability limit temperature, etc.), wear of engine parts (lubricity, cleaning effect, viscosity, compatibility with materials used to manufacture the fuel system, etc.).

3.1 Chemical composition of biodiesel

The elemental composition (carbon – C, hydrogen – H and oxygen – O), the C/H ratio and the chemical formula of diesel and biodiesel produced from different feedstocks is shown in Table 10 (Barabás & Todoruț, 2010; Chuepeng &Komintarachat, 2010). The elemental composition of biodiesel varies slightly depending on the feedstock it is produced from. The most significant difference between biodiesel and diesel fuel composition is their oxygen content, which is between 10 and 13%. Biodiesel is in essence free of sulfur.

Fuel	C	H	O	C/H	Empirical formula
Diesel	86.5	13.5	0	6.24	C <sub>15.05</sub> H <sub>27.94</sub>
RME	77.2	12.0	10.8	6.45	C <sub>19.03</sub> H <sub>35.17</sub> O <sub>2</sub>
SME	77.2	11.9	10.8	6.60	C <sub>19.05</sub> H <sub>34.98</sub> O <sub>2</sub>
PME	76.35	11.26	12.39	6.16	C <sub>18.07</sub> H <sub>34.93</sub> O <sub>2</sub>

Table 10. Elemental composition of diesel fuel and biodiesel, % (m/m)

Unlike fuels of petroleum origin, which are composed of hundreds of hydrocarbons (pure substances), biodiesel is composed solely of some fatty acid ethyl and methyl esters; their number depends on the feedstock used to manufacture biodiesel and is between 6 and 17 (Shannon & Wee, 2009). The fatty acid methyl and ethyl esters in the composition of biodiesel are made up of carbon, hydrogen and oxygen atoms that form linear chain molecules with single and double carbon-carbon bonds. The molecules with double bonds are unsaturated. Thus, fatty acid esters take the form *Cnc:nd* (lipid numbers), where *nc* is the number of carbon atoms in the fatty acid and *nd* is the number of double bonds in the fatty acid (e.g., 18:1 indicates 18 carbon atoms and one double bond). The ester composition of biodiesel (methyl and ethyl esters) is shown in Table 11 (Bamgboye & Hansen, 2008; Barabás & Todoruț, 2010; Chuepeng &Komintarachat, 2010). The highest concentrations are C18:1, C18:2, C18:3, followed by C18:0. A significant exception is biodiesel from coconut oil, in the case of which the highest concentration is C12:0, C14:0 and C16:0, hence this biodiesel is more volatile than the others. The physicochemical properties of biodiesel produced from a given feedstock are determined by the properties of the esters contained.

3.2 Cetane number

Cetane number (CN) is a dimensionless indicator that characterizes ignition quality of fuels for compression ignition engines (CIE). Since in the CIE burning of the fuel-air mixture is initiated by compression ignition of the fuel, the cetane number is a primary indicator of fuel quality as it describes the ease of its self-ignition.

Theoretically, the cetane number is defined in the range of 15-100; the limits are given by the two reference fuels used in the experimental determination of the cetane number:

Ester <sup>2</sup>	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	Others	Obs.
ALME	-	-	-	0.6	6.9	3	75.2	12.4	1.2	0.4	-	0.3	-
RME	-	-	-	-	3.8	1.9	63.9	19	9.7	0.6	-	1.1	-
REE	-	-	-	-	4.9	1.6	33.0	20.4	7.9	-	-	22.2	22.2% C22:1
CME	-	-	-	-	4.2	2	57.4	21.3	11.2	1.2	2.1	0.60	-
SME	-	-	-	-	9.4	4.1	22	55.3	8.9	-	-	0.3	-
SEE	-	-	-	-	10.8	3	26.5	47.3	9	-	-	3.40	-
SFME	-	-	-	-	4.2	3.3	63.6	27.6	0.2	-	-	1.1	-
PME	-	-	0.2	0.5	43.4	4.6	41.9	8.6	0.3	0.3	-	0.2	-
COME	-	-	-	-	12.1	1.8	27.2	56.2	1.3	0.4	-	1	-
AME	-	-	-	-	11.6	4.4	49.6	33.7	0.7	-	-	-	-
OEE	-	-	-	-	11.6	3.1	74.9	7.8	0.6	-	-	2	-
TME	-	-	0.2	2.9	24.3	22.8	40.2	3.3	0.7	0.2	0.6	4.8	-
FOME	-	-	0.2	7.7	18.8	3.9	15	4.6	0.3	0.2	1.4	47.9	25.1% - C20:5
JME	-	-	-	-	12.7	5.5	39.1	41.6	0.2	0.2	-	0.7	-
JME	-	-	-	-	12.5	30.9	34.4	20.4	-	-	-	1.8	-
WCOME	-	-	0.1	0.1	11.8	4.4	25.3	49.5	7.1	0.3	-	1.4	-
WCOEE	-	-	2.0	-	15.7	3.1	29.6	41.5	1.0	-	-	7.1	-
SAFME	-	-	-	-	7.3	1.9	13.6	77.2	-	-	-	-	-
CCME	6.3	6	49.2	18.5	9.1	2.7	6.5	1.7	-	-	-	-	-
CCEE	7.5	6	53.3	17.1	7.3	1.9	5.5	1.4	-	-	-	-	-
YMME	-	-	-	-	2.6	1.2	20.6	20.6	13.3	0.9	10.7	30.1	25.6% - C20:1
YGME	-	-	0.1	0.5	14.3	8	35.6	35	4	0.3	-	2.2	-

Table 11. Fatty acid composition of different biodiesels (methyl and ethyl esters), % (m/m)

a linear-chain hydrocarbon, hexadecane (C<sub>16</sub>H<sub>34</sub>, also called n-cetane), very sensitive to ignition, having a cetane number of 100, and a strongly branched-chain hydrocarbon, 2,2,4,4,6,8,8-heptamethylnonane (HMN, also called isocetane), having the same chemical formula C<sub>16</sub>H<sub>34</sub>, with high resistance to ignition, having a cetane number of 15. The cetane number is the percentage by volume of normal cetane in a mixture of normal cetane and HMN, which has the same ignition characteristics as the test fuel. Thus the cetane number is given by the formula: CN = n-cetane [%, v/v] + 0.15\*HMN [%, v/v]. Determination of the cetane number on the monocyliner engine specially designed for this purpose (EN ISO 5165, ASTM D613) is an expensive and lengthy operation. A cheaper and faster alternative is to determine the derived cetane number through ignition delay in a constant-volume combustion chamber (ignition quality tester – IQT), a widely accepted method described in ASTM D6890 and ASTM D7170, accepted by the biodiesel quality standard ASTM D6751. The cetane number indicates ignition delay, i.e. the time elapsed since the injection of fuel into the combustion chamber and self-ignition of the fuel-air mixture. Thus, ignition time lag

<sup>2</sup> C8:0 – caprylate, C10:0 – caprate, C12:0 – laurate, C14:0 – myristate, C16:0 – palmitate, C18:0 – stearate, C18:1 – oleate, C18:2 – linoleate, C18:3 – linolenate, C20:0 – arachidate, C22:1 – erucate.

means a low cetane number and vice versa. The upper and lower limits of the cetane number ensure the proper functioning of the engine. If the cetane number is too low, starting the engine will be difficult, especially at low temperatures and the engine will function unevenly and noisily, with cycles without combustion, it will warm more slowly, combustion will be incomplete and engine pollution will increase, especially hydrocarbon emissions. In case of a fuel with a very high cetane number, ignition will be carried out before a proper mix with air, resulting in incomplete combustion and the increase of the amount of exhaust smoke. Also, if the cetane number is too high the fuel will ignite close to the injector causing it to overheat, and unburned fuel particles can plug the injector nozzles. The optimal range of the CN (Fig. 1) is between 41 and 56, but must not be higher than 65 (Băţaga et al., 2003). The minimum cetane number of biodiesel is 51 in the European Union, 47 in the United States and 45 in Brazil. The minimum CN for diesel oil is 40 in the USA (ASTM D 975) and 51 in Europe (EN 590). The cetane numbers of the main pure methyl and ethyl esters are shown in Table 12 (Bamgboye & Hansen, 2008; Barabás & Todoruţ, 2010).

Acid (Cnc:nd)	Cetane number		Heat of combustion, kJ/kg	
	Methyl ester	Ethyl ester	Methyl ester	Ethyl ester
Caprylate (C8:0)	n.d.	n.d.	34907	35582
Caprate (C10:0)	48.53	55.6	36674	37178
Laurate (C12:0)	61.99	73	37968	n.d.
Myristate (C14:0)	69.48	69.45	38431	n.d.
Palmitate (C16:0)	81.17	86.55	39449	n.d.
Palmitoleate (C16:1)	53.80	n.d.	39293	n.d.
Stearate (C18:0)	88.57	86.83	40099	n.d.
Oleate (C18:1)	62.39	64.57	40092	40336
Linoleate (C18:2)	42.10	40.37	39698	n.d.
Linolenate (C18:3)	32.20	26.7	39342	n.d.
Arachidate (C20:0)	100.00	n.d.	n.d.	n.d.
Erucate (C22:1)	76.00	n.d.	n.d.	n.d.

Table 12. Cetane number and heat of combustion for fatty acid esters

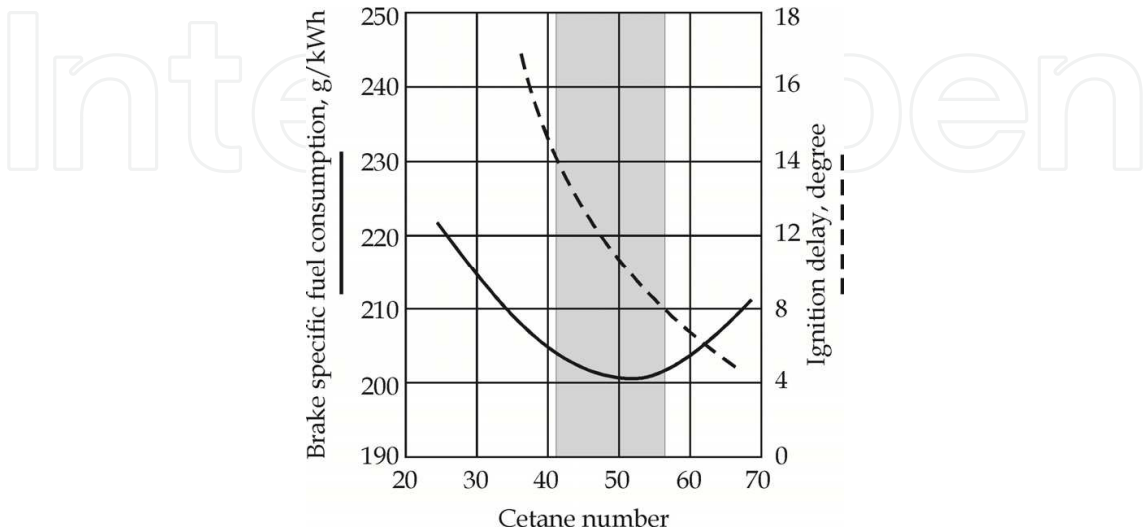


Fig. 1. Brake specific fuel consumption and ignition delay vs. fuel cetane number.



The cetane number of a substance depends on its molecular structure. The cetane number decreases with the number of double bonds, *nd*, in fatty acid ester molecules (degree of unsaturation, characterized by the iodine number) and increases with the number of carbon atoms, *nc*. Generally, the cetane number of ethyl esters is higher than that of methyl esters. Methyl- and ethyl palmitate as well as methyl- and ethyl stearate have a high cetane number, but methyl- and ethyl linoleate has a low cetane number. The cetane number of biodiesel depends on the cetane number and the concentration of the esters it is made up of. The cetane number of biodiesels is higher than that of the vegetable oils from which they are produced ( $34.6 < \text{CN} < 42$ ), and is between 39 and 67. The cetane number values of biodiesel produced from various feedstocks are presented in Table 13 (Anastopoulos et al., 2009; Barabás & Todoruț, 2010; Chuepeng & Komintarachat, 2010; Shannon et al., 2009; Fan et al., 2009).

Ester	CN	$Q_g$ , kJ/kg	$Q_n$ , kJ/kg	$\nu$ , mm <sup>2</sup> /s	$\rho$ , kg/m <sup>3</sup>
AME	n.d.	n.d.	n.d.	4.52	879
CCEE	67.4	38158	n.d.	3.08	n.d.
CCME	57.4	n.d.	n.d.	n.d.	n.d.
CME	n.d.	n.d.	n.d.	4.34 – 4.84	883 – 888
COME	65	n.d.	38480	4.18 – 4.52	884
CSOME	45.5 – 51.2	40600	n.d.	4.06	874 – 884
FOEE	n.d.	n.d.	n.d.	3.98	887
FOME	51	n.d.	37800	4.96 – 5.76	850
JME	48	n.d.	38450	4.8 – 5.56	870 – 880.3
OEE	n.d.	38200	n.d.	4.0	881.5
OME	61	n.d.	37287	4.70	n.d.
PEE	56.2	39070	n.d.	n.d.	n.d.
PME	n.d.	39837	37500	3.70	864.4 – 870
REE	59.7 – 67.4	38300 – 40663	37820	4.84 – 6.17	876 – 881.2
RME	56 – 61.8	40540	37300 – 37780	4.83 – 5.65	880.2
SAFEE	62.2	39872	n.d.	4.31	n.d.
SAFME	49.8	40060	n.d.	4.03	880
SEE	48.2	40160	n.d.	4.40 – 5.03	833
SME	50.9	40400	37000	4.8	n.d.
SFEE	n.d.	38600	n.d.	4.43	882.7
SFME	45.5 – 58	n.d.	38472	4.03	878 – 884
SME	37 – 51.5	39871	37388	3.97 – 4.27	872 – 885
TEE	n.d.	n.d.	n.d.	5.20	n.d.
TME	58 – 61.8	39961-40200	37531	4.1 – 4.99	876 – 887
WCOEE	n.d.	37800 – 40500	37200	5.81	888.5
WCOME	n.d.	40110	n.d.	5.78 – 6.0	920
YMEE	54.9	40679	n.d.	5.66	n.d.

Table 13. Cetane number, gross and net heat of combustion, viscosity and density of biodiesels from different feedstoks



### 3.3 Heat of combustion

The heat of combustion (heating value) at constant volume of a fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quantity of heat liberated when a unit quantity of the fuel is burned in oxygen in an enclosure of constant volume, the products of combustion being gaseous carbon dioxide, nitrogen, sulfur dioxide, and water, with the initial temperature of the fuel and the oxygen and the final temperature of the products at 25°C. The unit quantity can be mol, kilogram or normal square meter. Thus the units of measurement of the heating value are kJ/kmol, kJ/kg. The volumetric heat of combustion, i.e. the heat of combustion per unit volume of fuel, can be calculated by multiplying the mass heat of combustion by the density of the fuel (mass per unit volume). The volumetric heat of combustion, rather than the mass heat of combustion is important to volume-dosed fueling systems, such as diesel engines.

The gross (or high, upper) heating value ( $Q_g$ ) is obtained when all products of the combustion are cooled down to the temperature before the combustion and the water vapor formed during combustion is condensed. The net or lower heating value ( $Q_n$ ) is obtained by subtracting the latent heat of vaporization of the water vapor formed by the combustion from the gross or higher heating value. The net heat of combustion is related to the gross heat of combustion:  $Q_n = Q_g - 0.2122 \cdot H$ , where  $H$  is the mass percentage of hydrogen in the fuel. As in internal combustion engines the temperature of exhaust gases is higher than the boiling temperature of water (water vapor is discharged), for assessing the heating value of the fuel, the lower heating value of the biodiesel is more relevant. The heating value of fatty acid esters (Table 12) increases with molecular chain length (with the number of carbon atoms,  $nc$ ) and decreases with their degree of unsaturation (the number of double bonds,  $nd$ ). The mass heating value of unsaturated esters is lower than that of saturated esters, but due to their higher density, the volume heating value of unsaturated esters is higher than that of saturated esters. For example, methyl stearate ( $nd=0$ ) has a mass heating value of 40099 kJ/kg, and methyl oleate ( $nd=1$ ) has 40092 kJ/kg. Reported to the volume unit, the heating value of methyl stearate is 34070 kJ/L, while the volume heating value of methyl oleate is 34320 kJ/L. The presence of oxygen in the esters molecules (Table 1) decreases the heating value of biodiesel by 10...13% compared to the heating value of diesel fuel (see Table 13). Due to the fact that fuel dispensing in CIE is volumetric, the energy content of the injected dose will be more reduced in the case of biodiesel, therefore, the specific fuel consumption for biodiesel will be higher. This is partially compensated by the fact that the density of biodiesel is higher than that of diesel fuel.

### 3.4 Density of biodiesel

Fuel density ( $\rho$ ) is the mass of unit volume, measured in a vacuum. Since density is strongly influenced by temperature, the quality standards state the determination of density at 15 °C. Fuel density directly affects fuel performance, as some of the engine properties, such as cetane number, heating value and viscosity are strongly connected to density. The density of the fuel also affects the quality of atomization and combustion. As diesel engine fuel systems (the pump and the injectors) meter the fuel by volume, modification of the density affects the fuel mass that reaches the combustion chamber, and thus the energy content of the fuel dose, altering the fuel/air ratio and the engine's power. Knowing the density is also necessary in the manufacturing, storage, transportation and distribution process of biodiesel as it is an important parameter to be taken into account in the design of these processes. The density of esters depends on the molar mass, the free fatty acid content, the water content

and the temperature. Density values determined for pure esters are presented in Table 14 and for different biodiesel feedstock are listed in Table 13. The density of biodiesel is typically higher than that of diesel fuel and is dependent on fatty acid composition and purity. As biodiesel is made up of a small number of methyl or ethyl esters that have very similar densities, the density of biodiesel varies between tight limits. Contamination of the biodiesel significantly affects its density; therefore density can also be an indicator of contamination.

### 3.5 Viscosity of biodiesel

The viscosity of liquid fuels is their property to resist the relative movement tendency of their composing layers due to intermolecular attraction forces (viscosity is the reverse of fluidity). Viscosity is one of the most important properties of biodiesel. Viscosity influences the ease of starting the engine, the spray quality, the size of the particles (drops), the penetration of the injected jet and the quality of the fuel-air mixture combustion (Alptekin and Canakci 2009). Fuel viscosity has both an upper and a lower limit. The fuel with a too low viscosity provides a very fine spray, the drops having a very low mass and speed. This leads to insufficient penetration and the formation of *black smoke* specific to combustion in the absence of oxygen (near the injector) (Băţaga et al., 2003). A too viscous biodiesel leads to the formation of too big drops, which will penetrate to the wall opposite to the injector. The cylinder surface being cold, it will interrupt the combustion reaction and *blue smoke* will form (intermediate combustion product consisting of aldehydes and acids with pungent odor) (Băţaga et al., 2003). Incomplete combustion results in lower engine power. Too high viscosity leads to the increase of combustion chamber deposits and the increase of the needed fuel pumping energy, as well as the increased wear of the pump and the injector elements due to higher mechanical effort. Too high viscosity also causes operational problems at low temperatures because the viscosity increases with decreasing temperature (for temperatures at or below -20 °C viscosity should be at or below 48 mm<sup>2</sup>/s). Viscosity also influences the lubricity of the fuel as some elements of the fuel system can only be lubricated by the fuel (pumps and injectors). Due to the presence of the electronegative oxygen, biodiesel is more polar than diesel fuel; as a result, the viscosity of biodiesel is higher than that of diesel fuel. The viscosity of pure ethyl esters are higher than viscosity of methyl esters (Table 14). The viscosities of biodiesels from different feedstocks are presented in Table 13.

### 3.6 Cold flow properties

Generally, all fuels for CIE may cause starting problems at low temperatures, due to worsening of the fuel's flow properties at those temperatures. The cause of these problems is the formation of small crystals suspended in the liquid phase, which can clog fuel filters partially or totally. Because of the sedimentation of these crystals on the inner walls of the fuel system's pipes, the flow section through the pipes is reduced, causing poor engine fueling. In extreme situations, when low temperatures persist longer (e.g. overnight), the fuel system can be completely blocked by the solidified fuel.

The cold flow performances of the fuels can be characterized by the cloud point (CP), the pour point (PP), the cold filter plugging point (CFPP) and viscosity ( $\nu$ ). An alternative to CFPP is the low-temperature flow test (LTFT). Recently, the U.S. introduced a new method for assessing the cold flow properties of biodiesel, called cold soak filtration test (CSFT).

Acid ( <i>Cnc:nd</i> )	Density, kg/m <sup>3</sup>				Dynamic and kinematic viscosity			
	Methyl ester		Ethyl ester		Methyl ester		Ethyl ester	
	15 °C	40 °C	15 °C	40 °C	mPa·s	mm <sup>2</sup> /s	mPa·s	mm <sup>2</sup> /s
Caprylate (C8:0)	881.5	859.6	871.6	850.0	1.0444	1.2150	n.d.	n.d.
Caprate (C10:0)	876.4	856.0	868.4	848.0	1.4773	1.7258	1.6000	1.8868
Laurate (C12:0)	873.7	853.9	866.4	846.8	2.0776	2.4331	2.2198	2.6214
Myristate (C14:0)	n.d.	852.2	864.8	845.8	2.8447	3.3381	2.9928	3.5384
Palmitate (C16:0)	n.d.	850.8	n.d.	n.d.	3.7551	4.4136	3.9558	n.d.
Palmitoleate (C16:1)	872.8	853.8	n.d.	n.d.	2.6162	3.0642	n.d.	n.d.
Stearate (C18:0)	n.d.	849.8	n.d.	844.8	4.9862	5.8675	5.0823	6.0160
Oleate (C18:1)	877.7	859.5	874.1	855.8	3.9303	4.5728	4.2137	4.9237
Linoleate (C18:2)	889.9	871.5	886.3	867.8	3.2270	3.7028	3.4060	3.9249
Linolenate (C18:3)	905.7	887.0	897.0	878.3	2.9253	3.2980	2.9750	3.3872
Erucate (C22:1)	874.3	856.5	n.d.	n.d.	5.9575	6.9556	n.d.	n.d.

Table 14. Density and viscosity of fatty acid esters

3.6.1 Cloud point (CP)

The cloud point (CP) is the temperature at which crystals first start to form in the fuel. The cloud point is reached when the temperature of the biodiesel is low enough to cause wax crystals to precipitate. Initially, cooling temperatures cause the formation of the solid wax crystal nuclei that are submicron in scale and invisible to the human eye. Further decrease of temperature causes these crystals to grow. The temperature at which crystals become visible (the crystal’s diameter ≥ 0.5 μm) is defined as the cloud point because the crystals form a cloudy suspension. Below the CP these crystals might plug filters or drop to the bottom of a storage tank. The CP is the most commonly used measure of low-temperature operability of the fuel. The biodiesel cloud point is typically higher than the cloud point of conventional diesel. The cloud point of biodiesel depends on the nature of the feedstock it was obtained from (Table 15) (Barabás & Todoruț, 2010; Fan et al., 2009), and is between -5 °C (ALME) and 17 °C (TME).

3.6.2 Pour point (PP)

The pour point is the temperature at which the fuel contains so many agglomerated crystals that it is essentially a gel and will no longer flow. This occurs if the temperature of the biodiesel drops below CP, when the microcrystals merge and form large clusters, which may disrupt the flow of the biodiesel through the pipes of the engine’s fuel system. Similarly to the cloud point, the pour point values also depend on the feedstock the biodiesel was produced from (see Table 15). Pour point values are between -15 °C (REE and YMEE) and 16 °C (PME). Although CP and PP are relatively easily determined, they only provide indicative values for the minimum temperature at which the fuel can be used. While at cloud point the fuel can still be used in acceptable conditions, at pour point this is no longer possible. In other words, cloud point overestimates minimum operating temperature and pour point underestimates it.

3.6.3 Cold filter plugging point (CFPP)

The cold filter plugging point is the lowest temperature at which 20 mL of fuel passes through a filter within 60 s by applying a vacuum of 2 kPa. The CFPP test employs rapid

cooling conditions. For this reason, CFPP does not reflect the actual limit of the fuel’s operability temperature. The test does not take into account the fuel systems specially designed to operate at low temperatures (heavy-duty vehicles and some light-duty vehicles). Nevertheless, most standards require the determination of this parameter and its value is regulated depending on the climatic conditions of each region or country. The values of the CFPP of biodiesel produced from various feedstocks are listed in Table 15. CME has the lowest value, while TME has the highest. Biodiesel produced from the most common feedstocks has inferior cold flow properties compared to conventional diesel fuel (has a higher cloud point and pour point compared to petroleum diesel), which can lead to operational issues in cold climates, such as filter plugging due to wax buildup or reduced fuel flow. Conventional diesel blends with 10 % (v/v) biodiesels typically have significantly higher CP, PP and CFPP than petroleum diesel fuel.

Ester	CP, C	PP, °C	CFPP, °C	LTFT, °C	CSFT, s
ALME	-5	n.d.	-7	n.d.	85
CCEE	5	-3	n.d.	n.d.	n.d.
CCME	0	n.d.	-4	n.d.	49
CEE	-1	-6	n.d.	n.d.	n.d.
CME	-3...1	-9...-4	-13...-4	n.d.	113
COME	-3	-4	-3...-7	n.d.	131
CSOME	6	-4...0	3	n.d.	n.d.
FOME	4	n.d.	0	n.d.	68...81
JME	n.d.	-1	n.d.	n.d.	n.d.
OEE	7	-5	-3	n.d.	n.d.
OME	-2	-3	-6	n.d.	n.d.
PEE	8...16	6...12	n.d.	n.d.	n.d.
PME	13...16	14...16	10...14	n.d.	88
REE	-2...1	-15...-12	1	n.d.	n.d.
RME	-3...1	-9...-11	-10...-6	n.d.	233
SAFEE	-6	-6	n.d.	n.d.	n.d.
SAFME	n.d.	-6	n.d.	n.d.	n.d.
SEE	-2...15	-6...5	n.d.	n.d.	n.d.
SME	-2...3	-7...-1	-4...-2	-2...0	67
SFEE	-1...2	-6...-5	-3	n.d.	n.d.
SFME	0...4	-4...-3	-4...-2	n.d.	107
TEE	15	3...12	8	13	n.d.
TME	9...17	9...15	9...14	20	76
WCOEE	9	-1...8	3	n.d.	n.d.
WCOME	-2...3	-3...-6	-2...-9	n.d.	233
YGME	6	n.d.	2	n.d.	95
YMEE	1	-15	n.d.	n.d.	n.d.
YMME	4	n.d.	-5	n.d.	n.d.

Table 15. Cold flow properties of biodiesels from different feedstoks

### 3.6.4 Low-temperature flow test (LTFT)

Although CFPP is accepted almost worldwide as the minimum temperature at which fuel can be exploited, mainly because of the rapid cooling of the sample, the test does not entirely reflect real cooling conditions of the fuel. The Low-Temperature Flow Test (LTFT) is a similar attempt to the test determining the CFPP, the major difference being the cooling speed of the fuel sample, which in this case is 1 °C/h, reflecting more accurately the real conditions, when for example the fuel in the fuel system of a vehicle is cooled over a frosty night. In determining the low temperature flow temperature the sample volume is 180 mL, the filter is finer, and the vacuum filtration pressure is higher. Like CFPP, LTFT is defined as the lowest temperature at which 180 mL of fuel safely passes through the filter within 60 s. Since the LTFT is not included in biodiesel quality standards, currently there is very limited information about its values for biodiesel (see Table 15).

### 3.6.5 Cold soak filtration test (CSFT)

This test is the newest requirement under ASTM D6751, added in 2008 in response to data indicating that in blends with petroleum diesel of up to 20% some biodiesels could form precipitates above the cloud point. Some substances that are or seem to be soluble at ambient temperature come out of the solution if temperature decreases or biodiesel is stored at ambient temperature for a longer period. This phenomenon was observed both in the case of pure biodiesel and its blends with diesel fuel.

Solid or semi-liquid substances can, in turn, cause filter clogging. The CSFT allows highlighting this danger and improving biodiesel due to this phenomenon. Cold soak consists of chilling a 300 ml sample for 16 hours at 4 °C, then warming it up to ambient temperature (68-72 °F, 20-22 °C) and filtering with a 0.7 micron glass fiber filter with a stainless steel filter support. The result of this test is filtering time. There are two time limits for filtration: in the case of net biodiesel for use throughout the year, the filtration time is 360 seconds or less; if the seller claims the post-blended biodiesel is fit for use in temperatures below 10 °F (-12 °C) the filtration time is 200 seconds or less. The test result depends mainly on the type and quality of the used feedstock, the purity of biodiesel, the soap value, the total glycerin, etc. The higher the soap value, the higher the cold soak filtration results. In addition it was found that total glycerin can also negatively influence the cold soak filtration results. When the total glycerin is within the ASTM D 6751 standard's limits ( $\leq 0.24\%$ ), it will show no negative effect on the cold soak filtration results (Fan et al., 2009). Because CSFT has only recently been included in biodiesel quality standards, at present there is very little reported data on this parameter (Table 15).

## 3.7 Biodiesel lubricity

Lubricity describes the ability of the fuel to reduce the friction between surfaces that are under load. This ability reduces the damage that can be caused by friction in fuel pumps and injectors (Schumacher, 2005). Lubricity is an important consideration when using low and ultra-low sulfur fuels (ULSD). The fuel lubricity can be measured with High Frequency Reciprocating Rig (HFRR) test methods as described at ISO 12156-1. The maximum corrected wear scar diameter (WS 1.4) for diesel fuels is 460  $\mu\text{m}$  (EN 590). Reformulated diesel fuel has a lower lubricity and requires lubricity improving additives (which must be compatible with the fuel and with any additives already found in the fuel) to prevent excessive engine wear. The lubricity of biodiesel is excellent. Biodiesel may be used as a



lubricity improver. The lubricity of some biodiesels and the influence of biodiesel concentration on this parameter in blends with diesel fuel are shown in Table 16 (Barabás & Todoruț, 2010; Schumacher, 2005). The lubricity of biodiesel depends on the feedstock it is produced from. Biodiesel from jatropha oil has the highest and biodiesel sunflower oil has the lowest lubricity. Generally, it can be stated that 1% (v/v) biodiesel mixed with ultra-low sulfur diesel fuel (ULSD) already provides lubricity that meets the requirements of the commercial diesel fuel’s lubricity quality standards.

Biodiesel	Biodiesel concentration, % (v/v)					
	0	0.25	0.5	1	2	100
CME	735	n.d.	n.d.	n.d.	351	n.d.
COME	735	n.d.	n.d.	n.d.	366	n.d.
JME	570	345	325	265	165	95
PME	570	490	380	265	185	135
RME	520	518	517	395	n.d.	n.d.
SFME	735	n.d.	n.d.	n.d.	429 (2 % w/w)	n.d.
SME	735	n.d.	n.d.	n.d.	375	n.d.
SME	n.d.	485	525	325	n.d.	n.d.

Table 16. The effect of the biodiesel additive in ULSD on WS1.4 (μm)

3.8 Flash point (FP)

The flash point is the minimum temperature calculated to a barometric pressure of 101.3 kPa at which the fuel will ignite (flash) on application of an ignition source under specified conditions. It is used to classify fuels for transport, storage and distribution according to hazard level. The flash point does not affect the combustion directly; higher values make fuels safer with regard to storage, fuel handling and transportation. FP varies inversely with the fuel’s volatility. For biodiesel the minimum flash point is 93 °C in the United States, 100 °C in Brazil and 120 °C in Europe. Biodiesel’s flash point decreases rapidly as the amount of residual (un-reacted) alcohol increases (methanol’s flash point is 11-12 °C, and ethanol’s is 13-14 °C). Thus, measuring the biodiesel flash point helps indicate the presence of methanol or ethanol. For example, the presence of 0.5% methanol in biodiesel reduces biodiesel flash point from 170 °C to 50 °C. If flash point is used to determine the methanol content, the ASTM standard imposes for it a minimum value of 130 °C. This limit may be considered too severe, because at the maximum permissible concentration of methanol of 0.2% w/w biodiesel flash point drops below 130 °C. The flash point of biodiesel produced from various feedstocks are presented in Table 17 (Anastopoulos et al., 2009; Barabás & Todoruț, 2010; Barabás et al., 2010; Chuepeng & Komintarachat, 2010; Pinyaphong et al., 2011; Shannon et al., 2009; Fan et al., 2009).

3.9 Acid value

The acid value (AV), also called neutralization number or acid number is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize the acidic constituents in one gram of sample. The acid value determination is used to quantify the presence of acid moieties in a biodiesel sample. In a typical procedure, a known amount of sample dissolved in organic solvent is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a color indicator. The acidic compounds that could possibly be

found in biodiesel are: 1) residual mineral acids from the production process, 2) residual free fatty acid from the hydrolysis process or the post- hydrolysis process of the esters and 3) oxidation byproducts in the form of other organic acids (Berthiaume & Tremblay, 2006). This parameter is a direct measure of the content of free fatty acids, thus the corrosiveness of the fuel, of filter clogging and the presence of water in the biodiesel. A too high amount of free glycerin can cause functioning problems at reduced temperatures and fuel filter clogging. This parameter can also be used to measure the freshness of the biodiesel. Fuel that has oxidized after long-term storage will probably have a higher acid value.

Ester	FP, °C	AV, mg KOH/g	IV, g Iodine/100 g FAME	Oxidation stability, hours
ALME	>160	n.d.	n.d.	8.5 – 11.0
CCEE	190	n.d.	n.d.	n.d.
CCME	115	n.d.	n.d.	35.5
COME	111 - 170	0.15	101.0 – 119.18	n.d.
CSOME	110	n.d.	n.d.	n.d.
FOME	>160	1.11	n.d.	0.2
JME	170	0.38	105.0	2.3
OEE	182	n.d.	n.d.	n.d.
OME	178	0.13	84.0	3.3
PME	176	0.12	57.0 – 59.0	n.d.
REE	170 – 181	n.d.	99.7	2.0. – 7.6
RME	166 – 179	0.14 – 0.16	97.4 – 109.0	n.d.
SAFEE	178	n.d.	n.d.	n.d.
SAFME	149..180	n.d.	139.83	n.d.
SEE	55	0.28	123.0	n.d.
SME	171	0.14	120.52 – 133.2	n.d.
SFEE	178	0.15	132.0 – 136.0	n.d.
SFME	85 – 177	0.15	n.d.	0.8...0.9
SME	120 – 190	0.30	n.d.	2.1
TME	96 – 188	n.d.	n.d.	1.6
WCOEE	124	n.d.	n.d.	0.33
WCOME	141	0.14 – 0.69	n.d.	>6
WCOME	110...160	0.14	n.d.	1.0
YGME	>160	n.d.	n.d.	5.2
YMEE	183	n.d.	n.d.	n.d.
YMME	n.d.	n.d.	n.d.	1.1

Table 17. Flash point, acid value, iodine value and oxidation stability of biodiesels from different feedstoks



### 3.10 Iodine value

The iodine value (IV) or iodine number was introduced in biodiesel quality standards for evaluating their stability to oxidation. The IV is a measurement of total unsaturation of fatty acids measured in g iodine/100 g of biodiesel sample, when formally adding iodine to the double bonds. Biodiesel with high IV is easily oxidized in contact with air. The iodine value highly depends on the nature and ester composition of the feedstocks used in biodiesel production. Therefore the IV is limited in various regions of the world depending on the specific conditions: 120 in Europe and Japan, 130 in Europe for biodiesel as heating oil, 140 in South Africa, in Brazil it is not limited and in the U.S., Australia and India it is not included in the quality standard (it would exclude feedstocks like sunflower and soybean oil). Biodiesel with high IV tends to polymerize and form deposits on injector nozzles, piston rings and piston ring grooves. The tendency of polymerization increases with the degree of unsaturation of the fatty acids.

### 3.11 Biodiesel stability

Biodiesel quality can be affected by oxidation during storage (in contact with air) and hydrolytic degradation (in contact with water). The two processes can be characterized by the oxidative stability and hydrolytic stability of the biodiesel. Biodiesel oxidation can occur during storage while awaiting distribution or within the vehicle fuel system itself.

The stability of biodiesel can refer to two issues: *long-term storage stability or aging* and *stability at elevated temperatures or pressures* as the fuel is recirculated through an engine's fuel system (NREL 2009).

For biodiesel, storage stability is highly important. Storage stability refers to the ability of the fuel to resist chemical changes during long term storage. These changes usually consist of oxidation due to contact with oxygen from the air (Gerpen, 2005).

Biodiesel composition greatly affects its stability in contact with air. Unsaturated fatty acids, especially the polyunsaturated ones (e.g. C18:2 and C18:3) have a high tendency to oxidation. After oxidation, hydroperoxides (one hydrogen atom and 2 oxygen atoms) are attached to the fatty acid chain. Oxidation reactions can be catalyzed by some of the materials present (the material the reservoir is produced from) and light. After the chemical oxidation reactions hydroperoxides are produced that can, in turn, produce short chain fatty acids, aldehydes, and ketones. Hydroperoxides can polymerize forming large molecules. Thus, oxidation increases the viscosity of biodiesel. In addition, oxidation increases acid value, the color changes from yellow to brown, solid deposits can form in the engine fuel system (pipes and filters), the lubricity and heating value of the biodiesel is reduced.

When water is present, the esters can hydrolyze to long chain free fatty acids, which also cause the acid value to increase (Gerpen, 2005). These acids can catalyze other degradation reactions such as reverse trans-esterification and oxidation. The water required for hydrolysis can be present as a contaminant (Engelen, 2009). For determining the oxidation stability of biodiesel two types of tests are currently used: the Rancimat test, contained in EN 14214 and the oxidative stability index (OSI) included in ASTM D6751.

*The Rancimat test method* (EN 14112, EN 15751) is an accelerated oxidation test in which the biodiesel to be tested is run at elevated temperatures (110 °C) whilst exposing the sample to a stream of purified air (10 L/hour) accelerating the oxidation process of the oil. After passing through the biodiesel, the air is fed into a collection flask containing distilled water and a probe to measure conductivity. As the biodiesel sample degrades, the volatile organic acids produced are carried to the collection flask, and the conductivity of the solution is

recorded by the probe. Oxidation stability will be given by the induction period, defined as the time between the start of the test and the sudden conductivity increase of the solution in the collection flask. This results in auto-oxidation in a few hours, instead of months.

The *oxidative stability index* (OSI) is another measurement method of the conductivity increase caused by the formation of secondary products in the oxidation process. The OSI is defined as the time until the conductivity of a biodiesel sample rises most rapidly during an accelerated oxidation test. The oxidation of biodiesel is influenced by its composition (increases with the level of unsaturation of fatty acids in its composition), i.e. the feedstock used to manufacture the biodiesel. For example, the content of oleic acid methyl ester in the case of biodiesel produced from sunflower oil may vary between 48 and 74%. In addition, the induction period of biodiesel made from rapeseed oil is 12 times greater than those obtained from soybean oil and 25 times higher than those produced from linseed oil. The presence of metals (the tank walls and metals contained in the biodiesel) can accelerate the oxidation process, whereas sulfur is an antioxidant (Berthiaume & Tremblay, 2006). Oxidation stability can be improved by using the appropriate additives. Additives such as tert-butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PrG) and alpha-tocopherol (vitamin E) have been found to enhance the storage stability of biodiesel. Biodiesels produced from some feedstocks (e.g. soybean oil) naturally contain some antioxidants. Any fuel that will be stored for more than 6 months, whether it is diesel fuel or biodiesel, should be treated with an antioxidant additive (Gerpen, 2005).

### 3.12 Water and sediments

Water content is a purity indicator for the biodiesel. Biodiesel should be dried after water washing to get the water specification below 500 ppm (0.050 %). Even when biodiesel is dried properly by the producer, water can accumulate during storage and transportation.

The moisture accumulated in biodiesel leads to the increase of free fatty acid concentration, which can corrode metal parts of the engine's fuel system. Biodiesel is much more hygroscopic (it attracts water) than diesel oil. The biodiesel absorbs water during storage when the temperature is higher and the water absorbed is precipitated at lower temperatures. Following these repeated processes, the accumulated water is deposited on the bottom of the tank. Water in biodiesel facilitates microbial growth and the formation of sediments. To measure the water and sediment content, a 100 mL sample of undiluted fuel is centrifuged at a relative centrifugal force of 800 for 10 minutes at 21 to 32°C (70 to 90°F). After centrifugation, the volume of water and sediment which has settled into the tip of the centrifuge tube is read to the nearest 0.005 mL and reported as the volumetric percent of water and sediment.

### 3.13 Other properties

*Sulfated ash* is a measure of ash formed from inorganic metallic compounds. After the burning of biodiesel, in addition to CO<sub>2</sub> and H<sub>2</sub>O a quantity of ash is formed consisting of unburned hydrocarbons and inorganic impurities (e.g. metal impurities). Metallic ash is very abrasive and may cause excessive wear of the cylinder walls and the piston ring.

*Carbon residue* indicates the presence of impurities and deposits in the engine combustion chamber, and is also an indicator of the quantity of glycerides, free fatty acids, soaps and transesterification reaction catalyst residues.

*Copper-strip corrosion* is an indicator of the corrosiveness of biodiesel, of the presence of fatty acids derived from materials which did not enter into reaction during the production process.

*Content of metals* (Ca, Na, Mg, K and P) can lead to combustion chamber deposits, filter- and fuel injection pump clogging, and can harm the catalyst.

#### 4. Monitoring the quality of biodiesel

Biodiesel quality can be provided efficiently if its entire manufacturing process is monitored: from monitoring feedstock acidity, assuring complete separation of biodiesel from glycerin, to removing the excess of alcohol and contaminants before its marketing. Quality assurance and monitoring should include storage, testing, blending and distribution. Fuel quality monitoring is conducted by independent laboratories that can accredit manufacturers, distributors and quality analysis laboratories. One example is the BQ-9000® program in the United States of America, a program based on voluntary cooperation, which accredits manufacturers, marketers and biodiesel quality analysis laboratories. Monitoring the quality of biodiesel contributes to its promotion and public acceptance.

#### 5. Conclusions

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. Therefore, quality requirements for the marketing of biodiesel vary from region to region. The largest differences are found in cetane number, oxidation stability, iodine value, density and viscosity. Other reasons for these differences are the weather conditions, reflected in the regulations of properties describing performances of biodiesel at low temperatures. Due to these major differences, unifying the standards for biodiesel is not possible. This could be a serious impediment for both biodiesel imports and exports among different regions of the world, as well as automotive producers, who must adapt their engines to the quality of biodiesel in the region where the vehicles will be used.

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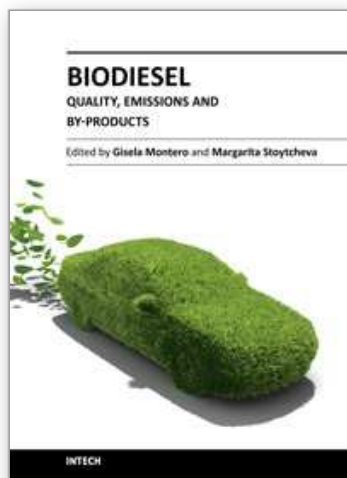
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## **Biodiesel- Quality, Emissions and By-Products**

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This book entitled "Biodiesel: Quality, Emissions and By-products" covers topics related to biodiesel quality, performance of combustion engines that use biodiesel and the emissions they generate. New routes to determinate biodiesel properties are proposed and the process how the raw material source, impurities and production practices can affect the quality of the biodiesel is analyzed. In relation to the utilization of biofuel, the performance of combustion engines fuelled by biodiesel and biodiesels blends are evaluated. The applications of glycerol, a byproduct of the biodiesel production process as a feedstock for biotechnological processes, and a key compound of the biorefinery of the future is also emphasized.

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