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REVIEW

Biodiesel production from various feedstocks and their effects on the fuel properties

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Abstract Biodiesel, which is a new, renewable and biological origin alternative diesel fuel, has been receiving more attention all over the world due to the energy needs and environmental consciousness. Biodiesel is usually produced from food-grade vegetable oils using transesterification process. Using food-grade vegetable oils is not economically feasible since they are more expensive than diesel fuel. Therefore, it is said that the main obstacle for commercialization of biodiesel is its high cost. Waste cooking oils, restaurant greases, soapstocks and animal fats are potential feedstocks for biodiesel production to lower the cost of biodiesel. However, to produce fuel-grade biodiesel, the characteristics of feedstock are very important during the initial research and production stage since the fuel properties mainly depend on the feedstock properties. This review paper presents both biodiesel productions from various feedstocks and their effects on the fuel properties.

Keywords Biodiesel · Feedstocks · Transesterification · Fuel properties

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Introduction

The share of diesel engine vehicles in the total vehicle amounts is increasing rapidly. In addition, diesel engines have wide usage in the industrial area as well [71]. Thus, diesel fuel has the biggest usage share among the petroleum-derived engine fuels, and this ratio is raising continuosly each passing day. However, most of the countries import their petroleum and petroleum-derived products, because the world petroleum reserves are in certain regions of the world, such as the Middle East and Middle Asia.

When thought about the limited energy sources, increasing amount of diesel fuel usage and share of diesel engines in the atmospheric pollution [13], the importance and necessity of an alternative diesel fuel, which is domestically available, renewable and environmentally friendly, is clearly understood.

Vegetable oils usage as a diesel engine fuel

When considering that Rudolph Diesel first operated his engine with peanut oil in the Paris Exhibition of 1900, it is seen that the use of vegetable oils as a diesel fuel is as old as diesel engine. Vegetable oils had been used as a diesel fuel in 1930s and 1940s but generally in emergency conditions such as World War II [37]. Although possitive results were obtained at first, a number of severe engine problems such as injector tips cooking, deposition of combustion chamber, deterioration of lubricating oil and consequently piston ring sticking, polimerisation and oxidation of vegetable oils were observed when the usage durations were extended [54, 77]. The use of vegetable oils as a diesel fuel was abandoned due to these bad results as well as due to the presence of inexpensive petroleum-derived diesel fuel.

However, as a result of oil crisis in 1970, the investigations on the vegetable oils for diesel engines started again. In the experiments done, the problems mentioned above were observed once again but this time they were more serious since modern diesel engines have direct injection (DI) fuel systems which are more susceptible to fuel quality and atomization than in-direct injection (IDI) systems [16, 56, 65, 76]. The fundamental reasons for these engine problems are high viscosities and low volatilities of vegetable oils. The viscosities of vegetable oils are much higher than that of conventional petroleum diesel fuel. The high viscosities of vegetable oils are caused from their molecular weights and chemical structures. The molecular weight of diesel fuel is less than that of any vegetable oil [18, 28]. The chemical structures of vegetable oils are significantly different from that of diesel fuel. Thus, it will be benefical to understand the chemical structure of the oils that are feedstocks for biodiesel production.

The chemical structure of oils and fats

The main constituent of oils and fats is triglycerides, which compose about 90–98% of total mass [71]. Figure 1 shows the chemical structure of a triglyceride molecule, where R_1, R_2, and R_3 represent the fatty acid radicals.

Triglycerides are composed of three fatty acids (R–COOH) and one glycerol [$C_3H_5(OH)_3$]. In a triglyceride molecule, the weight of the glycerol is about 41 g whereas the weights of fatty acid radicals are in the range from 650 to 790 g. Thus, it is understood that fatty acid radicals comprise most of the reactive groups in the triglyceride molecule and they greatly affect the characteristics of oils and fats'. Therefore, the importance of comprehensive investigation on fatty acids comprising about 94–96% (w/w) of the triglyceride molecule is clearly seen. The chemical structure of a free fatty acid molecule is shown in Fig. 2.

Fig. 1 The chemical structure of a triglyceride molecule

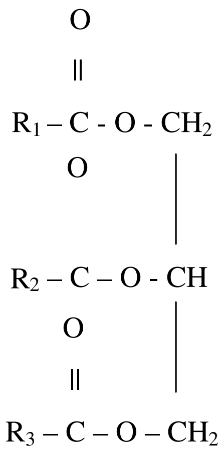
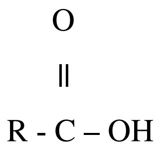


Fig. 2 Free fatty acid molecule


$$R-\overset{\overset{O}{\|}}{C}-OH$$

Fatty acids vary in their carbon chain length and in the number of double bonds (unsaturation level), and are shown by two figures. The former represents the number of carbon atoms in the fatty acid chain, and the latter shows the number of double bonds. For example, C18:3 (linolenic acid) implies that this fatty acid has 18 carbon atoms and 3 double bonds. The common fatty acids, which exist in the triglyceride molecule, are shown in Table 1. The physical and chemical fuel properties of biodiesel basically depend on the fatty acids distribution of the triglyceride used in the production. The fatty acid distributions of some feedstocks commonly used in biodiesel production are shown in Table 2.

What is biodiesel? Its production and superiorities over diesel fuel

Biodiesel is defined as the fatty acid alkyl monoesters derived from renewable feedstocks, such as vegetable oils, animal fats, etc. There are four chemical processes used to solve the high viscosity problem of triglycerides: dilution, microemulsification, pyrolysis (thermal cracking), and transesterification [67]. Among these four ways, the most commonly preferred process is transesterification. Transesterification is an ester conversion process that splits up the triglycerides; that is, takes the glycerol of the triglyceride and replaces it with alkyl radical of the alcohol used. Through transesterification, high viscosity is reduced to a value closer to that of diesel fuel while cetane number and heating value are saved. As seen in Fig. 3, three moles of alcohol are used per mole of triglyceride for the stoichiometric transesterification reaction. This reaction results in three moles of fatty acid alkyl monoester (biodiesel) and a mole of glycerol that is the by-product of this reaction. Although the theoritical molar ratio is 3:1, the molar ratio of 6:1 is generally used to complete the reaction accurately [25, 53, 71].

In the transesterification reaction, a catalyst is used to enhance the reaction rate and improve the produced fuel's features. Among the catalysts used for transesterification, alkaline catalysts (NaOH, KOH, $NaOCH_3$, etc.) are most commonly preferred when compared to acid (H_2SO_4, HCl, etc.) and lipase (biologic) catalysts since they are faster, and lower catalyst amount is sufficient to carry out the reaction. Biodiesel fuels produced using an alkaline catalyst are not corrosive for engine's metallic parts. Moreover,

Table 1 The chemical structures of common fatty acids

Fatty Acid	Chemical Structure
Myristic (14:0)	$CH_3(CH_2)_{12}COOH$
Palmitic (16:0)	$CH_3(CH_2)_{14}COOH$
Stearic (18:0)	$CH_3(CH_2)_{16}COOH$
Oleic (18:1)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Linoleic (18:2)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Linolenic (18:3)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Arachidic (20:0)	$CH_3(CH_2)_{18}COOH$
Behenic (22:0)	$CH_3(CH_2)_{20}COOH$
Erucic (22:1)	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$

Table 2 The fatty acid distributions of some biodiesel feedstocks

Feedstock	Fatty acids (% w/w)							Saturation level (%)	Reference No.
	14:0	16:0	16:1	18:0	18:1	18:2	18:3		
Sunflower	–	6.08	–	3.26	16.93	73.73	–	9.34	[28]
Rapeseed	–	3.49	–	0.85	64.40	22.30	8.23	4.34	[28]
Soybean	–	10.58	–	4.76	22.52	52.34	8.19	15.34	[10]
Soybean soapstock	–	17.2	–	4.4	15.7	55.6	7.1	~17	[30]
Used frying oil	–	12	–	–	53	33	1	~12	[3]
Tallow	3–6	24–32	–	20–25	37–43	2–3	–	47–63	[44, 48]
Lard	1–2	28–30	–	12–18	4–50	7–13	–	41–50	[44, 48]
Yellow grease	2.43	23.24	3.79	12.96	44.32	6.97	0.67	38.63	[10]
Brown grease	1.66	22.83	3.13	12.54	42.36	12.09	0.82	37.03	[10]

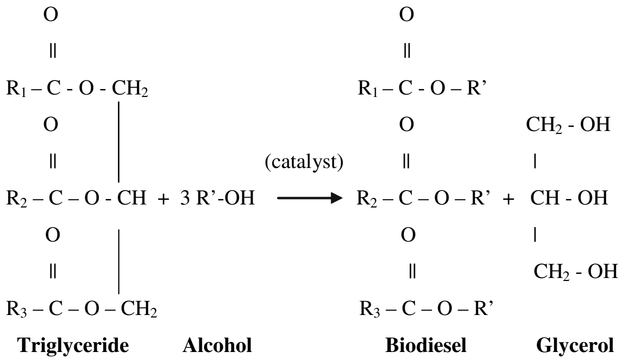


Fig. 3 Stoichiometric transesterification reaction

acid-catalyzed transesterification requires more alcohol ratios than alkaline-catalyzed reactions [8, 24, 49, 70, 79]. As a result of all these positive properties of alkaline catalysts, most of the transesterification reaction is fulfilled with one of them.

Biodiesel is a biodegradable, non-toxic, almost sulfurless and non-aromatic environmentally friendly alternative diesel fuel. When a diesel engine is operated with biodiesel, exhaust emissions decrease; approximately 20% in CO, 30% in HC, 40% in particulate matter (PM), and 50% in soot emission, compared to the diesel fuel. In contrast to these decreases, its NO_x emission increases about 10–15% [13, 29, 41, 57, 60]. However, the high NO_x problem can be overcome by retarding the injection timing [59]. Lubricity property of biodiesel is much better than that of diesel fuel, especially low-sulfur diesel fuel. Little biodiesel additive, even as little as 1%, is enough to significantly improve the conventional diesel fuel's lubricity [26, 34].

Industrial scale biodiesel production in Europe and USA

In Europe, commercial use of biodiesel began after the year 1980 [83]. Its usage has greatly increased, in particular during the last few years. Biodiesel production in the European Union (EU) has increased approximately more than 2.5 times in the last 3 years raising from 1.9 million tonnes in 2004 to 4.9 million tonnes in 2006 [21]. In this increase, the effect of the directive promoting the use of biofuels in transport issued by the European Comission in 2003 is so important. This directive (2003/30) created two indicative targets for EU member states: 2% biofuels penetration by December 2005 and 5.75% by December 2010 [6]. In the EU, 82% of the total biofuel production is biodiesel [21]. The annual biodiesel production amounts in the EU and in the USA can be seen in Table 3. The amounts show that the EU is the worldwide leader in both biodiesel production and

Table 3 The EU and the USA annual biodiesel production amounts

Year	Biodiesel production amounts (million tonnes)		Reference No.
	The EU	The USA	
2004	1.90	0.10	[6, 62]
2005	3.20	0.25	[21, 55, 62]
2006	4.90	0.75	[21, 62]

capacities. In the year of 2006, the EU produced about 77% of the biodiesel produced all over the world. The USA is the second largest biodiesel producer in the world [6, 19, 21].

Economic assessment for biodiesel based on the feedstock

Biodiesel is currently produced from high quality food-grade vegetable oils (in the USA, soybean oil; in Europe, rapeseed oil) using methanol and an alkaline catalyst. The end cost of the biodiesel mainly depends on the price of feedstock. The high cost of the food-grade oils causes to increase the cost of biodiesel and prevents its usage, even if they have some superiorities mentioned above. Unfortunately, biodiesel's economic situation has gone from bad to worse because of the increase in the vegetable oil prices in the last years. In the middle of 1990s, the cost of feedstock accounted for 60–75% of the total cost of biodiesel fuel [40], but today about more than 85% of the costs of production are fied up in feedstock costs [31, 83]. To investigate the dependence of biodiesel production cost on the cost of the feedstock, Haas et al. [31] carried out a study. This study indicated a linear relationship between the two, with a change of US $0.020/l in the product cost per US $0.022/kg change in oil cost. This means that the relationship between the feedstock mass input and biodiesel mass output is about 1:1 ratio.

To become an economically viable alternative fuel and to survive in the market, biodiesel must compete economically with diesel fuel. However, the raw material cost of biodiesel is already higher than the final cost of diesel fuel. Nowadays, biodiesel unit price is 1.5–3.0 times higher than that of petroleum derived diesel fuel depending on feedstock [19, 82, 83].

In order to make biodiesel an economically suitable fuel and increase its marketability, its high cost must be lowered. The low-cost and profitable biodiesel can be produced from low-cost feedstocks such as used frying oils, animal fats, soapstocks, and greases [10, 61, 82]. The decrease in the feedstock costs will affirmatively affect the biodiesel break-even price, of course. And so, the great difference between the prices of biodiesel and diesel fuel can be lowered to an acceptable value. In the literature, there are several studies about cost accounting of biodiesel from various feedstocks. Some of them are presented in Table 4.

Low-cost feedstocks

Feedstocks with high free fatty acid

As mentioned before, the main obstacle for commercialization of biodiesel is its high cost. However, used frying oils, soapstocks, yellow and brown greases are potential feedstocks for biodiesel production to lower the cost of biodiesel. Used frying oils and fats are currently collected from large food processing and service facilities where they are rendered and used primarily in animal food. Soapstock is the by-product of edible oil refining that is substantially less expensive than edible-grade refined oils. Its market value is about one-fifth of the crude vegetable oil prices [30]. Rendered animal fats and used frying oils with free fatty acids (FFA) level of less than 15% are known as yellow grease. If the FFA level exceeds 15%, it is named as brown grease. These feedstocks are attractive with their low cost. However, their transesterification reactions are much more difficult compared to those of food-grade high quality oils. They generally contain large amounts of FFA and water that cannot be converted to biodiesel using an alkaline catalyst. Waste greases typically contain FFA in the range from 10 to 25%. During the summer months, the FFA levels of the animal fats and greases increase as shown in Fig. 4. These high FFA levels are associated with the rapid degradation of animal carcasses during hot weather [7].

Biodiesel production from low-cost feedstocks

When FFAs react with an alkaline catalyst, as seen in Fig. 5, they cause soap and water formation which decrease

Table 4 Some economic assessment studies for biodiesel based on the feedstock

Feedstock type	Biodiesel price (US $/l)	Year	Reference
Soybean, canola, sunflower, rapeseed	0.54–0.62	1999	[5]
Waste grease	0.34–0.42	1999	[5]
Soybean	0.428	2001	[9]
Yellow grease	0.324	2001	[9]
Brown grease	0.246	2001	[9]
Canola	0.72	2003	[82, 83]
Waste cooking oil	0.54–0.74	2003	[82, 83]
Soybean	0.53	2005	[31]
Edible and inedible beef tallow	0.22–0.63	2006	[64]

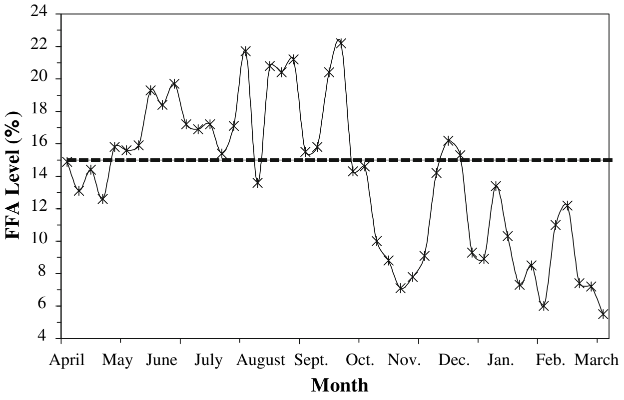
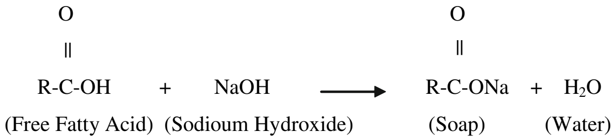


Fig. 4 The change in the FFA level of the animal fat during a year [7]

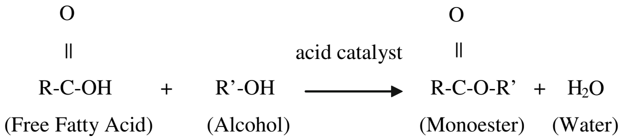


$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}OH} + \mathrm{NaOH} \longrightarrow \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}ONa} + \mathrm{H_2O}$$

Fig. 5 Soap formation reaction

the ester yield and prevent the separation of ester, glycerol, and wash water. Moreover, soap formation raises the viscosity and causes gel formation [10, 25, 30, 53, 80]. If FFA concentration of the feedstock is higher than the level of 0.5%, alkaline catalyst should not be used in the transesterification due to the soap formation [2, 10, 22, 36, 46, 49, 51, 80]. Nevertheless, in the literature there are some works, which state that an alkaline catalyst can be used in the transesterification up to the FFA level of 5% [27]. When feedstocks with high FFA are transesterified, acid catalysts which are much more tolerant to FFAs should be used [36, 46, 49]. Acid catalysts are too slow for converting triglycerides into biodiesel, but they are fast enough to convert FFAs to esters.

The acid-catalyzed process is named as pretreatment. This reaction is an esterification reaction, not an ester change reaction. Through pretreatment, FFAs are converted to monoesters as shown in Fig. 6. The molar alcohol ratio and the catalyst amount to be used in the pretreatment reaction are calculated according to the initial FFA content of the feedstock [10]. The main obstacle for the pretreatment is the water formation. When FFAs react with an alcohol, water also forms together with the monoesters and inhibits the conversion of FFAs to esters [8, 10, 25, 51, 68, 70]. The effect of water on the reaction is shown in Fig. 7. Another important point for biodiesel production from these feedstocks is the slow reaction rate. The alcohol used for the reaction has low dispersion rate in the feedstock. Therefore, more alcohol must be used and the mixture should be stirred vigorously [47, 50, 52].



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}OH} + \mathrm{R'{-}OH} \xrightarrow{\text{acid catalyst}} \mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'} + \mathrm{H_2O}$$

Fig. 6 Pretreatment reaction

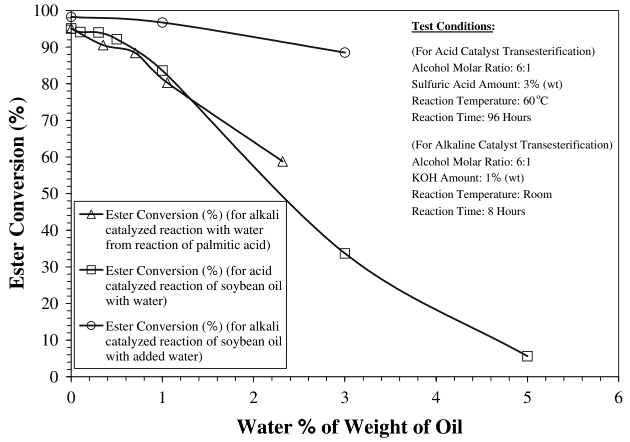


Fig. 7 Effect of water on the reaction [8]

In the indusrial area, most of the biodiesel production from high FFAs feedstocks is carried out using alkali-catalyzed reaction explained above. However, in the literature, there are some works, which state that the traditional alkali-catalyzed reaction using waste feedstocks would not improve the biodiesel unit price because of the pretreatment unit addition to reduce FFAs in the feedstock. For biodiesel production from low-cost feedstocks, there are some alternative methods other than the alkali-catalyzed process.

One of these alternative methods is the supercritical transesterification process. The advantages of this method: (1) Catalyst usage in the reaction is not required. Therefore, after the production process, the separation of the catalyst and saponified products from the fuel is not necessary [14, 17, 32, 75]. (2) Esterification of FFAs in the feedstock and transesterification of the triglycerides happen simultaneously. Hence, the reaction duration is significantly shorter than the traditional transesterification reaction [17, 69]. However, there are some studies using longer reaction durations ranging from 15 to 45 min to get high product yield [32, 78]. (3) The supercritical reaction is not sensitive to both FFA and water. Thus, low quality feedstocks can be used in this process [32, 42, 75]. As the supercritical method has some advantages, it has also some disadvantages that should be taken into account: (1) this method requires high molar ratio of alcohol to feedstock such as 40–42:1 [17, 32, 69]. (2) Since it requires high reaction pressures such as 35–40 MPa and reaction temperatures generally higher than 300°C, high-energy consumption will be necessary in the process. This will cause high operating cost and will increase the biodiesel's final price. (3) If the reaction parameters exceed the optimal level, side reactions such as thermal decomposition reactions and dehydrogenation reactions of unsaturated fatty acid methyl esters will occur and lead to yield drop [32, 69].

In the processing of the feedstocks with high FFAs, one alternative way is the acid-catalyzed transesterification, as well. Acid-catalyzed process is not sensitive to FFA content of the feestock and so does not require pretreatment reaction. This favorable property of the acid-catalysts makes the acid-catalyzed process using low cost feedstock with high FFA less complex than the traditional alkali-catalyzed process using these feedstocks. However, this process requires more alcohol and larger reactors. Besides, the presence of the acid catalyst in the reaction requires the use of stainless steel materials because of its corrosive feature. The sum of these two negative factors causes an increase in the equipment costs. Due to these problems of acid catalysts, no commercial biodiesel plants to date have been reported to use the acid-catalyzed process [82].

Fuel properties of biodiesel produced from high-quality oils and low-cost feedstocks

Some specifications are put into execuation so as to standardize the quality of biodiesel fuel worldwide (in the USA, ASTM D 6751; in Europe, EN 14214). By means of these mentioned standards shown in Tables 5 and 6, respectively, both the security of users and the opportunity of producing biodiesel from various feedstocks, just in case these specifications are ensured, are provided. Diesel engine producers approve the use of biodiesel on the condition that it is complied with these standards. At the end of the transesterification reaction, glycerol phase separation can be obtained, but all the features defined in the standards must be measured in order to determine whether the produced ester product is of fuel quality or not. On the condition that these standard values are met, biodiesel can be produced either from high-quality vegetable oils or from inexpensive poor quality feedstocks. In Tables 7 and 8, some critical properties of various vegetable oils commonly used in biodiesel production and some biodiesel (methyl ester) fuels produced from vegetable oils and low cost feedstocks are shown, respectively. In this section, the fuel properties of fatty acid alkyl monoesters are compared to each other.

Table 5 American standard specification for biodiesel (ASTM D-6751)

Property	Test method	Limits	Unit
Kinematic viscosity (at 40°C)	D 445	1.9–6.0	mm^2/s
Cetane number	D 613	47 min	–
Flash point (closed cup)	D 93	130.0 min	°C
Cloud point	D 2500	Report	°C
Water and sediment	D 2709	0.050 max	Volume (%)
Sulfated ash	D 874	0.020 max	Mass (%)
Sulfur	D 5453	0.05 max	Mass (%)
Copper strip corrosion	D 130	No. 3 max	–
Carbon residue (100% sample)	D 4530	0.050 max	Mass (%)
Acid number	D 664	0.80 max	Mg KOH/g
Free glycerol	D 6584	0.020 max	Mass (%)
Total glycerol	D 6584	0.240 max	Mass (%)
Phosphorus content	D 4951	0.001 max	Mass (%)
Distillation temperature (90% recovered)	D 1160	360 max	°C

Viscosity

The viscosity of an engine fuel is one of the most critical fuel features. It plays a dominant role in the fuel spray, mixture formation and combustion process. The high viscosity interferes with the injection process and leads to insufficient fuel atomization. Moreover, the mean diameter of the fuel droplets from the injector and their penetration increases with increasing fuel viscosity [15]. The inefficient mixing of fuel with air contributes to incomplete combustion in the engine. In addition to all these, high viscosity can cause early injection due to high line pressure, which moves the combustion of the fuel closer to top dead center, increasing the maximum pressure and temperature in the combustion chamber [15, 45, 73].

Viscosity of any fuel is releated to its chemical structure. Viscosity increases with the increase in the chain length and decreases with the increase in the number of double bonds (unsaturation level) [28, 29, 38]. In addition, viscosity and heat content of the feedstocks and biodiesel fuels tend to increase together [18, 28]. As seen in Table 8, viscosities of biodiesels from fats and greases are higher compared to those from vegetable oils since their saturation level are higher [4, 10, 29]. However, these differences in the viscosity values of the biodiesel fuels from oils and low cost feedstocks are mostly within the specification given in the standards and there is no problem in terms of this fuel property.

Density

The density of fuel has some effect on the break up of the fuel injected into the cylinder. In addition, more fuel is injected by mass as the fuel density increases. All biodiesel fuels regardless of produced from vegetable oils or from fats are denser and less compressible than the diesel fuel [11, 29, 38, 74]. Like viscosity, the density and compressibility have very important influences on the engine fuel

Table 6 European standard specifications for biodiesel (EN 14214)

Property	Test method	Limits	Unit
Kinematic viscosity (at 40°C)	EN ISO 3104	3.5–5.0	mm^2/s
Density (at 15°C)	EN ISO 3675/EN ISO 12185	860–900	Kg/m^3
Cetane number	EN ISO 5165	51 min	–
Flash point	ISO/CD 3679	120.0 min	°C
Water	EN ISO 12937	500 max	mg/kg
Sulfated ash	ISO 3987	0.02 max	Mass (%)
Sulfur	NF T 60-71/DIN 51680	10.0 max	mg/kg
Copper strip corrosion (3 h, at 50°C)	EN ISO 2160	No. 1	–
Carbon residue (10% sample)	EN ISO 10370	0.3 max	Mass (%)
Acid number	Pr EN 14104	0.5 max	mg KOH/g
Free glycerol	Pr EN 14105/Pr EN 14106	0.02 max	Mass (%)
Total glycerol	Pr EN 14105	0.25 max	Mass (%)
Phosphorus content	Pr EN 14107	10 max	mg/kg
Iodine number	Pr EN 14111	120 max	–
Oxidative stability (at 110°C)	Pr EN 14112	6 min	h
Monoglyceride content	Pr EN 14105	0.8 max	Mass (%)
Diglyceride content	Pr EN 14105	0.2 max	Mass (%)
Triglyceride content	Pr EN 14105	0.2 max	Mass (%)

Table 7 Some properties of vegetable oils commonly used in biodiesel production

Vegetable oil type	Kin. viscosity (mm^2/s, at 40°C)	Density (g/cm^3, at 21°C)	Cetane number	Flash point (°C)	Cloud point (°C)	Pour point (°C)	References
Soybean	33.1	0.914	38.1	254	−3.9	−12.2	[18, 28]
Rapeseed	37.3	0.912	37.5	246	−3.9	−31.7	[18, 28]
Sunflower	34.4	0.916	36.7	274	7.2	−15.0	[18, 28]
Corn	35.1	0.910	37.5	277	−1.1	−40.0	[18, 28]
Safflower	31.6	0.914	36.7	246	−3.9	−31.7	[18, 28]
Cottonseed	33.7	0.915	33.7	234	1.7	−15.0	[18, 28]
Peanut	40.0	0.903	34.6	271	12.8	−6.7	[18, 28]
Tallow	51.2	0.920	40.2	201	–	–	[4]

Table 8 Some properties of diesel fuel and biodiesel fuels produced from different feedstocks

Fuel	Kin. viscosity (mm^2/s, at 40°C)	Density (g/cm^3, at 21°C)	Cetane number	Flash point (°C)	Cloud point (°C)	Pour point (°C)	References
Diesel fuel	2.0–4.5	0.820–0.860	51.0	55	−18	−25	[11, 29, 43, 53]
Soybean methyl ester	4.08	0.884	50.9	131	−0.5	−4	[29, 30]
Rapeseed methyl ester	4.83	0.882	52.9	155	−4	−10.8	[1, 29]
Sunflower methyl ester	4.60	0.880	49.0	183	1	−7	[29, 71]
Tallow methyl ester	5.00	0.877	58.8	150	12	9	[4, 29, 81]
Yellow grease methyl ester	5.16	0.873	62.6	–	9	12	[11, 23]
Soapstock methyl ester	4.30	0.885	51.3	169	6	–	[30]

injection system. The injected fuel amount, injection timing and injection spray pattern are directly affected by these parameters [45]. With increasing density, the diameter of the fuel droplets increases. Since the inertia of the big droplets is big, their penetrations in the combustion chamber will be higher, as well [15]. When a fuel with lower density and viscosity is injected, improved atomization and better mixture formation can be attained. Like viscosity, the heating content of a fuel is a function of its density [18]. Fuel density also affects the exhaust emissions. The density can be correlated with particulate matter (PM) and NO_x emission. The fuel which has high density generally causes an increase in PM and NO_x emission in diesel engines [4, 72].

The chain length and saturation level of the fuel raise the density [29, 38, 43]. Thus, biodiesels produced from feedstocks such as fats or greases have more saturated fatty acids than the biodiesels produced from vegetable oils [4, 9, 29]. But, this rise in the density is not a problem in terms of the required standard value.

Cetane number

The cetane number is the prime indicator of fuel ignition quality and the opposite of octane number of a gasoline fuel. It can be defined as the measure of knock tendency of a diesel fuel. The cetane number is releated to the ignition delay time that is the time between the start of injection and start of combustion. As the cetane number increases, the ignition delay decreases and the main combustion phase (diffusion controlled combustion) increases. Long ignition delay is not acceptable since it causes diesel knock. Cetane number can also influence the cold engine starting and subsequent white smoke and noise emissions.

As low cetane number, too high cetane number is inconvenient, as well. If the cetane number of a diesel fuel is too high, this fuel will ignite in a short distance to the injector and cause excessive heating of the injector. As the result of the intense heating, cooked fuel particles inside the injector may plug the injector nozzle. Because of this, cetane number of a diesel fuel should not be higher than 65 [33].

To observe the effect of cetane number on a direct injection diesel engine performance, Icingur and Altiparmak [35] conducted engine tests. For this purpose, the fuels with 46, 51, 54.5 and 61.5 cetane number were tested at 150-bar injection pressure and full load conditions. The results showed that the engine torque and power output increased by 5 and 4%, when the cetane number was increased from 46 to 54.5, respectively. Nevertheless, when increasing the cetane number above 54.5, no significant increases were observed in the engine performance.

With increasing chain length, decreasing branching and unsaturation, cetane number increases [18, 28, 29, 38]. These chemical structures increase the heating value as well, so there is a tendency for cetane number to increase with viscosity and heating value [18]. Biodiesel has higher cetane number and consequently its ignition delay time is shorter compared to that of diesel fuel. The biodiesel fuels from feedstocks with long carbon chain and more saturated fatty acids such as fats or waste greases have higher cetane numbers than those of biodiesel produced from vegetable oils, as seen in Table 8. However, this difference may not significantly affect the combustion process [11].

Flash point

The flash point is the temperature at which the fuel will start to burn when it comes to contact with fire [4]. It is an important temperature from the safety point of view during storage and transportation. This temperature is correlated with its volatility, which is an important fuel feature for an engine's starting and warming. The combination of high viscosity and low volatility of a fuel causes bad cold engine start up, misfire and ignition delay [72]. A fuel with high flash point may cause carbon deposits in the combustion chamber.

As shown in Table 8, the flash point of all biodiesel feedstocks is far above that of diesel fuel, reflecting the involatile nature of the fuel. In spite of the fact that the flash points of feedstocks are reduced through transesterification, they are still higher than those of diesel fuel, regardless of whether the biodiesel is from high-quality vegetable oils or from low-cost feedstocks. However, if they are compared with each other, it is seen that the flash points of biodiesels from low-cost feedstocks are higher than those from vegetable oils since they have relatively more saturated fatty acid composition. With high cetane number and low volatility, the amount of fuel that burns in the premixed combustion decreases since the ignition delay ends sooner as well as the less fuel evaporates in this duration. Therefore, NO_x emission decreases due to low combustion pressure and temperature [13].

Cold-flow properties

Cold-flow quality of a fuel is determined by the cloud point and pour point. The cloud point is the temperature at which a cloud of wax crystals first appears in a liquid when cooled [4]. These formed crystals can cause operation problems because they can plug the fuel lines and filters. The pour point is the lowest temperature at which the fuel will still flow and can be pumped [44]. All biodiesel fuels regardless of its source have higher cloud and pour points than that of diesel fuel, and this poor cold flow property is one of the most critical obstacles against the widespread biodiesel usage. The fatty acid composition of biodiesel greatly influences its cold-flow properties. The freezing point of a biodiesel fuel increases with increasing carbon atoms in the carbon chain and decreases with increasing double bonds [18, 28, 29, 38]. According to this knowledge, it is an expected result that the biodiesel from feedstocks with large amounts of saturated fatty acids have higher cloud points and pour points. As a matter of fact, vegetable oil based biodiesel has lower cloud and pour point than that of the biodiesel from fats and greases, as seen in Table 8 [23, 44, 53, 71]. Tallow's saturated fatty acid concentration is about 50% while soybean oil is approximately 12–15% saturated. This higher saturation level increases the cloud point of animal fat based biodiesel.

The cold flow problem of biodiesel can be overcome by using branched chain alcohols such as iso-propanol, 2-butanol in the transesterification. Lee et al. [44] studied for improving the cold flow properties of biodiesel fuels both from oils and animal fats. They concluded that the cloud point for iso-propyl and 2-butyl esters of soybean oil were −9 and −12°C, which were 7 and 10°C lower, respectively, than that of the corresponding methyl esters. In addition, the crystallization onset temperatures of iso-propyl esters of lard and tallow are similar to that of methyl ester of soybean oil. But their cloud points and pour points are still too high to be used as a diesel fuel substitute. Moreover, branched chain alcohols can improve the cold-flow quality, but their reactions result in important amount of impurities such as monoglycerides, diglycerides and triglycerides showing the incompleteness of the transesterification. This is because of the low reactivities of these alcohols [43, 44]. This impurity can cause problems during the engine operation [39]. Furthermore, these alcohols have much more tendency of absorbing water during washing process than methanol. Branched chain alcohols are not economically feasible since they are more expensive. At the same time, their reactions require much more alcohol ratios such as 70:1 and their molecular weights are high which takes the production cost from bad to worse and lower yields can be obtained by their usage.

In terms of cold-flow properties, biodiesel fuels from greases are better than those from tallow esters [4, 20, 23]. This is because greases are mixtures of fats and oils. However, as mentioned above, all biodiesels regardless of their feedstocks have higher freezing points than that of diesel fuel limiting its usage. This is a big problem that should be solved, especially in cold climate operations.

Oxidation stability

Another important parameter of biodiesel is its oxidation stability. This property shows the fuel's resistance to oxidation during extended storage. Oxidation stability is determined by copper strip since it has the strongest catalyzing effect on oxidation. When oxidation occurs at ordinary temperatures, the initial products are hydroperoxides. As the oxidation continues, the peroxides may split and form aldehydes, ketones and short chain acids that produce unpleasant odors. Oxidation eventually deteriorates the fuel properties because of gum formation. This formed gum does not combust completely, resulting in carbon deposits in the combustion chamber and lubrication oil thickening [53]. Moreover, as it oxidizes, biodiesel becomes more viscous and its cetane number raises [12, 58]. Therefore, the oxidized biodiesel starts to burn earlier than the unoxidized one, and NO_x emission increases [59].

The chemical structure of biodiesel fuel is an important factor in the oxidation reaction [63, 66]. Oxidation is caused from the presence of double bonds in the chains, that is, feedstocks rich in polyunsaturated fatty acids are much more susceptible to oxidation than the feedstocks rich in saturated or monounsaturated fatty acids [29]. For instance, relative rates of oxidation are 1 for oleates, 41 for linoleates and 98 for linolenates [38]. Figure 8 shows the oxidation stability of methyl esters from five different vegetable oils. The methyl esters oxidized at different rates but appeared to reach a single maximum peroxide value of 300–350 meq/kg ester. The corn oil methyl ester might also follow this pattern but the test duration of 240 h was reached before the corn oil had oxidized to this level. The methyl esters of oils that are less saturated tend to have higher rates of oxidation.

Conclusions

The objective of this study was to present both the biodiesel productions from various feedstocks and their effects on the fuel properties. Even though biodiesel has some superiorities, the greatest barrier to biodiesel use is its cost compared to conventional diesel fuel. Therefore, it is necessary to economize biodiesel production to improve its marketability. Compared to high-quality vegetable oils, less expensive feedstocks, such as used frying oils, soapstocks, fats and greases, can be used to lower the cost of biodiesel. However, for these feedstocks, transesterification cannot be applied directly due to their high level of FFA. The cold-flow properties of the biodiesel, especially produced from fats are unacceptably worse since they have high saturation level. However, when branched-chain alcohols are used, possitive results in the cold-flow properties can be obtained. Therefore, the studies should focus on the improvement of

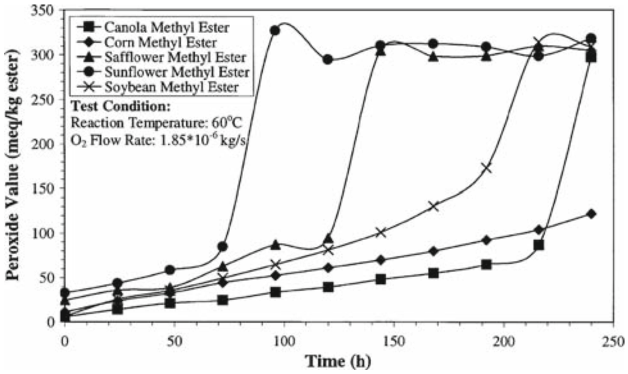


Fig. 8 Effect of feedstock on peroxide value [12]

the cold-flow properties of the biodiesels produced from the low-cost feedstocks.

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