Correlation Between Physicochemical Properties and Quality of Biodiesel

M.I. Jahirul, R.J. Brown and W. Senadeera

Abstract Biodiesel produced from renewable feedstocks represents a sustainable source of energy and will therefore play a significant role in providing the energy requirements for transportation in the near future. Biodiesel offers many benefits over conventional petroleum fuels, including the wide regional distribution of biomass feedstocks, high greenhouse gas reduction potential, biodegradability and a significant contribution to sustainability. Chemically, all biodiesels are fatty acid methyl esters (FAME), produced from raw vegetable oil and animal fat. However, clear differences in chemical structure are apparent when comparing one feedstock to the next in terms of chain length, degree of unsaturation and number of double bonds—all of which determine the fuel properties and quality of biodiesel as a diesel engine fuel. In this chapter, biodiesel feedstocks, production processes, chemical compositions, standards, physicochemical properties and in-use performance are discussed. A correlation study between the properties of biodiesel and its chemical composition is analysed using principal component analysis (PCA). The necessary data regarding the chemical composition and fuel properties of biodiesel were obtained from more than 100 papers published in recognised international journals. The PCA indicated that individual biodiesel properties have a complex correlation with the parameters of chemical composition. The average chain length and average number of double bonds are the most influential parameters that affect all biodiesel properties. The results of this analysis are presented graphically and discussed in this chapter. Therefore, this chapter will provide the reader a clearer understanding of the physicochemical properties of biodiesel.

Keywords Biodiesel · Chemical composition · Fuel properties · PCA

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1 Introduction

Globally, the transport sector occupies third place when total energy consumption and greenhouse gas emissions are considered (following the trade and building sectors). It is also the fastest growing sector. By 2030, the energy consumption and, therefore, the CO_2 emissions of this sector are predicted to be eight percent higher than current levels [86]. In addition, the energy supply depends heavily on non-renewable petroleum fuel (for production of gasoline and diesel) and currently consumes 30% of the world's petroleum oil, increasing to 60% by 2030 [85]. Furthermore, the supply of petroleum oil is geographically restricted, and the era of low-cost and secure oil is almost over. These facts have forced automobile researchers to look for alternative carbon-neutral transport fuels that promise a harmonious correlation with sustainable development, energy conversion, energy potency and environmental preservation [59]. However, such an alternative fuel for the transportation sector is yet to be developed. Moreover, cars with no greenhouse gas emissions (electric, solar, hydrogen, etc.) are far away from changing into mainstream vehicles. Therefore, development of a sustainable long-run alternative fuel has become essential, and biodiesel is receiving significant attention and is coming to the forefront as a sustainable alternative to standard fossil fuels [85].

Biodiesel is liquid fuel created from various oilseed crops and animal fat. Biodiesels offer many socio-economic advantages over petroleum-based fuels in automobile engine applications, in particular the fact that they are renewable, biodegradable, non-toxic and eco-friendly [61]. However, the majority of current vehicle engines are not optimised for the utilisation of biodiesel. Therefore, these engines are unlikely to be efficient when using biodiesel and show several technical issues such as carbon deposition, corrosion, high lubricating oil contamination, poor low-temperature performance and heavy gum and wax formation when compared to petroleum diesel [50]. The distinctions between petroleum diesel and biodiesel could be attributed to the variation of physical properties and chemical compositions. Petroleum diesel consists of hundreds of compounds boiling at completely different temperatures (determined by the petroleum refining method and crude oil raw material), whereas biodiesel contains compounds that are primarily eight to twenty-four carbon chain length alkyl esters (determined entirely by the feedstock) [57, 78]. Besides the main fatty ester components, the minor constituents of biodiesel embrace intermediary glycerides and free fatty acids resulting from the transesterification reaction, methanol, free fatty acids, etc. As engines are manufactured for petroleum diesel, original equipment makers (OEMs) and industry associations have shown a cautious response in their acceptance of biodiesel, especially those from new sources and the concept of using biodiesel blends as fuel [78].

2 Biodiesel

Fatty acid methyl or ethyl esters, commonly referred to as "biodiesel", are a liquid fuel alternative to diesel. They are made of agricultural products, forest organic matter and animal fat feedstocks. Biodiesel is the only currently available alternative transport fuel made from oilseed crops and animal fat which can be used directly in conventional, unmodified diesel engines. Biodiesel is safer to handle, store and transport compared to petroleum diesel because it is biodegradable, non-toxic and has a higher flashpoint than diesel [61]. One of the major advantages of biodiesel is that it has a potential to reduce dependency on imported petroleum through the use of domestic feedstocks for production [51].

In fuel property terms, biodiesel has a higher cetane rating than petroleum diesel, which improves engine performance. Also, it has better lubricant properties than petroleum diesel, which can extend engine life [50]. The use of biodiesel reduces particulate emissions by up to 75% when compared with conventional diesel fuel. Biodiesel also substantially reduces unburned hydrocarbons, carbon monoxides and particulate matters, including an elimination of sulphur dioxide in exhaust emissions. The exhaust emissions of particulate matter from biodiesel have been found to be 30% lower than overall particulate matter emissions from fossil diesel. The exhaust emissions of total hydrocarbons are up to 93% lower for biodiesel than for diesel fuel [105].

As a fuel, there are currently several disadvantages to using biodiesel in diesel engine applications. These mainly result from the differences in chemical composition between petroleum diesel and biodiesel. These major disadvantages are lower energy density, higher viscosity, higher copper strip corrosion and issues with the degradation of fuel in storage for prolonged periods. Biodiesel also has a higher cold-filter plugging point temperature than fossil diesel, which means it will crystallise into a gel at lower temperatures when used in its pure form. Biodiesel can also cause dilution of engine lubricant oil, requiring more frequent oil changes than when using petroleum diesel fuels in conventional diesel engines. This increase in dilution and polymerisation of engine sump oil is due to the higher viscosity at lower temperatures of biodiesel when compared to petroleum diesel.

3 Biodiesel Feedstock

Feedstocks for biodiesel production can be classified into four groups. These are (1) virgin vegetable oil feedstocks such as rapeseed, soya bean, sunflower and palm oil; (2) waste vegetable oils; (3) animal fats including beef tallow, lard and yellow grease; and (4) non-edible oils such as jatropha, neem oil and castor oil. The prevalence of these feedstocks varies around the world (Fig. 1). The regional availability of feedstocks for biodiesel production depends greatly on climate, soil conditions and options for alternate land use [83]. Consequently, different regions

Fig. 1 Biodiesel feedstocks around the world [55]

are focussing their efforts on different feedstocks. As an example, the widespread use of soya beans in the USA as a food product has led to the emergence of soya bean biodiesel in that country. In Europe, rapeseed is the most common source of biodiesel production. In India and south-east Asia, the jatropha tree is used in biodiesel production, and in Malaysia and Indonesia, palm oil is used as a significant biodiesel source.

4 Biodiesel Production

More than 100 years ago, Rudolf Diesel (1858–1913) demonstrated the operation of a diesel engine using vegetable oil as a fuel, so the potential of using these feedstocks has been long recognised. However, vegetable oils are extremely viscous, with viscosity ranging from 10 to 17 times higher than that of petroleum diesel [57]. This makes vegetable oil unsuitable to use as a direct fuel in the modern diesel engine. As a consequence, researchers and scientists have developed various methods to reduce the viscosity of bio-oils to make them suitable for diesel engine use. Some of these methods include dilution with other fuels, esterification, micro-emulsification, pyrolysis and catalytic cracking. Of these techniques, esterification is the most promising and widely used solution due to its high conversion efficiency, simplicity, low conversion cost and the fuel qualities of the product.

Transesterification of bio-oils with alcohols to produce esters is a widely used technique for commercial biodiesel production [83].

Transesterification is a chemical reaction in which oils (triglycerides) are converted into esters as shown in Fig. 2. Triglycerides react with alcohols (e.g. methanol and ethanol) under acid- or base-catalysed conditions, producing fatty acid alkyl esters and glycerol. A catalyst is used to improve the reaction rate and yield. Because the transesterification reaction is reversible, excess alcohol is used to shift the equilibrium to favour production of the ester. The yield of biodiesel in transesterification is affected by several process parameters. These include the reaction temperature, the molar ratio of alcohol to oil, the type and concentration of catalyst and the reaction time [58]. After the reaction is complete, glycerol is removed as a by-product. The biodiesel produced may be denominated by the feedstock used and the ester formed including fatty acid methyl ester (FAME), fatty acid ethyl ester (FAEE), soya bean methyl ester (SME) and rapeseed methyl ester (RME). The total ester content in biodiesel is the measure of the completeness of the transesterification reaction [106].

Alkali-catalysed transesterification cannot be directly used to produce high-quality biodiesel from feedstocks containing high levels of free fatty acids (FFAs). This is because FFAs react with the catalyst to form soap (Fig. 3), resulting in emulsification and separation problems. To overcome this problem, a pre-esterification process may be used to reduce the content of FFAs in the feedstock. A typical pre-esterification process uses homogeneous acid catalysts, such as sulphuric acid, phosphorous acid combined with sulphonic acid, or heterogenous “solid-acid” catalysts, to esterify the free fatty acids as shown in Fig. 4.

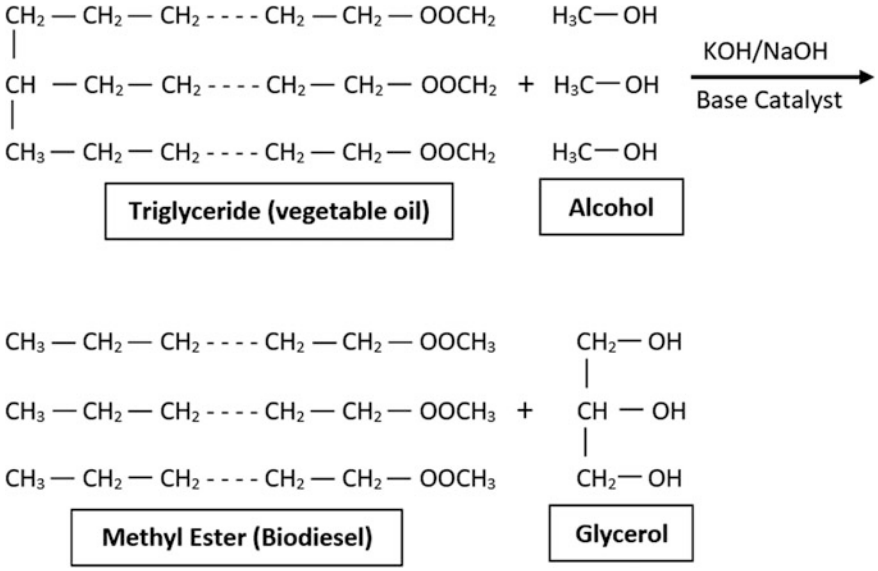

Fig. 2 Transesterification reaction [55]

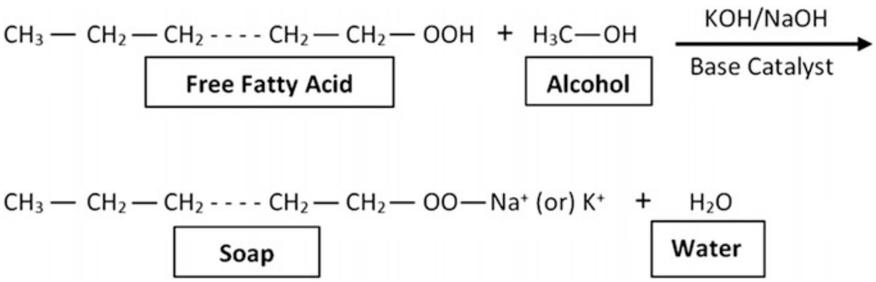

Fig. 3 Soap formation during biodiesel production [55]

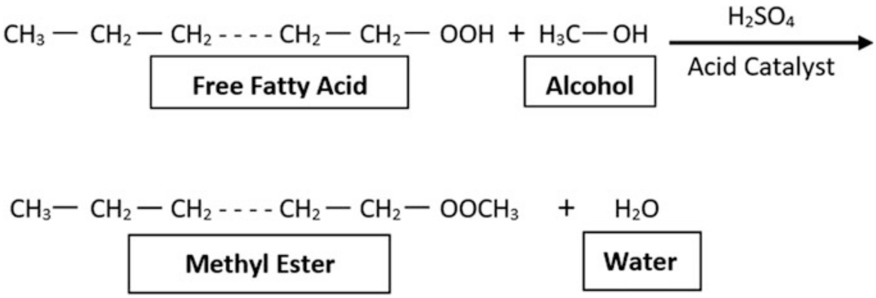

Fig. 4 Acid pre-esterification [55]

5 Biodiesel Standards

Quality standards are crucial for the commercial use of any fuel product. They serve as guidelines for production, assure customers that they are buying high-quality fuels and provide authorities with approved tools for a common approach to transport, storage and handling. Modern diesel engines using common rail fuel injection systems are more sensitive to fuel quality. Therefore, engine and automotive manufacturers rely on fuel standards in determining consumer warranties. However, the chemical compositions of biodiesel and petroleum diesel are very different, and these differences result in varying physicochemical properties. To improve the viability of biodiesel for use as a commercial fuel for direct replacement of petroleum diesel, the properties of biodiesel need to reflect a functional equivalence with diesel.

Biodiesel can be used as a pure fuel (B100) or blended with petroleum diesel in varying concentrations. For B100, the most internationally recognised standards are EN14214 (Europe) and ASTM D-6751 (USA). Both standards are similar in content, with only minor differences in some parameters. Many other countries have defined their own standards, which are frequently derived from either EN14214 or ASTM D-6751 [51]. As a part of the Fuel Quality Standards Act 2000,

Table 1 International standards of biodiesel [18, 126]

Properties	Units	USA ASTM D-6751	Europe EN 14214	Australia
Viscosity, 40 °C	mm^2/s	1.9–6.0	3.5–5.0	3.5–5.0
Density	gm/m^3	n/a	0.86–0.90	0.86–0.90
Cetane number	–	47 min	51 min	51 min
Flashpoint	°C	130 min	120 min	120 min
Cloud point	°C	Report	Report	Report
Acid number	mg KOH/g	0.80 max	0.5 max	0.8 max
Free glycerine	wt%	0.02 max	0.02 max	0.02 max
Total glycerine	wt%	0.24 max	0.25 max	0.25 max
Iodine number	–	–	120 max	n/a
Oxidation stability	h	–	6 min	n/a
Monoglyceride	Mass (%)	–	0.8 max	n/a
Diglyceride	Mass (%)	–	0.2 max	n/a
Triglyceride	Mass (%)	–	0.2 max	n/a

the Australian government released a biodiesel fuel standard, “Fuel Standard (Biodiesel) Determination 2003”. A summary of the major fuel quality parameters in these standards is detailed in Table 1.

6 Data Collection

Data were collected from more than 150 papers, mostly published in the last decade, and which contain experimental results of the chemical composition of biodiesel along with corresponding fuel properties. During data collection, special care was taken to ensure the quality of the data and to eliminate duplication. Data have been taken only from literature in which the experiments were conducted following recognised international standards. Some extreme data have been excluded from the database due to unexpected results contained therein. Data were also eliminated from the database if it was found to differ greatly to fuel properties in the primary data collection results. Furthermore, the experimental results for density and kinematic viscosity of biodiesel are highly dependent on temperature. Although 15 and 40 °C temperatures are recommended for density and kinematic viscosity respectively, some researchers did not mention the test temperature. Therefore, those data have also been excluded from the database. Since the properties of particular biodiesels can be varied depending on the type of alcohol (methyl, ethyl, etc.) used in the production process, this study only considers the methyl esters for inclusion in the database. The list of papers including feedstock use and the country of the authors is given in Table 2.

Table 2 Biodiesel datasets investigated in this study

Feedstock	References
Algae	[37, 54]
Almond	[10, 46]
Babassu	[12, 89, 94, 114, 118]
Beauty leaf	[56]
Camelina	[27, 44, 91, 118, 129, 137]
Canola	[2, 21–23, 31, 37, 40, 49, 52, 69, 73, 88, 118]
Coconut	[6, 21, 40, 43, 75, 92, 114, 118, 131]
Coffee	[32, 133]
Corn	[29, 30, 81, 114, 123]
Cottonseeds	[2, 35, 89, 111, 115, 132]
Fish oil	[13, 82, 113]
Grape	[29, 109]
Hazelnut	[35, 73, 90]
Hepar	[118]
Jatropha	[8, 22–24, 26, 60, 76, 118, 120, 125, 133, 135]
Lard	[15, 36, 69, 80, 138]
Linseed	[41, 48, 79, 101, 103, 114, 117]
Mahua	[34, 45, 47, 66]
Mustard	[11, 62]
Neem	[8, 103, 104, 119, 128]
Olive	[21, 29, 38, 65, 109]
Palm	[12, 14, 21, 28, 29, 37, 63, 64, 67, 74, 84, 88, 93, 97, 99, 109, 122, 134]
Peanut	[12, 29, 31, 68, 81, 90, 99, 109, 130]
Poppyseed	[35]
Rapeseed	[21, 35, 44, 67, 79, 81, 97, 99, 109, 110, 116, 122, 133, 136]
Rice bran	[127]
Rubber seed	[53, 107]
Safflower	[110]
Sesame	[1, 16]
Soya bean	[2–5, 9, 12, 17, 19–21, 31, 40, 43, 48, 69, 81, 87–89, 97–99, 102, 109, 114, 120, 121, 124, 132, 136, 138]
Soap nut	[22, 23]
Sunflower	[7, 12, 29, 35, 41, 65, 81, 88, 99, 109, 112, 115, 120, 123]
Tallow	[3, 7, 12, 29, 35, 65, 79, 88, 95, 99, 108, 112]
Terebinth	[96]
Terminalia	[39]
Turnip	[124]
Walnut	[90]
Waste cooking oil	[3, 21, 25, 33, 42, 48, 73, 77, 81, 82, 100]
Yellow grease	[19, 69]
Pure methyl ester	[70–72, 89, 114]

7 Chemical Composition of Biodiesel

Petroleum diesel fuels are saturated straight-chain hydrocarbons with carbon chain lengths of 12–18, whereas vegetable oils and animal fats consist of 90–98% triglycerides, small amounts of monoglycerides and free fatty acids. The fatty acid compositions of triglycerides differ in chain length, the degree of unsaturation and the presence of other functional groups. The fatty acid compositions are feedstock-dependent and are affected by factors such as climatic conditions, soil type, plant health and plant maturity upon harvest. Using the carboxyl reference system, fatty acids are designated by two numbers: the first number denotes the total number of carbon atoms in the fatty acid, and the second is the number of double bonds indicating the degree of unsaturation. For example, 18:1 designates oleic acid which has 18 carbon atoms and one C=C double bond. The most common fatty acids found in biodiesels and their structures are listed in Table 3.

The biodiesels are mainly comprised of the methyl esters of various fatty acids. The most common components found in biodiesel samples are mono-unsaturated oleic acid (C18:1) and di-unsaturated linoleic acid (C18:2) methyl esters. These two fatty acids (C18:1 and C18:2) were found in almost every biodiesel sample with an average weight percentage of 34.9 and 24.7, respectively, as shown in Fig. 5. Also, a significant amount of unsaturated erucic acid (22:1) and oleic acid (18:1) methyl ester were found in biodiesels. Furthermore, the oleic (C18:1) and linoleic (C18:2) are not only most commonly found in the biodiesel samples, but also showed highest in average weight percentage in the biodiesel samples, at approximately 40 and 32%, respectively. By contrast, an average of 7.5 and 6.5% of linolenic acid (C18:3) and stearic (18:0) acids methyl esters were present in the samples. Apart from fatty acid methyl esters, other chemical compositions usually found in the biodiesel are mainly unreacted monoglycerides and free fatty acids represented as the acid value.

Table 3 Chemical structure of common fatty acids in biodiesels

Fatty acid		Chemical structure
1.	Caprylic (8:0)	$CH_3(CH_2)_6COOH$
2.	Capric (10:0)	$CH_3(CH_2)_8COOH$
3.	Lauric (12:0)	$CH_3(CH_2)_{10}COOH$
4.	Myristic (14:0)	$CH_3(CH_2)_{12}COOH$
5.	Palmitic (16:0)	$CH_3(CH_2)_{14}COOH$
6.	Palmitoileic (16:1)	$CH_3(CH_2)_6$ CH=CH $(CH_2)_6$ COOH
7	Stearic (18:0)	$CH_3(CH_2)_{16}COOH$
8.	Oleic (18:1)	$CH_3(CH_2)_7$ CH=CH $(CH_2)_7$ COOH
9.	Linoleic (18:2)	$CH_3(CH_2)_4$ CH=CHCH$_2$CH=CH $(CH_2)_7$ COOH
10.	Linolenic (18:3)	$CH_3(CH_2)_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7$ COOH
11.	Gondonic (20:1)	$CH_3(CH_2)_7$ CH=CH $(CH_2)_9$ COOH
12.	Erucic (22:1)	$CH_3(CH_2)_9$ CH=CH $(CH_2)_9$ COOH

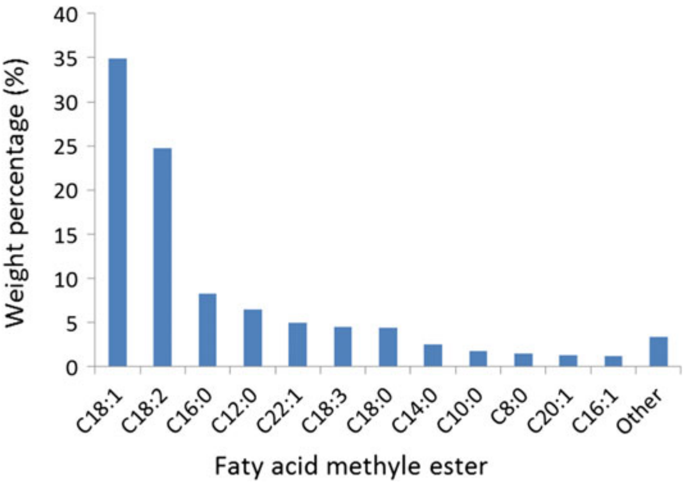

Fig. 5 Average weight in percentages of fatty acid methyl esters found in the collected data samples

8 Fuel Properties

The quality of biodiesel and its performance as an internal combustion engine application is largely determined by the fuel properties. One important liquid fuel property is kinematic viscosity (KV), which indicates the resistance or flow of liquid fuel. It plays a dominant role in the fuel spray, fuel–air mixture formation and the combustion process in diesel engine application. In a diesel engine, the liquid fuel is sprayed into compressed air and atomised into small droplets near the nozzle exit. In the engine combustion chamber, the fuel forms a cone-shaped spray at the nozzle exit which is affected by the viscosity. In addition to that viscosity also affects the fuel atomisation quality, penetration and size of the fuel droplet [18]. Higher viscosities result in higher drag in the fuel line and injection pump, higher engine deposits, higher fuel pump duties and increased wear in the fuel pump elements and injectors. Moreover, the mean diameter of the fuel droplets from the injector and their penetration increases with an increase in fuel viscosity. Higher pressure in the fuel line can cause early injection, moving the combustion of the fuel closer to top dead centre, thus increasing the maximum pressure and temperature in the combustion chamber [80]. Studies show that in a light-duty diesel engine, the CO and UHC could increase by 0.02% (by volume) and 1 ppm (by volume), respectively, with 1 cSt. increase of fuel viscosity [72]. On the other hand, low fuel viscosity is undesirable because it does not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear [50]. Therefore, all biodiesel standards define the upper limit and lower limit of viscosity. Heating value is another fuel property indicating the energy content in the fuel, along with biodiesel density. It determines the amount of energy taken by the engine in certain volume. When injecting the fuel in a diesel engine, the fuel pumps measure fuel on the basis of volume, not by mass. Therefore, the change in biodiesel density directly affects the engine output power and hence engine performance. This property is also correlated with engine exhaust emissions, particularly particulate matter (PM), nitrogen oxides (NOX) and carbon mono-oxides (CO) [105]. This is because the higher density of biodiesel increases the diameter of the fuel droplets in the combustion chamber, which consequently affects the fuel atomisation, combustion process and exhaust emission formation. Another significant fuel property that directly affects engine output power is the higher heating value (HHV). It determines the suitability of biodiesel as an engine fuel, as it indicates the energy content in the fuel. In general, biodiesels are approximately 10% less energy dense as compared with petroleum diesel, depending on the oxygen content in the hydrocarbon molecules. Furthermore, of great concern when considering biodiesels for engine fuel is oxidation stability (OS), which reflects resistance to oxidation during long-term storage. Biodiesels from any sources usually show very poor oxidation stability when compared with mineral diesel due to their chemical composition. During the oxidation process, the quality of fuel declines due to gum formation which remains in the biodiesel. This gum does not combust completely, resulting in poor combustion, carbon deposits in the combustion chamber and lubrication oil thickening. Therefore, high oxidation stability is desirable for a good quality biodiesel.

The average fuel properties reported in the collected data were found to be within the limits of European (EU), American (US) and Australian (AU) biodiesel standards, except for oxidation stability (OS). The average OS was found to be 4.73 h, which is much lower than the minimum OS requirement (6 h minimum) of EU and AU biodiesel standards. These results indicate that a vast number of the investigated biodiesels were unlikely to fulfil EU biodiesel standards, and this may be one of the major issues that restrict the widespread use of biodiesel in conventional diesel engines. The biodiesels that showed poor OS and which were rich in unsaturated FAME include soya bean, sunflower, safflower, corn, cottonseeds, linseeds, jatropha and camelina. European and Australian biodiesel standards also impose tight restrictions on kinematic viscosity (KV), limiting it to a minimum of 3.5 and a maximum of 5 cSt. However, the KV of biodiesels in the secondary data ranged from 0.99 to 7.21 cSt, which means that many of them would be unlikely to meet EU and AU biodiesel standards regarding KV. US biodiesel standards are laxer regarding KV (1.9–6 cSt). However, they place tighter restrictions on other biodiesel properties, which means that many biodiesels identified in the secondary dataset would still be unlikely to meet US standards. Overall, most of the maximum and minimum values for fuel properties were outside the range of biodiesel standards, demonstrating the significant level of variation in the data. This was not unexpected because the data were collected from a large number of different biodiesels with a wide variety of chemical structures. Therefore, the collected secondary data were useful for conducting an in-depth correlation study between fuel properties and the chemical composition of biodiesel (Table 4).

Table 4 Summary of data for biodiesel properties

Properties	Biodiesel standard			Max.[a]	Min.[a]	Ave.[a]
	ASTM D7651	EN 4214	Australian			
Kinematic viscosity (cSt.)	1.9–6	3.5–5	3.5–5	6	2.15	4.42
Density (kg/l)	n/a	0.86–0.9	0.86–0.90	0.924	0.829	0.876
Higher heating value (Mj/kg)	n/a	n/a	n/a	41.6	35.86	39.91
Oxidation stability (h)	3 min	6 min	6 min	11.4	0.2	4.73

[a] Max. = maximum value; Min. = minimum value; Ave. = average value

9 Correlation of Chemical Composition and Fuel Properties

The fuel properties of biodiesel are generally controlled by its chemical composition. Due to variations in the chemical structure in fatty acid methyl esters, the fuel properties of biodiesel significantly differ from one another. Figure 6 shows the effect of average chain length (ACL) on kinematic viscosity (KV), density, higher heating value (HHV) and oxidation stability (OS). The ACL was correlated with all the fuel properties investigated in this study. There was a very strong positive correlation with KV, as shown in Fig. 4a. This is mainly due to the increase in carbon content, as well as random intermolecular interaction in the FAME, which consequently increased the KV. For the same reason, ACL was also found to have a strong positive correlation with density and HHV. It is also interesting to found that biodiesels with an ACL less than 14 were unlikely to meet the lower limit of both US and EU standards. On the other hand, biodiesel with a very high ACL (over 19) is more likely to exceed the upper limit of biodiesel standards regarding KV.

The average number of double bonds (ANDB) in the biodiesel (which indicates the concentration of unsaturated fatty acid methyl esters) was found to be another influential factor affecting most of the biodiesel properties investigated in this study. Figure 7 shows the effect of ANDB on the kinematic viscosity (KV), density, higher heating value (HHV) and oxidation stability (OS). Oxidation stability (OS) may have a slight negative correlation with ACL, as shown in Fig. 4d. However, this property has a very strong negative correlation with ANDB. Figure 5d indicates that the OS of biodiesel decreased rapidly with an increase in ANDB. This is because a higher number of double bonds in the fatty acid chain of biodiesel make it much more susceptible to oxidation. ANDB also has a moderate

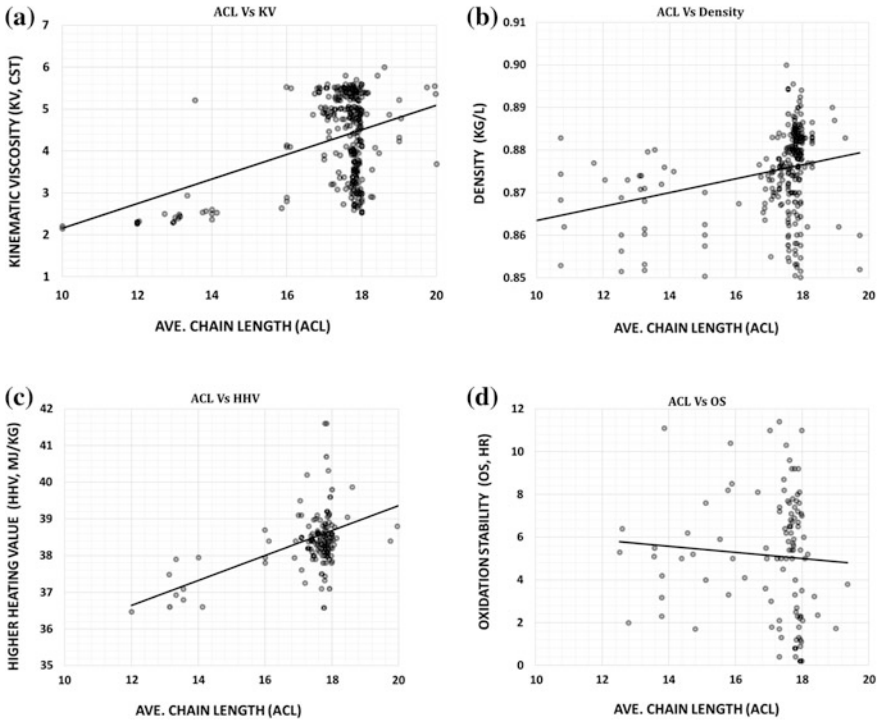

Fig. 6 Effect of ACL on biodiesel **a** kinematic viscosity (KV), **b** density, **c** higher heating value (HHV) and **d** oxidation stability (OS)

positive correlation with density and HHV, but no correlation was found between ANDB and KV, as shown in Fig. 5a.

The result of this analysis indicated that ACL and ANDB have certain effects on the four biodiesel properties investigated in this study. However, with a close look at Figs. 4 and 5, it can be seen that ACL and ANDB are the only parameters that control all fuel properties of biodiesel, rather other parameters and their combined effect may involve in determining the properties. Therefore, a multicriteria data analysis is required to investigate the correlation of biodiesel's properties with its chemical composition, and this is investigated in the next section.

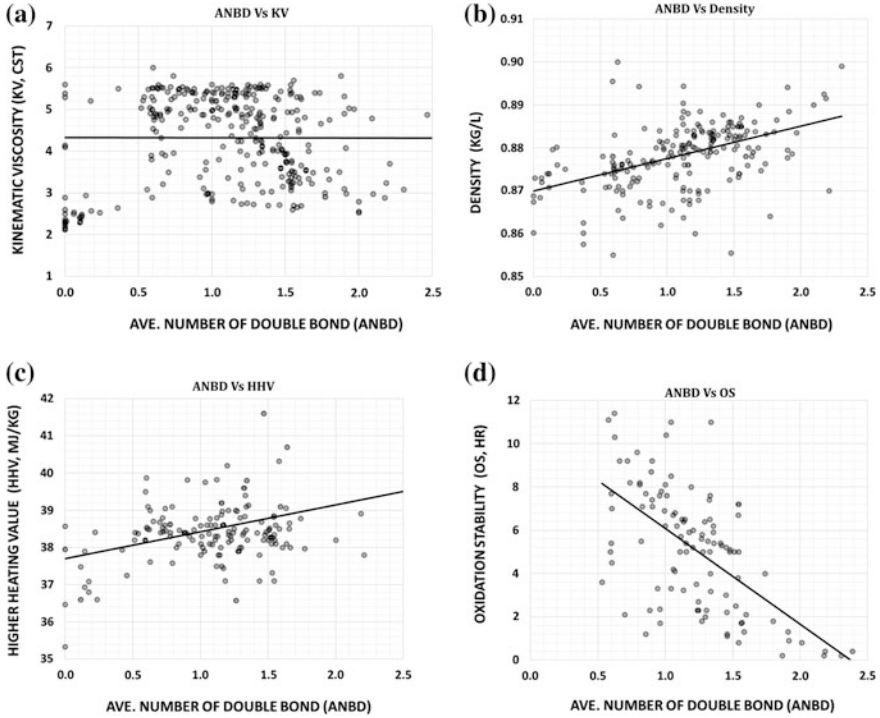

Fig. 7 Effect of ANDB on biodiesel **a** kinematic viscosity (KV), **b** density, **c** higher heating value (HHV) and **d** oxidation stability (OS)

10 Principal Component Analysis

The findings of the correlation study reported in the previous section indicate a complex relationship between biodiesel quality and its chemical composition. A particular fuel property does not depend on a single chemical parameter; rather it is influenced by multiple parameters and factors. Therefore, multivariate data analysis is required to gain a detailed understanding of this relationship. Principal component analysis (PCA) is one of the popular multivariate data analysis techniques used by almost all scientific disciplines. PCA is used to analyse datasets with highly intercorrelated dependent variables. It reduces the complexity and dimensionality of the problem, thereby extracting the most important information and analysing the structure of the observations and variables. PCA changes the input variables into principal components (PCs) that are an independent and linear combination of input variables. PCA also represents patterns in the observations and variables by displaying them as points on a diagram. In this study, PCA was conducted using Microsoft XLSTAT software to observe the influence of chemical composition on individual fatty acid compositions. The variables used for the principal components were individual fatty acid methyl esters chain length ranging from 8 to 22, while the interaction terms included average chain length (ACL), average number of double bonds (ANDB) and weight percentages of oxygen (O_2), hydrogen (H), carbon (C), saturation (percentage of saturated fatty acid), mono-unsaturated fraction (MUFA) and poly-unsaturated fraction (PUFA). The variables also included the most commonly found impurities in biodiesel, namely monoglyceride and free fatty acid contents regarding acid number (AN). In general, variables which lie close to (±45°) an observation are correlated, those lying in opposite directions (135°–225°) are anti-correlated, and those lying in an orthogonal direction have less or no influence. The direction and length of the variables are indicative of their influence on the observation, with a short length indicative of little influence. The results of four fuel properties are graphically shown in Figs. 8, 9, 10 and 11.

As discussed earlier, the results of principal component analysis as shown in Fig. 8 also indicate a strong positive correlation between KV and ACL. Therefore, fatty acid methyl esters (FAME) with a carbon chain length 18 or above increase the KV, and the inverse is true for short chain fatty acids (<C16). Moreover, the presence of unsaturated FAME also had a moderate positive influence on KV. Among the unsaturated FAME, MUFA has more influence compared to PUFA on KV. The presence of other parameters that increase the KV of biodiesel are impurities and carbon content. On the other hand, an increase in the oxygen percentage reduces the KV of biodiesel. The influence of free fatty acid and hydrogen

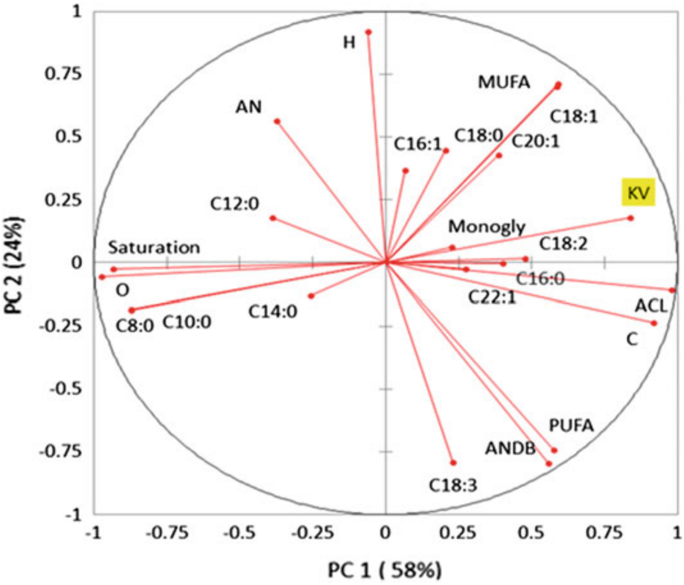

Fig. 8 Principal component analysis and correlation of kinematic viscosity with chemical composition of biodiesel

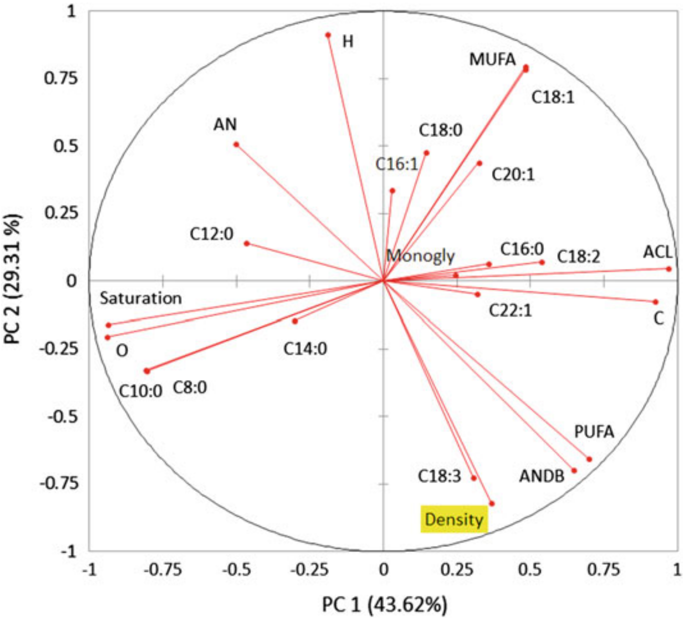

Fig. 9 Principal component analysis and correlation of density with chemical composition of biodiesel

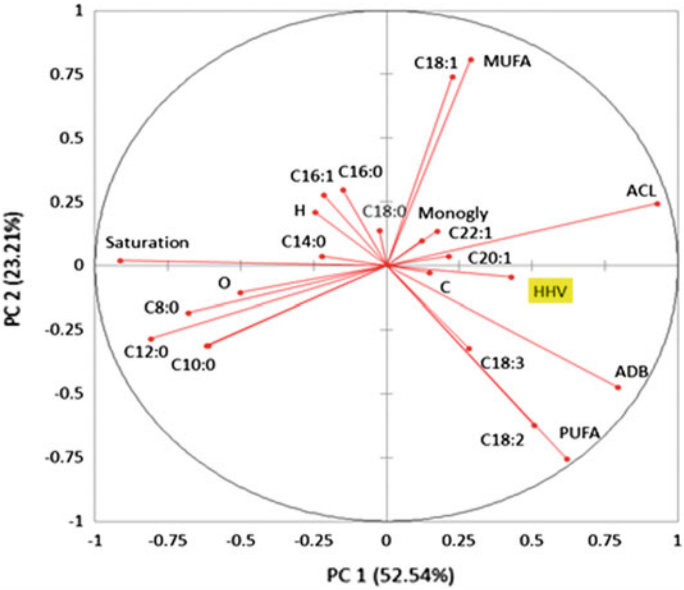

Fig. 10 Principal component analysis and correlation of higher heating value with chemical composition of biodiesel

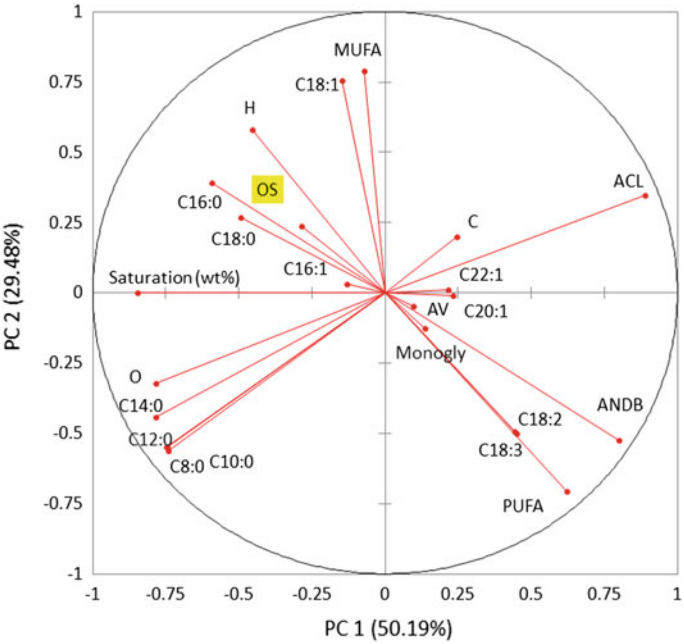

Fig. 11 Principal component analysis and correlation of oxidation stability with chemical composition of biodiesel

content on KV is insignificant. In contrast, the density of biodiesels is significantly affected by ANDB, and PUFA is shown in Fig. 9. In the PCA plan, the line for linolenic (C18:3) FAME lies very close to the density line which indicates a strong positive relationship between them. The other parameter which strongly influences the density of biodiesel is the percentage of hydrogen and AN with opposite correlations. The presence of saturated FAME significantly reduces the HHV of biodiesel as shown in Fig. 10. This figure also shows that ACL and ANDB have a positive correlation with HHV. Therefore, biodiesel with a high content of long-chain unsaturated FAME always shows a higher HHV. But the opposite correlation is evident in Fig. 11, where long-chain unsaturated FAME significantly reduces the OS of the biodiesel. It can be argued that biodiesel with a higher HHV may have less OS and vice versa.

11 Conclusion

In this chapter, a detailed investigation of key physicochemical properties of biodiesel has been carried out. During the last few decades, numerous types of biodiesel have been investigated. Formulated from a wide variety of sources, biodiesels differ from one to another as regards fuel properties and chemical composition. The aim of this chapter was to investigate the correlation between the fuel properties of biodiesel and its chemical composition, based on data collected from published literature. The fuel properties considered in this study were kinematic viscosity, density, higher heating value and oxidation stability. An investigation was conducted using principal component analysis (PCA) data analysis tool. A complex relationship was found between chemical composition and biodiesel properties. PCA indicated that the fuel properties of biodiesels are determined by a number of parameters and by the combination of different chemical compositions. An average number of double bonds (ANDB) and an average chain length (ACL) may well be the most influential parameters affecting most of the properties of biodiesels. Parameters relating to biodiesel production and purification, such as free fatty acids and glycerol content, also influence certain biodiesel properties found in this study. Thus, the future challenge is to develop an accurate model for estimating biodiesel properties and to find an optimum combination of the chemical composition of biodiesel for enhanced performance in automotive applications.

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