

Biodiesel fuels

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ABSTRACT

The mono-alkyl esters, most commonly the methyl esters, of vegetable oils, animal fats or other materials consisting mainly of triacylglycerols, often referred to as biodiesel, are an alternative to conventional petrodiesel for use in compression-ignition engines. The fatty acid esters that thus comprise biodiesel largely determine many important fuel properties. In turn, the composition of the biodiesel depends on the composition of the parent feedstock because feedstocks with widely varying fatty acid composition can be used for biodiesel production. The use of different feedstocks is also significant under aspects of increasing biodiesel supply and socio-economic issues. In this article, biodiesel production is briefly described, followed by a discussion of biodiesel fuel properties and the influence of varying fatty acid profiles and feedstocks. It is shown that the properties of biodiesel least influenced by minor components can be determined by a straightforward equation in which the properties of the biodiesel fuel are calculated from the amounts of the individual component fatty esters and their properties. Optimizing biodiesel composition is also addressed.

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1. Introduction

The search for a variety of energy sources is nearly as old as mankind's need for energy. Increasing industrialization commencing in the 19th century, spurred by the development of machines converting the energy stored in a variety of resources to power, caused this search to intensify. The internal combustion engine, in its two major variations, the spark-ignition and compression-ignition (diesel) engines, is a prime example. While fuels obtained from fossil sources were investigated from the onset of these engines, biogenic materials also found some interest, primarily ethanol in the case of the spark-ignition engine [1] and vegetable oils in the case of the compression ignition engine [2]. Due to a variety of factors, petroleum became the major source of fuels for both engines, although research, testing and some use of the "alternative" biogenic fuels continued for many years through approximately World War II and then resumed with ever-increasing intensity, in the late 1970s and early 1980s as a result of the energy crises of the 1970s.

That operational problems were associated with the use of vegetable oils in a diesel engine was recognized early [2], with high viscosity being defined as a major cause of these problems. While one paper states [3] that it is "academically necessary to split off the glycerides and to run on the residual fatty acid," other work goes a step further by interchanging glycerol for ethanol by preparing the ethyl esters of palm oil through a transesterification reaction, with the Belgian patent 422877 probably being the first report of what is termed biodiesel today [4,5] and testing them in an urban bus [6]. This is probably the first documented use of what is now termed biodiesel [7,8], namely the mono-alkyl esters of vegetable oils or animal fats or other triacylglycerol-containing feedstocks. This approach was then rediscovered approximately forty years later [9] in the early stages of renewed interest in vegetable oils and their derivatives as diesel fuel.

Besides preparing biodiesel, several other approaches have been investigated over time with the objective of reducing the viscosity of triacylglycerol-containing materials. These approaches are dilution with petrodiesel, microemulsification, and pyrolysis [10]. Besides these four approaches, more recently another approach based on a catalytic reaction termed hydrodeoxygenation, which affords a mixture of hydrocarbons probably best called "renewable diesel"

and simulating the composition of petroleum-derived diesel fuel (petrodiesel), has been developed [11,12]. The present article is, however, concerned with biodiesel and the other approaches are not discussed here.

With ever-increasing research interest as well as production and use of methyl esters of plant oils as biodiesel, especially since the mid- to late 1990s, standards were developed tailored largely toward these methyl esters. The first standard was established in Austria in 1991 followed by other European standards, most notably the German standard DIN 51606. Standards in individual European countries have been superseded by the European standard EN 14214 [13]. In the United States, concurrently the biodiesel standard ASTM D6751 [14] was developed. It may be noted that ASTM D6751 states that biodiesel meeting its specifications is to serve as blend stock for blends with petrodiesel and therefore is applied to neat biodiesel. Relatedly, the standard ASTM D7467 covers blends at levels of 6–20% biodiesel [15] and an ASTM specification WK52154 for blends >20% is under development [16]. Blends of up to 5% biodiesel with petrodiesel are covered by the petrodiesel standard ASTM D975 [17] with these blends required to meet the specifications for neat petrodiesel. The EN and ASTM standards now often serve as reference standards for other biodiesel standards world-wide. These standards address a variety of fuel quality issues caused by the properties of the major fuel components, the mono-alkyl esters of fatty acids, and by minor constituents (contaminants). It may be noted that viscosity, in the form of kinematic viscosity, as the major issue for using biodiesel instead of vegetable or plant oils, is limited in these standards to ensure that alkyl (usually methyl) esters are indeed used as biodiesel. Selected current specifications in the aforementioned two standards are listed in Table 1.

Besides overall favorable properties for use as transportation fuel, biodiesel has numerous other potential uses, although none of these uses can compete with fuel in terms of volume. These uses include heating oil [18,19], power generation [20], lubricants [21], plasticizers [22], high boiling absorbents for cleaning of gaseous industrial emissions [23], as well as various solvent applications, which are also discussed here briefly. It is biodegradable [24–26] and, relatedly, has also been tested as a possible oil spill remediation agent [27–31]. This application relates to the solvent properties briefly discussed at the end of this article. A detailed discussion of the applications

Table 1
Selected technical specifications in the biodiesel standards ASTM D6751 [14] and EN 14214 [13].

Specification	ASTM D6751		EN 14214	
	Limit	Method	Limit	Method
Kinematic viscosity	1.9–6.0 mm ² /s	D445	3.5–5.0 mm ² /s	EN ISO 3104
Cetane number	47 min	D613, D6890	51 min	EN ISO 5165
Cloud point	Report		– ^b	
Oxidation stability	3 h min	EN 14112	8 h min	EN 14112, EN 15751
Density	–	–	860–900 kg/m ³	
Free glycerol	0.02% mass max	D6584	0.02% mass max	EN 14105
Monoacylglycerols	0.4% mass max	D6584	0.7% mass max	EN 14105
Total glycerol	0.24% mass max	D6584	0.25% mass max	EN 14105
Acid value	0.5 mg KOH/g max	D664	0.5 mg KOH/g max	EN 14104
Na K combined	5 ppm (μg/g) max	EN 14538	5 mg/kg max	EN 14108, EN 14109
S	0.015 or 0.05% mass, max ^a	D5453	10 mg/kg	EN ISO 20846, EN ISO 20884
P	0.001% mass, max	D4951	4 mg/kg	EN 14107
Ca Mg combined	5 ppm (μg/g)	EN 14538	5 mg/kg	EN 14538

Max = maximum; min = minimum.

^a Depends on the grade of petrodiesel to be blended with.

^b Cold filter plugging point with varying limits depending on geography and time of year.

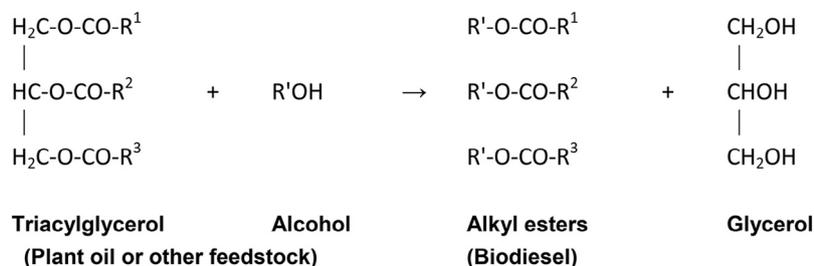


Fig. 1. The transesterification that produces biodiesel. R^1 , R^2 and R^3 represent different fatty acid chains. R^1 , R^2 and R^3 may or may not be identical. Methanol ($R' = \text{CH}_3$) is the most commonly used alcohol with sodium methoxide (NaOCH_3) being the preferable catalyst.

of biodiesel other than those discussed here is beyond the scope of this article.

Besides the aforementioned driving forces, advantages of biodiesel are low or no sulfur content, no aromatics content, high flash point, inherent lubricity, biodegradability, reduction of most regulated exhaust emissions, miscibility with petrodiesel in all blend ratios and compatibility with the existing fuel distribution infrastructure. Technical challenges associated with biodiesel include reduction of NO_x exhaust emissions and improvement of oxidative stability and cold flow properties. While the biodegradability of biodiesel is frequently cited as an advantage, for example, in case of spills in the environment, this also means that bacterial biomass may grow during storage and form deposits that clog engines and fuel lines [32,33].

The overall environmental benefit or damage derived from the production and use of biodiesel needs to be evaluated on a “cradle-to-grave” basis through life-cycle analyses (LCA). Biodiesel from terrestrial sources is generally computed to have a positive energy balance; i.e., more fuel energy is derived from the product than was consumed to produce it. For example a life-cycle analysis for soybean-derived biodiesel showed a positive energy ratio [34] and a review of palm biodiesel LCA showed uniformly positive energy ratios with dependence on system boundaries [35]. Aquatic feedstock like microalgae though may result in a negative energy balance.

While biodiesel was initially assumed to be “carbon-neutral,” the agricultural inputs needed to grow the feedstock and the incurred carbon debt from land-use change often mean that biodiesel use may actually result in greater greenhouse emissions than if petrodiesel were used [35]. Increased agriculture may also have negative impacts on waterways because of nitrification from fertilizer runoff. So, while biodiesel has distinct advantages over petrodiesel for the local environment, its impact on the global environment is less clear. LCAs are dependent on system definition and the availability and quality of data. Value judgments will also have to be made on the relative importance of each environmental impact. Which one is more important than the other? Further developments in the assessment of the desirability of a product will be necessary before this question can be answered.

The economics of biodiesel have made it often dependent on incentives in the form of subsidies, tax reductions or other regulations to be competitive with petrodiesel. Therefore, it is of interest to investigate other potential applications where biodiesel may be technically and economically competitive. Development of other products from non-oil feedstock components would also be critical, to improve both business and environmental profiles. The business challenges faced by the biodiesel industry have led to the slow adoption of innovative new manufacturing technologies in spite of their many advantages as many of these require significant capital inputs. Thus, while biodiesel has become a widely adopted alternative fuel, there remain many challenges that may prevent it from being more widely used.

This article is concerned primarily with fuel properties largely determined by the major components of biodiesel as each component has a different combination of properties. Properties that will be discussed here and how they are affected by the composition of biodiesel from various feedstocks are the cetane number (CN), cold flow, oxidative stability, kinematic viscosity, lubricity, and density. How fuel properties can be influenced by minor constituents will also be addressed.

Biodiesel is obtained by transesterifying vegetable oils or other materials are largely comprised of triacylglycerols with monohydric alcohols, most commonly methanol, to give the corresponding mono-alkyl esters (Fig. 1) [7,8]. Thus, the fatty acid profile of biodiesel corresponds to that of the parent oil or fat from which it is produced. As the least expensive alcohol, methanol has been commonly used to produce biodiesel. Thus, biodiesel is often referred to as the fatty acid methyl esters (FAME) of a vegetable oil or animal fat or other triacylglycerol-containing material. Both moieties, the fatty acid chain and the alcohol functionality, contribute to the overall properties of a fatty ester and therefore the properties imparted by other alcohols (yielding fatty acid alkyl esters; FFAE) that could be used for producing biodiesel should be considered. Accordingly, both structural moieties will be discussed here.

2. Discussion

2.1. History and background

The diesel engine, a version of the internal combustion engine relying on self-ignition of a fuel under conditions of elevated heat and pressure (thus also often termed the compression-ignition engine), was developed in the 1890s. Its inventor, Rudolf Diesel (1858–1913), tested numerous fuels at that time as he describes in his book *Die Entstehung des Dieselmotors* [36]. As Diesel describes in this book and elsewhere [36–38], the first use of a vegetable oil as fuel for a diesel engine occurred at the World Exposition in Paris in 1900. At the request of the French Government, which at that time was interested in developing fuels of local origin for its African colonies for sake of energy independence, a small diesel engine ran on peanut (groundnut) oil. Apparently, this was only one of five diesel engines shown at that exposition [39]. In any case, as Diesel reports, the engine ran smoothly on this fuel with the onlookers not noticing this ongoing experiment. Later on, through the 1920s until approximately the end of World War II, there are numerous reports in the literature on the use of vegetable oils in diesel engines, often under the theme of energy independence [2]. During that time, several researchers recognized that the high viscosity of vegetable oils can lead to operational problems such as engine deposits. One suggestion was to split off the glycerol moiety and run the engine on fatty acids, although it was recognized that this approach could also cause operational issues [3]. Under current aspects, probably the most interesting and significant work was described

in Belgian patent 422877 issued in 1937 to Chavanne [4]. In this patent and some later publications [5,6], the ethyl esters of palm oil, obtained by transesterification of the oil with ethanol, are described. The first test of this fuel in 1938 in an urban bus is also discussed [6].

Research on alternative fuels remained largely dormant in the years after World War II until the energy crises of the 1970s spurred renewed interest in this subject. In this connection, vegetable oils were rediscovered as potential fuels for diesel engines. The probably first reports on esters of vegetable oils from this time date to 1980 [9]. In this work, researchers from South Africa describe the use of methyl esters of sunflower oil in a diesel engine and that the use of these esters alleviated the viscosity issue and subsequent operational issues. As mentioned in Section 1, besides the reduction of viscosity of a vegetable oil by transesterifying to alkyl esters, three other solutions to the issue of high viscosity exist, namely microemulsification, diluting with petrodiesel and pyrolysis. In any case, transesterification is the approach to viscosity reduction that ultimately received the most consideration and now alkyl esters of vegetable oils are known as biodiesel. Methyl esters are the most widely produced and used vegetable or plant oil esters, largely because methanol is the most common and least expensive alcohol available for this purpose. In more recent years, what may be seen as a fifth approach to producing fuels from vegetable/plant oils, and which has found some commercial application, has been developed. This process, giving a fuel probably best termed, as mentioned in Section 1, “renewable diesel,” is the production of hydrocarbons emulating the components of petrodiesel via a process termed hydrodeoxygenation [11,12]. In this process, the glycerol or carboxyl moiety is cleaved and the double bonds saturated so that largely alkanes of shorter chain length arise. Thus, the “ideal” product arising from triolein in this process would be heptadecane. The process can be tailored with subsequent isomerization of the hydrocarbon chain to give fuels with improved cold flow properties that are of interest as jet (aviation) fuels.

Besides the biodiesel standards mentioned above, numerous legislative and regulatory efforts promoting the cause of biodiesel have accompanied or facilitated its rising production and use. For example, in the United States, biodiesel production in 2014 was approximately 6.65 billion liters after about 6.84 billion liters in 2013 [40], and in the European Union it was approximately 10,367,000 metric tons (approximately 11.77 billion liters) in 2013 with a production capacity of 23,093,00 metric tons in 2014 [41]. Worldwide production in 2014 has been at given as 29.7 billion liters (approximately 26,144,000 metric tons), with the top producer being the United States (4.7 billion liters) followed by Brazil and Germany (3.4 billion liters each), Indonesia (3.1 billion liters), Argentina (2.9 billion liters), and France (2.1 billion liters), with the EU accounting for 11.6 billion liters [42]. Issues related to production that have affected biodiesel use include feedstock availability as not enough vegetable/plant oils are produced to replace all petrodiesel, and the so-called food vs. fuel issue which is based on the claim that fuel production from edible oils may increase their price and reduce their availability while also causing agricultural land to be used for fuel instead of food production.

The output of research papers on biodiesel and related aspects has increased exponentially, making biodiesel probably one of the most-researched alternative fuels. Considerable research has been devoted to addressing the technical issues facing biodiesel, which have impaired its even more widespread commercialization and use. These issues include the properties at low temperatures (cold flow issues), stability toward oxygen and other materials, especially while stored, and the reduction of nitrogen oxides (NO_x) exhaust emissions, one of the four kinds of exhaust emissions affected by regulations. The issue of feedstock availability mentioned above has caused a search for additional feedstocks. The transesterification

reaction has received considerable research attention also, mainly the search for additional and/or improved catalysts.

This article will focus on the technical issues that have been facing biodiesel, as well as discuss the fuel and physical properties of biodiesel, as these issues are largely a result of the properties of the components of biodiesel. The issue of feedstocks will be addressed by primarily focusing on their varying composition and how this may affect the use of the biodiesel fuels derived from them.

2.2. Biodiesel production

2.2.1. Transesterification

Summarily, transesterification is the production of one ester from another ester. In the case of biodiesel, this is the production of mono-alkyl esters from a vegetable/plant oil which consists largely of triacylglycerols, i.e., the glycerol esters of long-chain fatty acids, with a low molecular-weight alcohol. As indicated above, methanol is currently the preferred alcohol for this purpose, giving the methyl esters of the plant oil with a fatty acid profile corresponding to that of the parent oil.

The transesterification reaction is well-known and is, to a significant extent, textbook material. It can be catalyzed by both acids and bases, with base catalysis being considerably more rapid [43]. The overall reaction, which is reversible, is shown in Fig. 1.

The most advantageous reaction conditions were established as a molar ratio alcohol:oil of 6:1, 60 °C, 1 h with either 0.5% sodium methoxide (CH₃ONa) or 1% sodium hydroxide as preferred catalyst when using methanol as alcohol [43]. Generally, the reaction temperature should be slightly below the boiling point of the alcohol. The 6:1 molar ratio is a 100% increase over the theoretical amount, which is necessary to drive the equilibrium to the right. Furthermore, the free fatty acid content should be less than 0.5% (acid value of less than approximately 1) and the reaction system as free of moisture as possible. Thus, production of biodiesel is becoming more common on a commercial scale using sodium methoxide as catalyst because this catalyst helps maintain low moisture content. The reason is that when using an alkoxide, such as sodium methoxide as catalyst, the water-forming reaction



occurring when using hydroxide catalysts is avoided.

At the beginning of the transesterification reaction, the mixture of vegetable oil and methanol consists of two immiscible phases, the vegetable oil and the alcohol. This leads to a situation where mass transfer may be limiting the overall reaction rate rather than the actual chemical reaction. Similarly, at the end of the reaction two phases occur, the methyl esters product and glycerol as co-product. The two phases can be easily separated by gravity (settling of the phases) or centrifugation but the latter is energy intensive. Washing the product ester phase with water is necessary to remove the remaining catalyst and potential contaminants such as glycerol formed during the reaction.

The transesterification occurs stepwise, proceeding from the triacylglycerol starting material via the di- and monoacylglycerols to glycerol, with methyl ester being formed at each step. Although under optimal conditions, the transesterification reaction proceeds to a very high degree of conversion, minor to trace amounts of triacylglycerol starting material as well as mono- and diacylglycerols remain. Even very minor amounts of some of these materials can significantly influence fuel properties. Thus glycerol and the various triacylglycerols are limited in biodiesel standards as free and total glycerol, respectively, with monoacylglycerols being limited individually in both the ASTM and EN standards while the other acylglycerols are limited individually only in the EN standard.

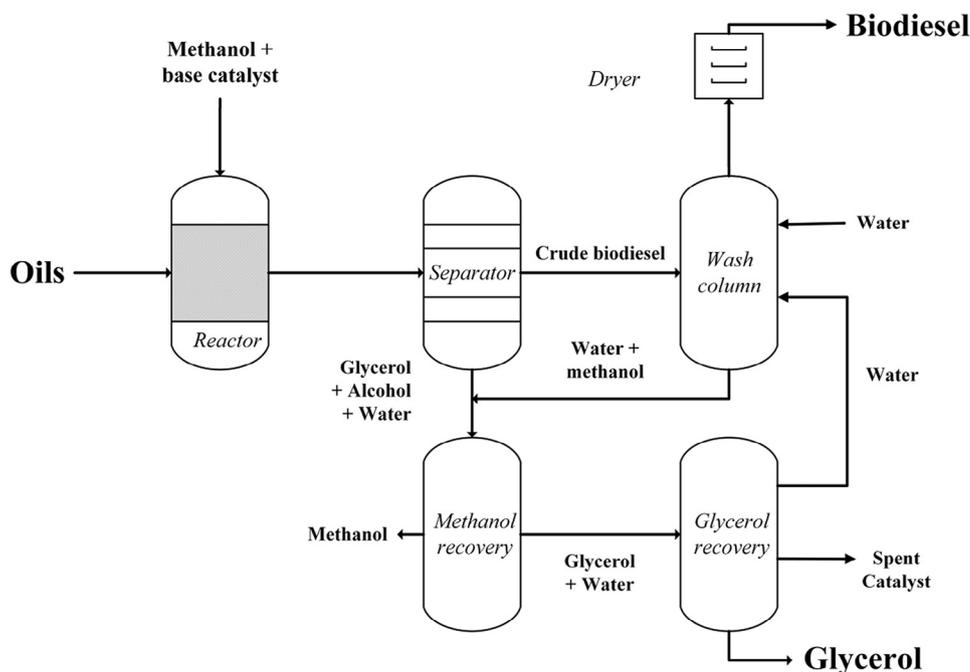


Fig. 2. Biodiesel production process, as commonly practiced in industry.

If the feedstock contains a significant amount of free fatty acids as is often the case with low-quality feedstocks such as used cooking oils, trap grease or animal fats, an acid pre-treatment step is usually employed to reduce the free fatty acid content [44]. This pretreatment consists of esterifying the free fatty acids in the feedstocks to the methyl esters using the desired alcohol and an acid catalyst (H_2SO_4), thereby reducing the acid value. The triacylglycerol portion of the feedstock can then be transesterified by base catalysis using the conditions described above.

The “conventional” process for biodiesel production is shown in Fig. 2. The aforementioned sensitivity of the transesterification reaction under what might be termed the “standard conditions” toward moisture, free fatty acid content, mass transfer limitations and other factors has caused significant research efforts toward developing other process systems. While it is beyond the scope of this article to deal with these aspects in detail, some salient aspects are briefly discussed here.

Process improvements have approached these concerns by: (a) improving contact between the oil and alcohol phases, either chemically or mechanically; (b) heterogeneous and enzymatic catalysts; (c) simultaneous extraction and reaction; (d) reaction with simultaneous removal of the product; and (e) microwave irradiation. Combinations of all of these have also been extensively studied.

2.2.2. Reducing or eliminating mass-transfer effects

Novel reactor designs have improved the contact between the oil and methanol phases beyond that which can be achieved using a common paddle-type impeller [45]. These include static mixers [46], micro-channel reactors [47], slit channel reactors [48], oscillatory flow reactors [49], and rotating tube reactors [50]. Particularly interesting is the use of ultrasound to induce the formation of cavitation microbubbles whose collapse induces better convection and mixing [51,52].

Mass transfer limitations have also been addressed by performing the transesterification at supercritical conditions: ~ 573 – 673 K and ~ 15 – 45 MPa [53]. At these conditions, the reaction mixture is in one phase only and thus interphase mass transfer constraints are eliminated. At supercritical conditions, the reaction proceeds

rapidly with a high yield without a catalyst and is insensitive to the presence of water and free fatty acids. Thus, the system provides twin advantages over the conventional process for transesterification. Waste and crude oils may be used without initial pretreatment. Furthermore, catalyst removal and separation will be unnecessary. The high pressures and temperatures would drive up capital equipment costs however. High alcohol-oil molar ratios are also necessary. Safety concerns have also been raised about the use of flammable solvents at very high temperatures and pressures. Jet fires having an effect as distant as 190 m have been predicted in the case of a methanol pump rupture [54].

Another approach for eliminating mass transfer limitations is the use of co-solvents like tetrahydrofuran [55], dimethyl ether [56] and methyl tert-butyl ether (MTBE) [57] to improve the miscibility of the oil and alcohol. With the co-solvents, the reaction mixtures are now single phase and the overall reaction rate is greatly enhanced.

2.2.3. Heterogeneous catalysts

Heterogeneous catalysts have found significant interest as they usually can be recycled many times and thus avoid having to use fresh methoxide (or hydroxide or other alkoxide) for each reaction batch. Separation is also simplified, the need for washing is reduced and continuous operation becomes simpler. The activity of these catalysts to affect the transesterification reaction diminishes with time. It also appears that many papers concerned with this kind do not address the question of catalyst leaching and how that may affect biodiesel storage and properties and meeting specifications, especially those addressing the heteroatoms Na, K, Mg, Ca, P and S (if the catalysts contain these elements) in biodiesel standards. Some catalysts may contain other heteroelements not addressed in biodiesel standards and the impact of these elements on fuel quality has not yet been fully addressed.

Research on various catalysts for the transesterification has been so extensive that numerous reviews now deal with specialized aspects such as certain classes of catalysts and even catalysts containing specific metals, etc. Recent reviews [58,59] cover most of the chemistry behind new heterogeneous catalysts. In these reviews and as in many other biodiesel heterogeneous catalysis papers,

mass-transfer effects are not considered extensively. If heterogeneous catalysts are used, the three phases arise: alcohol, oil and catalyst. Mass-transfer effects are often discussed only in the context of systems designed to eliminate or reduce mass-transfer-limitations, e.g. ultrasound [60]. Notable exceptions are studies concerning CaO catalysts [61,62]. Until the mass-transfer effects and leaching effects are addressed, it would be premature to discuss detailed kinetics of any of the other heterogeneous catalysts. Despite the innumerable reports on alternative catalysts for the transesterification reaction, it is unclear whether any have been used in commercial production due to a lack of reports in the open literature.

Enzymatic catalysis [63–65] shares many of the advantages of inorganic heterogeneous catalysts. Products are more easily recovered and, in general, product quality is improved. In addition, enzymes promise to be more environmentally friendly and are usually more tolerant toward moisture content and the quality of the feedstock. Reaction times are longer, however, and the enzymes are expensive. Costs are very system dependent but it is worth mentioning a study that determined that a biodiesel produced via an immobilized lipase system was about twice as expensive as one produced with a conventional alkali system [66].

Other means of catalyzing the transesterification process include whole-cell biocatalysts [67] and ionic liquids [68].

2.2.4. Direct contact between feedstock and alcohol

Integration of the oil extraction step with the transesterification step has been investigated [69], a process called *in situ* transesterification or reactive extraction. This process could eliminate the use of hexane as extraction solvent for the oil feedstock. Some good results have been obtained but most of these processes have required high solvent-to-oil ratios, thus deviating from the “standard” conditions mentioned in Section 2.2.1., possibly because a large amount is necessary to physically cover dry feedstocks [70]. It is a method, however, to be investigated in connection with the transesterification of feedstocks of aqueous origin like microalgae [71] because it eliminates the drying step that is a major energy load on microalgal processes. Like the heterogeneous catalytic systems, *in situ* transesterification will yield a three-phase system (alcohol, oil and feedstock solids), hence *in situ* transesterification is often combined with the methods to promote mass transfer mentioned earlier. These include co-solvents [70], ultrasound [51] and operating at supercritical conditions [58].

2.2.5. Early product removal to drive equilibrium

In conventional transesterification, a large excess of alcohol, usually 100% more than theoretical, is fed in order to ensure that the equilibrium is driven forward and the limiting reactant (oil) is consumed. While the methanol may be recovered and recycled, this increases the cost for separation. One of the techniques being studied to avoid this is the use of membrane reactors, which allow continuous separation of the reactants from the products as they are formed [72]. A similar concept is reactive distillation wherein a reactive middle section is sandwiched between a top section where recovery of solvents can be done and recovery of the heavier FAME product can be done. Because it also involves heat integration, reactive distillation has been shown to be an effective solution both in theory [73] and in experiments [74].

2.2.6. Microwave irradiation

The use of microwave irradiation for heating chemical reactions is not simply a more efficient method for heating. Microwaves promote selective heating of polar molecules which result in local temperatures that are actually higher than the bulk temperature [75]. The *apparent* activation energy is thus lower and the overall reaction rate is higher. Catalyst requirements can also be reduced. The

use of microwaves, however, places restrictions on the reaction vessel size and shape.

2.3. Biodiesel feedstocks

The starting materials used for biodiesel production are vegetable oils (or more generally, plant oils) or other oils and fats consisting largely of triacylglycerols. The most common feedstocks in the past and up to the present have been commodity vegetable oils such as rapeseed (low-erucic variety; canola being similar to low-erucic rapeseed), palm, soybean and coconut. This observation is confirmed by the historical research described above carried out on oils such as peanut, palm and sunflower. The issue of expanding the base of feedstocks has led to significant interest in other potential source of triacylglycerol-based oils [76].

A common feature of most vegetable/plant oils is that most of their fatty acid profile is comprised of the five most common fatty acids palmitic (hexadecanoic), stearic (octadecanoic), oleic (9(Z)-octadecenoic), linoleic (9(Z),12(Z)-octadecadienoic) and linolenic (9(Z),12(Z),15(Z)-octadecatrienoic). The amounts of these acids vary among the oils though, and because their methyl esters have different properties the biodiesel fuels derived from these oils also show varying properties. Some plant oils, on the other hand, for example castor, coriander, cuphea and meadowfoam, exhibit fatty acid profiles with other fatty acids as major components, again significantly influencing the fuel properties of the biodiesel derived from these oils. Minor components, however, which may include other fatty acid methyl esters in the fatty acid profile, as well as steryl glucosides, monoacylglycerols and other acylglycerols remaining in the product after the transesterification reaction, and materials carried over from the feedstock often can significantly influence biodiesel fuel properties.

As the cost of biodiesel production is largely (about 75–80%) determined by the cost of the feedstock, less expensive feedstocks have been of interest for a considerable length of time. These low-cost feedstocks include used cooking oils, greases and animal fats. While their cost is lower, they also usually are of lower quality, almost always exhibiting high acid values and/or water content and presence of extraneous materials, necessitating quality improvement before biodiesel production.

Several other issues have led to an intense search for other vegetable/plant oils as additional feedstocks. These issues include (a) expanding the base of feedstocks to potentially increase biodiesel supply; (b) the use of commodity oils for nutritional purposes and the claim that therefore the production of biodiesel from them affects food prices; (c) the issue of land-use change, i.e., the use of agricultural land for “growing fuel” instead of food or change of use of virgin land to agricultural use for this purpose of “growing fuel”; and (d) the use of pesticides and fertilizers needed to grow these feedstocks and which can leach into groundwater or bodies of water. Therefore, “alternative” sources of biodiesel are often waste or inedible oils and/or plants growing on land unsuitable for agriculture. A prominent example of an “alternative” feedstock presented often as very promising is jatropha [77,78]. In some recent publications it has been discussed, however, that the hopes and assumptions associated with this potential feedstock have been overstated [79–81]. While most of these feedstocks, including jatropha, exhibit the aforementioned five most common fatty acids as the major components of their fatty acid profiles, some feedstocks may have fatty acid profiles deviating more strongly from the five major fatty acids as major components, so that property assessment is critical here, too.

Terrestrial plants that have been investigated as biodiesel sources are listed in Tables 2 and 3, which are updates of tables previously published [82]. Table 2 lists those that have been investigated on a laboratory scale while Table 3 lists those that have been investigated in an engine, including those that have indicated that the

Table 2
Terrestrial plant sources for FAME that have been physico-chemically tested for fuel properties.^a The plant part is usually the seed unless indicated otherwise.

Common name	Scientific name	Family	Reference(s)
Amygdalus	<i>Amygdalus pedunculata</i> (<i>Prunus pedunculata</i>)	Rosaceae	[83]
Annona (Chirimuya)	<i>Annona cherimola</i>	Annonaceae	[84]
Avocado	<i>Persea americana</i>	Lauraceae	[85]
Babassu	<i>Orbignya oleifera</i>	Arecaceae	[86]
Baobab	<i>Adansonia digitata</i>	Bombacaceae	[87]
Bitter almond	<i>Prunus dulcis</i>	Rosaceae	[88]
Black currant	<i>Ribes nigrum</i>	Grossulariaceae	[89]
Blessed milk thistle	<i>Silybum marianum</i>	Asteraceae	[90]
Borage	<i>Borago officinalis</i>	Boraginaceae	[89]
Brazilian mustard	<i>Brassica juncea</i>	Brassicaceae	[91]
Camelina	<i>Camelina sativa</i>	Brassicaceae	[92]
Cardoon	<i>Cynara cardunculus</i>	Asteraceae	[92]
Cedar mangrove	<i>Xylocarpus moluccensis</i>	Meliaceae	[93]
Chinese pepper	<i>Zanthoxylum bungeanum</i>	Rutaceae	[94,95]
Chinese soapberry	<i>Sapindus mukorossi</i>	Sapindaceae	[96]
Chinese spicehush	<i>Lindera communis</i>	Lauraceae	[97]
Chinese tallow tree	<i>Sapium sebiferum</i>	Euphorbiaceae	[98]
Coffee defective beans	<i>Coffea</i> spp.	Myrtaceae	[99]
Coffee grounds	<i>Coffea</i> spp.	Myrtaceae	[100]
Coriander	<i>Coriandrum sativum</i>	Apiaceae	[101]
Cuphea	<i>Cuphea viscosissima</i> × <i>C. lanceolata</i>	Lythraceae	[102]
Date palm	<i>Phoenix dactylifera</i>	Arecaceae	[103]
Egusi	<i>Citrullus colocynthis</i>	Cucurbitaceae	[104]
Field pennycress	<i>Thlaspi arvense</i>	Lauraceae	[105]
Garden cress	<i>Lepidium sativum</i>	Brassicaceae	[106]
Harmal	<i>Rhazya stricta</i>	Apocynaceae	[107]
Hazelnut	<i>Corylus avellana</i>	Betulaceae	[108]
Hemp	<i>Cannabis sativa</i>	Cannabaceae	[109]
Honesty	<i>Lunaria annua</i>	Brassicaceae	[110]
Ilama	<i>Annona diversifolia</i>	Annonaceae	[111]
Indian milkweed	<i>Calotropis gigantea</i>	Asclepiadaceae	[112]
Jimsonweed	<i>Datura stramonium</i>	Solanaceae	[98,113]
Kapok	<i>Ceiba pentandra</i>	Malvaceae	[114]
Kenaf	<i>Hibiscus cannabinus</i>	Malvaceae	[115]
Lavender croton	<i>Croton gratissimus</i>	Euphorbiaceae	[116]
Lesquerella	<i>Lesquerella fendleri</i>	Brassicaceae	[117]
Dishrag gourd; sponge gourd; loofah; smooth loofah	<i>Luffa cylindrica</i> (<i>Luffa aegyptiaca</i>)	Cucurbitaceae	[118]
Madre de cacao	<i>Gliricidia sepium</i>	Fabaceae	[119]
Mandarin orange	<i>Citrus reticulata</i>	Rutaceae	[120]
Marama bean	<i>Tylosema esculentum</i>	Fabaceae	[121]
Marula (sea mango)	<i>Cerbera odollam</i>	Apocynaceae	[122]
Marula	<i>Sclerocarya birrea</i>	Anacardiaceae	[121]
Milkweed	<i>Asclepias syriaca</i>	Asclepiadaceae	[123]
Milo	<i>Thespesia populnea</i>	Malvaceae	[124]
Mongongo	<i>Schinziophyton rautanenii</i>	Euphorbiaceae	[121]
Moringa	<i>Moringa oleifera</i>	Moringaceae	[125]
Okra	<i>Hibiscus esculentus</i>	Malvaceae	[126]
Olive	<i>Olea europaea</i>	Oleaceae	[85]
Osage orange	<i>Maclura pomifera</i>	Moraceae	[127]
Papaya	<i>Carica papaya</i>	Caricaceae	[128]
Pequi	<i>Caryocar brasiliensis</i>	Caryocaraceae	[129]
Perilla	<i>Perilla ocyroides</i>	Lamiaceae	[130]
Pili pulp	<i>Canarium ovatum</i>	Burseraceae	[131]
Pumpkin	<i>Cucurbita pepo</i>	Cucurbitaceae	[132]
Rocket (arugula)	<i>Eruca sativa</i>	Brassicaceae	[133]
Roselle	<i>Hibiscus sabdariffa</i>	Malvaceae	[134]
Rough cocklebur	<i>Xanthium sibiricum</i>	Asteraceae	[135]
Seashore mallow	<i>Kosteletzkya pentacarpos</i>	Malvaceae	[136,137]
Shepherd's purse	<i>Capsella bursa-pastoris</i>	Brassicaceae	[133]
Spanish bayonet	<i>Yucca aloifolia</i>	Asparagaceae	[138]
Syringa berries	<i>Melia azedarach</i>	Meliaceae	[139]
Tomato	<i>Solanum lycopersicum</i>	Solanaceae	[140]
Tropical almond	<i>Terminalia catappa</i>	Combretaceae	[141]
Tucum	<i>Astrocaryum vulgare</i>	Arecaceae	[142]
Tung	<i>Aleurites fordii</i>	Euphorbiaceae	[142,143]
Upland Cress	<i>Barbarea verna</i>	Brassicaceae	[133]
Walnut	<i>Juglans regia</i>	Juglandaceae	[108]
White mustard	<i>Sinapis alba</i>	Brassicaceae	[144]
Winged bean	<i>Psophocarpus tetragonolobus</i>	Fabaceae	[131]
Wonder tree	<i>Idesia polycarpa</i>	Salicaceae	[145]
Yellow nutsedge tuber	<i>Cyperus esculentus</i>	Cyperaceae	[146]
Yellow oleander	<i>Thevetia peruviana</i>	Apocynaceae	[147]

^a The reader is advised to use caution when referring to some data in some references given here as some data in these references may be erroneous. This list was compiled without checking data in the references for accuracy.

Table 3
Alternative terrestrial plant sources for FAME that has been engine tested.^a

Common name and plant part ^b	Scientific name	Family	Reference(s)
Apricot	<i>Prunus armeniaca</i>	Rosaceae	[148]
Beach almond	<i>Terminalia belerica</i>	Combretaceae	[149]
Camelina	<i>Camelina sativa</i>	Brassicaceae	[150–152]
Caper Spurge	<i>Euphorbia lathyris</i>	Euphorbiaceae	[153]
Castor	<i>Ricinus communis</i>	Ricinus	[117,154]
Chinese parasol	<i>Firmiana platanifolia</i>	Malvaceae	[155]
Chinese pistache	<i>Pistacia chinensis</i>	Anacardiaceae	[156]
Desert Date	<i>Balanites aegyptica</i>	Zygophyllaceae	[157]
Ethiopian mustard	<i>Brassica carinata</i>	Brassicaceae	[158]
Hazelnut	<i>Corylus avellana</i>	Betulaceae	[159]
Jatropha	<i>Jatropha curcas</i>	Euphorbiaceae	[77–81,160]
Jajoba	<i>Simmondsia chinensis</i>	Simmonsniaceae	[160]
Karanja	<i>Pongamia pinnata</i>	Fabaceae	[161,162]
Kuntze tea	<i>Camelia sinensis</i>	Theaceae	[163]
Kusum	<i>Schleichera oleosa</i>	Sapindaceae	[164,165]
Linseed	<i>Linum usitatissimum</i>	Linaceae	[166]
Mahua	<i>Madhuca indica</i>	Sapotaceae	[167]
Manchurian apricot	<i>Prunus mandshurica</i>	Rosaceae	[168]
Moringa	<i>Moringa oleifera</i>	Moringaceae	[169]
Mukinduri	<i>Croton megalocarpus</i>	Euphorbiaceae	[170,171]
Neem	<i>Azadirachta indica</i>	Meliaceae	[172]
Niger	<i>Guizotia abyssinica</i>	Asteraceae	[173]
Olive pomace	<i>Olea europaea</i>	Oleaceae	[174]
Paradise tree	<i>Simarouba glauca</i>	Simaroubaceae	[175]
Pilu	<i>Salvadora oleoides</i>	Salvadoraceae	[176]
Polanga	<i>Calophyllum inophyllum</i>	Clusiaceae	[177]
Poon	<i>Sterculia foetida</i>	Malvaceae	[178,179]
Radish, Turnip	<i>Raphanus sativus</i>	Brassicaceae	[180,181]
Ribbed melon	<i>Hodgsonia macrocarpa</i>	Cucurbitaceae	[182]
Rice bran	<i>Oryza sativa</i>	Poaceae	[183]
Rocket	<i>Eruca sativa</i>	Brassicaceae	[184]
Rubber	<i>Hevea brasiliensis</i>	Euphorbiaceae	[161,185]
Safflower	<i>Carthamus tinctorius</i>	Asteraceae	[186]
Sesame	<i>Sesamum indicum</i>	Pedaliaceae	[187,188]
Siberian apricot	<i>Prunus sibirica</i>	Rosaceae	[168]
Terebinth	<i>Pistacia terebinthus</i>	Anacardiaceae	[189]
Tobacco	<i>Nicotiana tabacum</i>	Solanaceae	[155,190]
Weeping forsythia	<i>Forsythia suspense</i>	Oleaceae	[191]
Yellow horn	<i>Xanthoceras sorbifolia</i>	Sapindaceae	[192]

^a The reader is advised to use caution when referring to some data in some references given here as some data in these references may be erroneous. This list was compiled without checking data in the references for accuracy.

^b Plant part is seed unless indicated otherwise.

cetane number was tested using a cetane engine. Splitting the list into these two scales of development is a useful indicator of the level of interest in the feedstock and the availability of materials for more extensive testing. The feedstocks from the family Fabaceae are interesting because these plants are diazotrophic or nitrogen-fixing, that is, they are able to utilize nitrogen from the air. This ability makes the use of fertilizers unnecessary and reduces cultivation costs and environmental impact. Halophytic plants like polanga (*Calophyllum inophyllum*) and sea mango (*Cerbera odollam*) share the ability to grow in salty soil with more established oil crops like palm and coconut. Seashore mallow (*Kosteletzkya pentacarpos*) is an example of a temperate zone plant that can grow in salty environments. The Brassicaceae and Euphorbiaceae are also interesting because these are mostly herbs or shrubs, which reduce the cost of harvesting. In contrast to large trees, there is also less biomass “overhead” required to grow the plant. Other noteworthy plants are those that are commonly regarded as weeds such as yellow nut sedge (*Cyperus esculentus*) and Indian milkweed (*Calotropis gigantea*) since these indicate that they are easy to grow.

Many of the plants listed in Tables 2 and 3 are significant agricultural wastes including rubber seed, rice bran, tobacco seed, coffee grounds, defective coffee beans olive pomace, pili pulp, papaya seed, tea seed, pumpkin seed and avocado seed. They are byproducts from the production of a more highly valued product and so are essentially

free. Utilization of these would eliminate or mitigate a waste stream. Multi-product plants like moringa are also noteworthy.

Animal fats have been studied in a similar context as waste cooking oils [193–196]. The waste animal cooking oils originate from commercial-scale livestock or fish rendering operations and are thus easily collected from waste streams. Waste animal fats offer twin advantages of mitigating a waste stream and generating a side revenue. Because the feedstock cost is essentially zero, the resulting product is much less costly in spite of additional processing steps required to separate the oil from water and other impurities [197]. Compared to vegetable oils, animal fats have more saturated fatty acids, leading to some additional handling and distribution problems because the feedstock is often solid and the resulting product tends to have poor cold flow properties [149,195]. An exception is fish oils. Fish oils, similar to algal oils, usually contain considerable amounts of unsaturated fatty acids but these are mostly long-chain such that the net effect is still poor cold flow properties [198]. On the other hand, methyl esters from butter had approximately 20% C₆–C₁₂ methyl esters which led to poor results in flash point while oxidation stability was also low [199]. Nonetheless, in spite of some poor results at a lab scale, commercial scale biodiesel production from waste animal fats has been done in many locations around the world [81].

Waste vegetable oils have also been studied but other than the challenges of collection, pretreatment and variability of composition [200], it is not expected that there would be any significantly different treatment of the waste vegetable oils from virgin oils.

Biodiesel is one of the many biofuels that have been proposed to be obtainable from single-cell organisms such as microalgae, yeast, molds, cyanobacteria and bacteria [201]. Photosynthetic microalgae have attracted the most attention because they offer many advantages including a photosynthetic efficiency higher than terrestrial plants and the possibility of using non-arable land for cultivation [202]. Immense technical challenges, however, must be overcome before microalgal biofuels can reach commercial success. Many microalgal oils contain significant amounts of long-chain polyunsaturated fatty acids so these may negatively impact important properties such as oxidative stability [198]. On a life-cycle basis, as compared to terrestrial plants, microalgae require considerably more inputs such as nitrogen fertilizers and energy for harvest and post-harvest treatment. Microalgae are grown in either open ponds or closed photobioreactors and these consume significant amounts of energy. The most basic measure of the feasibility of an energy system may be the energy efficiency ratio (EER) or the energy return on investment (EROI), which is defined as the ratio of energy inputs required to the amount of energy produced. Thus, an EER of 1 indicates break-even. It has been suggested that an EROI or EER of more than 5 [203] or even 7 [204] is the minimum necessary for the sustainability of an energy system. While life-cycle assessments (LCA) are very system-dependent, reviews of extant LCA studies show that most fall far below this standard [203]. Many of the environmental impacts of large-scale microalgal culture are still incompletely known [205]. Using wastewater as a feed may alleviate some of the energy and environmental burdens but these may carry further complications like inconsistent composition and pathogens [205]. There have been many attempts to commercialize the technology with significant amounts of venture capital (see, for example [206]). While microalgal technology is conceptually attractive, there are many technological breakthroughs that must be achieved before viable commercial implementation can be achieved [207].

Cyanobacteria, also called blue-green algae, share many advantages with microalgae and have another advantage in that they are also capable of generating reactive or fixed nitrogen from the air. This removes the need for the addition of fertilizers to the culture media. This quality plus the production of other fuels from the cyanobacteria offers the possibility of a favorable energy balance [208].

The other single-cell organisms studied as biodiesel feedstock like yeast [209] and mold [210] are heterotrophic; i.e., they rely on chemical sources of energy and are not photosynthetic. While the focus has been mostly on using waste materials as substrates, we are not aware of any life-cycle assessments having been done for these systems. Given the unfavorable results for the photosynthetic microorganisms, it is unlikely that a favorable EROI would be achieved with these systems.

Insects have also been studied as possible feedstocks. The value of using insects as feedstock is premised on their use to degrade solid wastes [211] and the presence of significant amounts of lipids in insect biomass [212]. Some biodiesel fuel testing has been done and as with other animal-sourced biodiesels the cold-flow properties tend to be poor [213]. While automated harvesting systems have been developed [211], the cost trade-offs are unknown and it is difficult to see how this can be implemented on a sufficiently large scale.

2.4. Biodiesel analysis

A major issue ensuring the commercialization and marketability of biodiesel is fuel quality assurance, as indicated above, by limiting the extraneous materials that can be present as they can negatively influence fuel properties and performance. These undesirable components include minor constituents formed during the transesterification reaction such as glycerol and the various acylglycerols as mentioned in Section 2.2.1. The issue of the acylglycerols and glycerol is addressed in biodiesel standards by the specifications for monoacylglycerols as well as free and total glycerol, the latter specification encompassing all acylglycerols and glycerol (Table 1). Other possible minor components of biodiesel that can negatively affect fuel quality or performance and combustion behavior are trace elements (“heteroelements”) which can be caused by residual catalyst or carry-over from the feedstocks. The elements that are limited in biodiesel standards are Na, K, S, P, Ca and Mg (Table 1). The biodiesel should also be as free of fatty acid as possible as addressed by the acid value as free fatty acids may cause corrosion and have elevated melting points. Various other specifications in biodiesel standards address other issues, such as the flash point limiting residual alcohol, and some specifications are redundant.

Numerous analytical methods have been developed for these minor components. Especially noteworthy are the gas chromatographic methods for determining free and total glycerol which are the standards ASTM D6584 [214] and EN 14105 [215]. Overviews of various methods for analyzing different aspects of the finished biodiesel product as well as monitoring the transesterification reaction, which includes spectroscopic methods such as infrared (IR) and nuclear magnetic resonance (NMR), are available in the literature [216–220].

Another issue is that of determining blend levels of biodiesels in petrodiesel. For this purpose, IR spectroscopic methods are utilized in standards such as ASTM D7371 [221], ASTM D7806 [222] and EN 14078 [223], including for analysis of trace amounts of biodiesel in aviation fuel such as ASTM D7797 [224].

2.5. Biodiesel fuel properties

The properties that will be discussed here are those that are to a significant extent determined by the fatty ester composition of the diesel fuel. These are kinematic viscosity, cetane number and other combustion-related properties, cold flow, oxidative stability and density. Lubricity, which is not a performance issue with biodiesel and therefore influenced only marginally by the fatty acid profile, will also be discussed.

As will be obvious from the following discussion, the properties of mixtures that generally do not pose operational problems can be predicted by the general equation

$$Pr_{mix} = \sum A_c \times Pr_c \quad (2)$$

in which Pr_{mix} is the property of the mixture being predicted, A_c = the relative amount (vol.-%; or amount as determined by gas chromatography) of an individual neat ester in the mixture, and Pr_c is the property of the individual neat ester. In other words, these properties vary proportionally with the amounts of the individual components and their properties. These properties are kinematic viscosity, cetane number and density as discussed below in the corresponding sections.

On the other hand, the properties associated with operational problems when using biodiesel cannot be predicted using the appropriate variation of Eq. (2). These properties are oxidative stability and cold flow. Minor FAME components influence these properties more strongly than indicated by the amounts.

Correlations of properties are possible only for classes of compounds possessing the same structural features or well-defined parameters. Thus saturated compounds can be primarily compared only among themselves, monounsaturated compounds among themselves. For example, it is not possible to correlate kinematic viscosity only to the number of carbon atoms in the chain. Correlation in this case can be only among saturated or among monounsaturated or among diunsaturated compounds or among triunsaturated compounds, etc.

Furthermore, properties based primarily on the structure of the component fatty acid alkyl esters of biodiesel compound structure-based properties such as cetane number and kinematic viscosity, etc. cannot be correlated with properties such as flash point, etc., which primarily serve to limit certain minor constituents/contaminants in biodiesel.

The greatest change in properties occurs when going from the saturated FA chain to the monounsaturated FA chain. Subsequent transitions to even more double bonds have less effect as evidenced by data for properties such as kinematic viscosity, cetane number, and oxidative stability.

2.5.1. Kinematic viscosity

Kinematic viscosity is the property of fatty compounds that is to a large extent the cause for the production of biodiesel, thus being a major reason why neat vegetable oils have been largely abandoned as alternative diesel fuel. Viscosity not only affects flow at all temperatures a fuel may be exposed to but also strongly influences the atomization of a fuel upon injection into the combustion chamber and ultimately the possible formation of engine deposits. The higher the viscosity, the greater is the tendency of the fuel to cause such problems. The viscosity of biodiesel in the form of methyl esters is about an order of magnitude lower than that of the parent oil. Kinematic viscosity has been included in most biodiesel standards and can be determined by standards such as ASTM D445 [225] or ISO 3104 [226].

The kinematic viscosity of individual fatty acid alkyl esters is affected by structural factors such as chain length as well as the number and nature of double bonds. Viscosity increases with chain length (number of carbon atoms) and with increasing degree of saturation. This holds also for the alcohol moiety, the viscosity of ethyl esters being slightly higher than that of methyl esters. Double bond configuration also influences viscosity. Compounds with *cis* double bonds exhibit lower viscosity than those with *trans* configuration, the kinematic viscosity of the latter being relatively close to that of the saturated compounds with the same number of carbon atoms [227]. Branching in the ester moiety, however, has little influence on viscosity, showing that this is a technically promising approach

Table 4
Kinematic viscosity (40 °C) of fatty acid methyl esters.^a Data from Refs. [227,228] unless indicated otherwise.

Saturated fatty acid methyl esters		Unsaturated fatty acid methyl esters	
Fatty acid methyl ester	Kinematic viscosity (mm ² /s)	Fatty acid methyl ester	Kinematic viscosity (mm ² /s)
8:0	1.19	16:1 Δ9c	3.67
10:0	1.72	18:1 Δ9c	4.51
12:0	2.43	18:1 Δ9t	5.85
14:0	3.30	18:2 Δ9c,12c	3.65
16:0	4.38	18:3 Δ9c, 12c, 15c	3.14
18:0	5.86	18:3 Δ6c, 9c, 12c	3.01 [89]
20:0	(7.40) ^b	20:1 Δ11c	5.77
22:0	(9.31) ^b	20:4 Δ5c, 8c, 11c, 14c	3.11 [229]
24:0	(11.53) ^b	22:1 Δ13c	7.33
		22:6 Δ4c, 7c, 10c, 13c, 16c, 19c	2.97 [229]
		24:1 Δ15c	8.87
		18:1 Δ9c 12-OH	15.44

^a The numbers denote the number of carbons and double bonds. For example, in oleic acid, 18:1 stands for eighteen carbons and one double bond with position and configuration of the double bond indicated by Δ9c. Trivial or common names as well as systematic names of the acids listed here: 8:0 10:0 12:0 14:0 16:0 18:0 20:0 22:0 24:0 16:1 Δ9c 18:1 Δ9c 18:1 Δ9t 18:2 Δ9c,12c 18:3 Δ9c, 12c, 15c 18:3 Δ6c, 9c, 12c 20:1 Δ11c 20:4 Δ5c, 8c, 11c, 14c 22:1 Δ13c 22:6 Δ4c, 7c, 10c, 13c, 16c, 19c 24:1 Δ15c 18:1 Δ9c 12-OH.

^b Solid at 40 °C. The value given in parentheses is a calculated viscosity contribution as described in Section 2.5.1.

for improving low-temperature properties (see discussion on cold flow properties below) without significantly affecting other fuel properties. Table 4 contains experimental kinematic viscosity data (at 40 °C) for common fatty acid methyl esters as they occur in biodiesel. Kinematic viscosity data at temperatures below 40 °C are available in other literature [230]. Other literature often presents dynamic viscosity data for biodiesel and its components, but these data are not included in Table 4 as kinematic viscosity is prescribed in biodiesel standards and dynamic viscosity can be easily calculated from kinematic viscosity by their relationship through density.

Most biodiesel fuels meet the kinematic viscosity range prescribed in biodiesel standards (Table 1) as most common fatty acid methyl esters possess kinematic viscosity values in that range, for example, the kinematic viscosity at 40 °C of methyl oleate is 4.51 mm²/s and that of methyl palmitate is 4.38 mm²/s. For the sake of comparison the kinematic viscosity values (40 °C) of some triacylglycerols are 32.94 for triolein, 24.91 for trilinolein and 17.29 for trilinolenin [227].

The kinematic viscosity of a mixture of fatty esters can be determined by an equation in which the overall kinematic viscosity is directly proportional to amounts and viscosities of the individual components [228]. This equation is

$$v_{\text{mix}} = \sum A_c \times v_c \quad (3)$$

in which v_{mix} = the kinematic viscosity of the biodiesel sample (mixture of fatty acid alkyl esters), A_c = the relative amount (%/100) of the individual neat ester in the mixture (as determined by, for example, gas chromatography) and v_c = kinematic viscosity of the individual esters. This approach is a simplification of the well-known Grunberg–Nissan equation usually applied for predicting dynamic viscosity.

As an example for the prediction of the kinematic viscosity of a mixture, the kinematic viscosity (40 °C) of soy methyl esters (SME) in the literature has usually been reported to be in the range of 4.0–4.1 mm²/s. This range for the kinematic viscosity of SME values agrees well with the application of this equation using the kinematic

viscosity values given in Table 1 to a typical fatty acid profile of SME being approximately 11% 16:0, 4% 18:0, 24% 18:1 Δ9c, 1% 18:1 Δ11c, 52% 18:2 and 8% 18:3. The effect on viscosity of blending biodiesel and petrodiesel was studied [231] and an equation was derived which allows the calculation of the viscosity of such blends.

The prediction of viscosity of fatty materials has received considerable attention in the literature with a variety of approaches having been established. An issue of interest in this connection is the contribution of compounds with melting points >40 °C to the overall kinematic viscosity of biodiesel at this temperature, which is the temperature prescribed in biodiesel standards. Fatty esters with melting points >40 °C are usually only saturated fatty esters with fatty acid chain lengths ≥C20. Obviously, their (hypothetical) kinematic viscosity is greater than that of the shorter-chain compounds that are liquids at 40 °C. As their contribution to the overall kinematic viscosity of a mixture cannot be determined directly, extrapolation of the kinematic viscosity of saturated fatty acid methyl esters with melting points <40 °C is applied. Thus a third-order polynomial equation

$$v = 0.30487 + 0.0265 \times C + 0.0066 \times C^2 + 0.000491 \times C^3 \quad (4)$$

in which v = kinematic viscosity as calculated viscosity contribution (CVC) and C = number of carbon atoms [228] was obtained. Calculated kinematic viscosity contributions (values in parentheses) for methyl eicosanoate (methyl arachidate), methyl docosanoate (methyl behenate), and methyl tetracosanoate are also given in Table 4. These values can be used like the experimental values for the other compounds for calculating overall kinematic viscosity according to Eq. (3).

2.5.2. Combustion-related properties: cetane number, speed of sound, heat of combustion, exhaust emissions

The final stage of the life cycle of a fuel is its combustion in an engine. Besides the technology level of the engine, numerous properties affect the efficiency and products of combustion of a diesel fuel. One of the most prominent properties in this connection is the cetane number (CN). Generally, the dimensionless CN is a prime indicator of diesel fuel quality as it relates to the ignition behavior of the fuel. The higher the CN, the shorter the ignition delay time, i.e. the time that passes between injection of the fuel into the cylinder and the onset of ignition and vice versa. Shorter ignition delay times are generally desirable.

A cetane scale has been established which is the basis of the determination of CNs by standards that have been established worldwide including ASTM D613 [232] in the United States and the International Organization for Standardization (ISO) standard ISO 5165. The American standard ASTM D975 [17] for petrodiesel requires a minimum CN of 40 and the European petrodiesel standard EN 590 [233] prescribes a minimum CN of 51 while the standards for biodiesel prescribe a minimum of 47 in ASTM D6751 or 51 in EN 14214. A long straight-chain hydrocarbon, hexadecane (C₁₆H₃₄; trivial name cetane), is the high quality standard on the cetane scale with an assigned CN of 100. Highly branched 2,2,4,4,6,8,8,-heptamethylnonane (HMN; also C₁₆H₃₄), which possesses poor ignition quality, is the low-quality standard with a CN of 15. The two reference compounds on the cetane scale show that the CN decreases with decreasing chain length and increasing branching. Aromatic compounds, which occur in significant amounts in petrodiesel, have low CNs but their CNs increase with increasing size of n -alkyl side chains [234,235]. Compounds with CN > 100 or CN < 15 have been identified on the cetane scale.

As CN determination by the traditional standard ASTM D613 consumes a significant amount of fuel sample, an apparatus termed the Ignition Quality Tester™ (IQT™) was developed, which also offers the benefit of easier use. It forms the basis of the standard ASTM

Table 5
Cetane numbers of fatty acid methyl esters (mostly determined as derived cetane numbers).

Saturated fatty acid methyl esters		Unsaturated fatty acid methyl esters	
Fatty acid methyl ester	Cetane number	Fatty acid methyl ester	Cetane number
8:0	39.75 [243]	16:1 Δ9c	56.6, 51.0 [237,243]
10:0	51.6 [243]	18:1 Δ6c	58.55 [238]
12:0	66.7 [243]	18:1 Δ9c	57 [238] ^a
14:0		18:1 Δ9t	57.15 [238]
16:0	85.9 [243]	18:1 Δ11c	53.9 [238]
18:0	101 [237]	18:2 Δ9c, Δ12c	38.2 [237]
20:0	112–120 ^b	18:2 Δ9t, Δ12t	43 [238]
22:0	125–130 ^b	18:3 Δ9c, Δ12c, Δ15c	22.7 [243]
24:0	135–145 ^b	18:3 Δ6c, Δ9c, Δ12c	29.2 [89]
		20:1 Δ11c	73.2 [105]
		20:4 Δ5c, Δ8c, Δ11c, Δ14c	29.6 [229]
		22:1 Δ13c	74.2 [105]
		22:6 Δ4c, Δ7c, Δ10c, Δ13c, Δ16c, Δ19c	24.4 [229]
		18:1 Δ9c 12-OH	37.4 [243]

^a Determined from averaging more than 20 datapoints.

^b Theoretical ranges determined as described in Ref. [238].

D6890 [236], in which a derived cetane number (DCN) is obtained that correlates with the CN obtained by the traditional standard. Most CN data presented here were obtained as DCNs using the IQT™ [237,238].

Probably the first CN test of what is now known as biodiesel was conducted with palm oil ethyl esters [2,6]. This material had a high CN, a result confirmed by later studies on many other vegetable oil-based diesel fuels and individual fatty compounds. Furthermore, as indicated above by the differing CNs of hexadecane and HMN, structural elements define the CN of a specific compound. Thus branching in the chain reduces CN as shown by the comparison of hexadecane and HMN; however, increasing unsaturation also decreases the CN. The double bond position also plays a role with CN having been predicted to be higher if the double bond is located toward one end of the chain than toward the middle of the chain [239]. Several reports on experimental cetane number determination confirm these insights [240–242]. Thus, one long straight chain suffices to impart a high CN even if the other moiety is branched. Accordingly, highly polyunsaturated FAME with C20 and C22 chain lengths as found in many algal oils therefore have low CNs [229]. On the other hand, double bond configuration does not significantly affect CN [238]. Branched esters, however, derived from alcohols such as isopropanol have CNs competitive with methyl or other straight-chain alkyl esters [237]. Branched esters are of interest because they exhibit improved low-temperature properties as discussed below.

Table 5 lists the CNs of FAMES, most of which were determined using ASTM D6890. Many FAMES have high CNs, imparting overall CNs to biodiesel higher than those of many petrodiesel fuels. Generally, the CNs of low-CN compounds show better agreement in the

literature than those of compounds with higher CNs. The cause of this is the non-linear relationship between the ignition delay time and the CN [237]. Thus, small changes at shorter ignition delay times result in greater changes in CN than at longer ignition delay times.

Similar to the approach used for kinematic viscosity, the CNs of mixtures such as biodiesel can be approximated by the equation in which the overall CN is proportional to the amount and CNs of the individual components

$$CN_{mix} = \sum A_c \times CN_c \quad (5)$$

in which CN_{mix} is the CN of the mixture, A_c = the relative amount (vol.-%) of an individual neat ester in the mixture, and CN_c is the CN of the individual neat ester [229,238]. With this equation and using data from Table 5, the CN of biodiesel from soybean oil (SBO) is approximately 50 when assuming a typical fatty acid profile of soy methyl esters as discussed above for kinematic viscosity. This result agrees well with published CN data for soy methyl esters which are usually in the upper 40s to low 50s.

Ideally, only carbon dioxide and water are the combustion products of a hydrocarbon. As combustion is not completely ideal, a variety of other products are formed. Among these other products are hydrocarbons, particulate matter, carbon monoxide and nitrogen oxides, which are also the species addressed by exhaust emissions regulations.

For petrodiesel, higher CNs were correlated with reduced nitrogen oxides (NO_x) exhaust emissions [244], although the relationship between the CN and engine emissions is complicated by many factors including the technology level of the engine, with older, lower injection pressure engines generally being more sensitive to CN. Despite the inherently relatively high CNs of fatty compounds, NO_x exhaust emissions usually increase slightly when operating a diesel engine on biodiesel [245]. The level of exhaust emissions is also proportional to the amount of biodiesel in blends thereof with petrodiesel [245]. The connection between the structure of fatty esters and exhaust emissions was investigated [246,247] by studying the exhaust emissions caused by enriched fatty acid alkyl esters (FAAE) as fuel. NO_x exhaust emissions increase with increasing unsaturation and decreasing chain length, which can also lead to a connection with the CNs of these compounds. While several fuel properties play a role in affecting the NO_x increase when using biodiesel as fuel, the key factors appear to be charge-gas mixtures that are closer to stoichiometric at ignition and in the standing pre-mixed autoignition zone near the flame lift-off length [248]. Other properties, notably (isentropic) bulk modulus and speed of sound, have been considered among the primary influencing factors due to their effect on the fuel injection system and combustion, ultimately elevating NO_x exhaust emissions [229,244–248]. Speed of sound, which decreases with increasing temperature, and isentropic bulk modulus tend to increase as the degree of unsaturation and chain length increase with the increase in isentropic bulk modulus being fairly uniform with the addition of each double bond (Table 6) [249–254]. The higher viscosity, higher cetane number, and

Table 6
Speed of sound and isentropic compressibility κ_s from Ref. [249] and Ref. [250] at 83 kPa.

	Speed of sound (m/s ⁻¹)	Isentropic compressibility (GPa ⁻¹)
10:0	1324.6 (20 °C); 1249.2 (40 °C)	0.654 (20 °C); 0.749 (40 °C) [249]
14:0	1299.5 (40 °C) [249]	0.695 (40 °C) [249]
16:0	1317.8 (40 °C) [249], 1320 (40 °C), 1303 (45 °C) [250]	0.677 (40 °C) [249]
18:0		1317 (45 °C) [250]
18:1 Δ9c	1408.8 (20 °C), 1337.7 (40 °C) [249]; 1389 (25 °C), 1318 (45 °C) [250]	0.577 (20 °C), 0.650 (40 °C) [249]
18:2 Δ9c,12c	1419.3 (20 °C), 1348.1 (40 °C) [249]; 1398 (25 °C), 1327 (45 °C) [250]	0.561 (20 °C), 0.632 (40 °C) [249]
18:3 Δ9c,12c, 15c	1411 (25 °C), 1340 (45 °C) [250]	
10:0 Et	1313.7 (20 °C), 1240.6 (40 °C) [249]	0.671 (20 °C), 0.766 (40 °C) [249]
14:0 Et	1360.5 (20 °C), 1288.7 (40 °C) [249]	0.627 (20 °C), 0.712 (40 °C) [249]

lower volatility of the biodiesel combine with the earlier injection timing to effect the start of combustion. Also, the higher bulk modulus of biodiesel compared to petrodiesel implies that biodiesel experiences a faster pressure rise than petrodiesel, resulting in earlier injection for biodiesel [251,252].

Particulate emissions, on the other hand, were hardly influenced by the aforementioned structural factors. Compared to neat alkanes, the “ideal” components of petrodiesel, biodiesel and its components lower PM exhaust emissions considerably while neat alkanes show lower NO_x exhaust emissions than biodiesel and its neat components [247]. Neat alkanes also exhibited lower PM and NO_x exhaust emissions than the petrodiesel fuel they were compared to [248], showing that components such as aromatics in petrodiesel fuel are likely responsible to a significant extent for its regulated exhaust emissions. This observation implies that the results of exhaust emissions testing of biodiesel vs petrodiesel depend on both fuels, also considering that petrodiesel has undergone changes over the years such as the introduction of ultra-low sulfur diesel fuels. Exhaust emissions control technologies, however, such as selective catalytic reduction (SCR; serving to reduce NO_x exhaust emissions) and diesel particulate filters (DPF; serving to reduce particulate emissions) which are increasingly penetrating the diesel engine market as older engines are retired have the effect of largely eliminating the effect of compound structure on exhaust emissions as they leave the tailpipe of a vehicle [255].

Another aspect of exhaust emissions is that of their effect on human health. In the United States, soy-derived biodiesel passed EPA Tier 2 Health effects testing required for registration under provisions of the Clean Air Act in the United States [256]. Generally, biodiesel and petrodiesel generate the same types of exhaust emissions but the detailed composition and morphology of the species in the exhaust emissions may differ, an effect also dependent on the engine and the conditions of the test. This holds for the particulate matter and hydrocarbons exhaust emissions addressed by regulations. Issues that have been investigated include mutagenicity and cytotoxicity with several reviews being available [257–259]. For example, despite overall lower particulate matter emissions, biodiesel generated smaller particles which are of concern because they can penetrate deeper into the lungs. Exhaust emissions control systems, however, may have significant effect on the remaining particles emitted. Aldehydes and alkanes, identified as ozone precursors, were increased in exhaust emissions from rapeseed methyl esters [260]. Emissions generated by rapeseed methyl esters had higher toxicity but mutagenicity was reduced by biodiesel, probably due to higher polyaromatic hydrocarbons in the case of petrodiesel [261,262], although newer “clean” petrodiesel fuels also perform better in this respect. Relatedly, both biodiesel and renewable diesel were found to be preferable to conventional petrodiesel for use in underground mining equipment [263]. Overall, the effect of biodiesel versus petrodiesel is mixed, being complicated by constantly evolving levels of engine and exhaust emissions control technology which may level the effects of fuel composition, varying fuel composition as well as the conditions of engines tests including geographical and meteorological conditions, so that the need for more research exists [259,264].

The suitability of fatty acid alkyl esters as petrodiesel alternative is also indicated by the heat of combustion. The heats of combustion of virtually all fatty acid methyl esters occurring in biodiesel exceed 35,000 kJ/kg (35 MJ/kg), the minimum heat of combustion value prescribed in the European standard EN 14213 [265] when using biodiesel for heating purposes. Heat of combustion of a compound generally increases with chain length and increasing saturation. Some experimental [266] and calculated [243] values for heat of combustion are given in Table 7. For comparison purposes, an experimental value for the heat of combustion of hexadecane is 47,180 kJ/kg [266]. Thus, the lower heat of combustion

Table 7

Heat of combustion. Experimental data from Ref. [266] and calculated data from Ref. [243].

Saturated fatty acid methyl esters		Unsaturated fatty acid methyl esters	
Fatty acid methyl ester	Heat of combustion [kJ/kg]	Fatty acid methyl ester	Heat of combustion [kJ/kg]
8:0	34840 [266], 34907 [243]	16:1 Δ9c	39293 [243]
10:0	36590 [266], 36674 [243]	18:1 Δ9c	39930 [266], 40092 [243]
12:0	37910 [266], 37968 [243]	18:2 Δ9c, Δ12c	39650 [266], 39698 [243]
16:0	39630 [266], 39449 [243]	18:3 Δ9c, Δ12c, Δ15c	39342 [243]
18:0	40060 [266], 40099 [243]		

of biodiesel compared to petrodiesel causes slightly elevated fuel consumption which is partially compensated by the higher density of biodiesel, leading to a minor decrease when in terms of volume for commercial applications. It may be noted that heat of combustion is not included in the biodiesel standards ASTM D6751 and EN 14214.

2.5.3. Cold flow

Poor low-temperature flow properties are a major problem associated with the use of biodiesel and affect biodiesel both in its neat form and in blends with petrodiesel. Major operability problems are caused by solids and crystals rapidly growing and agglomerating, plugging fuel lines and filters. This issue is documented by many biodiesel fuels exhibiting a relatively high cloud point (CP; ASTM D2500 [267]) and pour point (PP; ASTM D97 [268]). For example, the CP of methyl soyate was given as 0 °C [82] and that of palm oil methyl esters, which contain high amounts of saturated fatty acids, as 16 °C [269]. The CP usually occurs at a higher temperature than the PP. The CP is the temperature at which a fatty material becomes cloudy due to the formation of crystals and solidification of saturates. When the temperature decreases further, even more solids form and the material approaches the PP, the lowest temperature at which it will still flow. Saturated fatty compounds have significantly higher melting points than unsaturated fatty compounds (Table 8; for a compilation of melting points of fatty acid

Table 8

Melting points of fatty acid methyl esters. Most data from Ref. [270] unless indicated otherwise.

Saturated fatty acid methyl esters		Unsaturated fatty acid methyl esters	
Fatty acid methyl ester	Melting point (°C)	Fatty acid methyl ester	Melting point (°C)
8:0	−37.4	16:1 Δ9c	−34.1
10:0	−13.5	18:1 Δ6c	−1.0
12:0	4.3	18:1 Δ9c	−20.2
14:0	18.1	18:1 Δ9t	9.9
16:0	38.5	18:1 Δ11c	−24.3
18:0	37.7	18:2 Δ9c, Δ12c	−43.1
20:0	46.4	18:3 Δ9c, Δ12c, Δ15c	< −50
22:0	53.3	20:1 Δ11c	−7.8
24:0	58.6	22:1 Δ13c	−3.0
Methyl dihydrosterculate	−4.4 ^a	18:1 Δ9c 12-OH	−5.85
Iso-stearate (16-methyl-heptadecanoate)	26.8		
Methyl vernolate	0.5 ^b		

^a From Ref. [124]. Methyl dihydrosterculate = C₂₀H₃₆O₂, methyl 9,10-methylene octadecanoate.

^b Determined in the course of this work by DSC analogous to Ref. [270]. Methyl vernolate = C₁₉H₃₄O₃, methyl 12,13-epoxy octadecanoate.

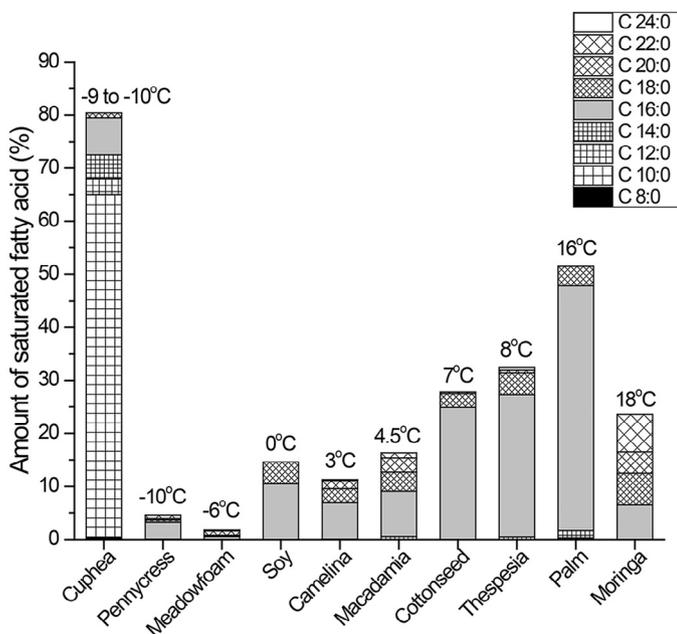


Fig. 3. Effect of amounts of selected individual saturated fatty acid methyl esters on the cloud point of biodiesel from left to right in order of increasing cloud point (inscribed). The effect of even minor amounts of high-melting FAMEs with ≥ 20 carbon atoms in the fatty acid chain is obvious.

esters, see also [270]), and therefore in a mixture they crystallize at higher temperature than their unsaturated counterparts. The CP depends on the nature and amounts of the saturated fatty compounds [271]. Thus, biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds will display higher CPs and PPs. Generally, the CP is more critical than the PP for improving low-temperature flow properties [272]. In Fig. 3, CP point data are compiled for the methyl esters of various oils which show the dependence of the cloud point or, more generally speaking, cold flow properties on the nature and amount of saturated fatty acid methyl esters.

Besides CP and PP, two other test methods for assessing the cold flow properties of petrodiesel are the low-temperature flow test (LTFT; used in North America; ASTM D4539 [273]) and cold filter plugging point (CFPP; used outside North America; see the European standard EN 116 [274]). Biodiesel and its blends with petrodiesel have been evaluated by these methods. Such low-temperature filterability tests have been stated to correlate better with operability tests than CP or PP [275]. For fuel formulations containing at least 10 vol.-% methyl esters, however, LTFT and CFPP are linear functions of CP [276]. More recently, the cold soak filterability test (CSFT; ASTM D7501 [277]) was developed which determines the filtration time through a specific filter of biodiesel stored at 4.5 °C and then warmed to 25 °C. An overview of these and other test methods is available in the literature [278].

Approaches investigated for improving the low-temperature problems of the mixtures of fatty acid methyl esters that are biodiesel include blending with petrodiesel, winterization, additives, esters with branching in the alcohol moiety or fatty acid chain, and bulky substituents in the chain. Blending of esters with petrodiesel is not discussed here.

Numerous additives, usually of polymeric nature, have been reported, mainly in patent literature, to lower PP or sometimes even CP. A brief overview of such additives has been provided in the literature [279]. Relatedly, the use of fatty compound-derived materials with bulky moieties in the chain at additive levels was investigated [280,281]. The background of this approach is that the bulky

moieties in these additives would destroy the harmony of the crystallizing solids. The effect of some additives appears to be limited, however, because they more strongly affect the PP than the CP or they had only a slight influence on CP.

The use of branched esters such as *iso*-propyl, *iso*-butyl and 2-butyl instead of methyl esters [195,282], based on their lower melting points compared to methyl esters (Table 8), is another approach for improving the low-temperature properties of biodiesel. Branched esters exhibit a lower T_{CO} (crystallization onset temperature) as determined by differential scanning calorimetry (DSC) for the isopropyl esters of SBO by 7–11 °C and for the 2-butyl esters of SBO by 12–14 °C [282]. CP and PP are also lowered by branched esters. The CP of *iso*-propyl soyate was given as –9 °C and that of 2-butyl soyate as –12 °C [195], comparing favorably with the CP of methyl soyate mentioned above. Only *iso*-propyl esters appear attractive as branched-chain esters under economic aspects, although they are even more expensive than methyl esters. Branching in the alcohol moiety of the ester functionality does not negatively affect the CNs of these compounds as discussed above. The approach of using esters other than methyl is of interest for “designer” biodiesel, i.e., optimizing the composition of biodiesel to improve properties, as discussed in the corresponding section below. A variation of this approach is the use of esters with branching in the fatty acid chain, for example methyl *iso*-oleate and methyl *iso*-stearate isomers, which improved the CP and PP of biodiesel fuels significantly at higher concentrations [283]. The effect of branching in the fatty acid chain is shown by the significantly lower melting point (>10 °C difference) of methyl *iso*-stearate compared to methyl stearate (Table 8).

Winterization [284,285] is based on the lower melting points of unsaturated fatty compounds vs. saturated compounds. This method removes by filtration solids, mainly saturated esters, formed during cooling of the plant oil esters, leaving a mixture enriched in unsaturated fatty esters and thus lower CP and PP. Repetition of this procedure further reduces CP and PP. Since saturated fatty acid alkyl esters also have higher CNs than their unsaturated counterparts as discussed above, winterization simultaneously decreases the CN of biodiesel while improving low-temperature properties. The removal of the saturated species also caused loss of unsaturated esters occluded in the solid material. Less material is lost when winterization is conducted in the presence of cold flow improvers or solvents such as hexane and *iso*-propanol [285].

Besides the saturated esters, minor constituents of biodiesel can also cause significant cold flow problems [286–292]. These minor components (may) have greater influence on cold flow of biodiesel than their amounts indicate. Among the most problematic species are monoacylglycerols (MAG), especially those of saturated fatty acids, formed as intermediates in the transesterification reaction, and steryl glucosides. This also affects low-level blends of biodiesel with petrodiesel with an increase of 0.01 wt.% saturated MAG in a biodiesel blend increasing CP by as much as 4 °C [292]. The high melting points of saturated monoacylglycerols (melting points of monopalmitin and monostearin >70 °C), which can precipitate in biodiesel in different crystal forms with different solubility [290], and free steryl glucosides (m.p. >240 °C) cause these materials to crystallize from biodiesel more readily under common storage conditions [287,289]. Steryl glucosides occur naturally in acylated form in plant oils and consist of a sterol and a carbohydrate (glucose) moiety [287,289]. The acylated form in which they occur naturally can be changed to the less-soluble free form during biodiesel production by the transesterification reaction.

Algae-derived biodiesel fuels, besides their often elevated content of high-melting saturated esters, may contain other components affecting cold flow as was shown for a biodiesel fuel derived from *Ischrysis* [293]. These materials are long-chain alkenones (usually C_{37} and C_{38}) with a keto group located at one end of the molecule and unsaturation at different positions in the chain and whose

melting point is around 70 °C. Removal of these alkenones improves the cold flow properties, although oxidative stability remains an issue due to the high content of polyunsaturated fatty esters [293].

2.5.4. Oxidative stability

Besides cold flow, oxidative stability of biodiesel is a subject of considerable interest research as it is also one of the major technical issues facing biodiesel. Some review articles on various aspects of biodiesel oxidative and storage stability are [294–297]. The issue of oxidation affects biodiesel primarily during extended storage.

Besides oxidation, it should be noted that other stability-related issues regarding biodiesel exist. These issues include stability toward water and microbial growth. For example, the saturation level of moisture in biodiesel is 15–25 times higher than that of petrodiesel in the temperature range of 4–35 °C [298]. This proclivity to take up moisture may promote the hydrolysis of biodiesel to fatty acids, besides the aspect of moisture enhancing oxidation and microbial growth [299,300].

The influence of parameters such as the presence of air, heat, light, traces of metal, antioxidants, and peroxides as well as the nature of the storage container was investigated in the aforementioned studies. Generally, factors such as the presence of air and/or light, elevated temperatures, the presence of metals or exposure to light facilitate oxidation. Studies performed with the automated oil stability index (OSI) method confirmed the catalyzing effect of metals on oxidation, with copper being among the most effective oxidation-promoting metals [301]. The influence of compound structure of the fatty esters, especially unsaturation as discussed below, was even greater [296].

Biodiesel standards call for evaluating oxidative stability with the so-called Rancimat method. During this procedure, air is bubbled through the sample at an elevated temperature (110 °C) and the effluent directed into water, the conductivity of which is continuously measured. The time of the greatest increase in the conductivity of the water is given as the induction time. Originally, the standard EN 14112 [302] using this method was developed for studying neat FAME. A modified version with reduced sample volatility, EN 15751 [303], was more recently developed for investigating blends of biodiesel with petrodiesel. The biodiesel standards ASTM D6751 and EN 14214 call for minimum oxidative stability times (induction times) of 3 h and 8 h, respectively. Numerous other methods such as DSC, but also including wet chemical procedures such as acid value and peroxide value, have been applied in oxidation studies of biodiesel. Despite addressing the issue of oxidation through determination of initial degradation products, the peroxide value, however, is not very suitable assessing the oxidation status of biodiesel. The reason is the formation of secondary oxidation products so that the peroxide value may decrease even in case of progressing oxidative degradation [304]. Another specification in EN 14214 purported to address the oxidation stability issue is the iodine value (IV), which is a measure of total unsaturation of a sample. The IV, however, is not suitable for this purpose because it is too unspecific as, for example, an infinite number of fatty acid profiles yield the same IV [305].

The presence of double bonds in the chains of many fatty compounds is the reason for their autooxidation. The autooxidation of unsaturated fatty compounds proceeds with different rates depending on the number and position of double bonds [306]. The positions allylic to double bonds are especially susceptible to oxidation. The *bis*-allylic positions in common polyunsaturated fatty acids such as linoleic acid (double bonds at C-9 and C-12, thus one *bis*-allylic position at C-11) and linolenic acid (double bonds at C-9, C-12, and C-15, thus two *bis*-allylic positions at C-11 and C-14) are even more prone to autooxidation than allylic positions. Relative rates of oxidation given in the literature [306] are 1 for oleates (methyl, ethyl esters), 41 for linoleates, and 98 for linolenates. This is essential

because most biodiesel fuels from plant oils contain significant amounts of esters of oleic, linoleic, or linolenic acids, which influence the oxidative stability of the fuels. Many algal oils contain even more highly unsaturated fatty acids with four, five or even six double bonds, usually of C20 and C22 chain lengths. These materials cause biodiesel from algal oils to be very susceptible to oxidation.

Oxidation is a very complex process causing the fuel to eventually deteriorate. The oxidation process begins with the formation of hydroperoxides with subsequent secondary reactions leading to a variety of products, including aldehydes, carboxylic acids, hydrocarbons, ketones, polymers and others [306], the discussion of which is beyond the scope of this article. It may be noted that other stability issues such as hydrolytic stability may affect the other major functional group in fatty acid alkyl esters, namely the ester moiety, through saponification.

Oxidation stability (induction times) determined for neat fatty acid esters using the Rancimat method is given in Table 9. As the data show, no neat unsaturated fatty acid methyl ester exhibits an induction time >3 h, which is the minimum specification in the ASTM biodiesel standard. This observation indicates that antioxidant additives are almost always necessary to attain the minimum oxidative stability specifications in biodiesel standards. Another issue in this respect is that, similar to the issue of cold flow, the presence of minor amounts of unsaturated fatty acid chains may have a greater influence on oxidative stability than their amounts indicate. Also, vegetable oils have naturally occurring tocopherols and their presence (or absence) may have a significant effect on the oxidation stability of biodiesel [307].

2.5.5. Lubricity

The issue of diesel fuel lubricity attained increasing significance with the advent of low-sulfur petrodiesel. The background is that hydrodesulfurization of petrodiesel reduces or eliminates the inherent lubricity of this fuel [308–311], which is essential for proper functioning of vital engine components such as fuel pumps and injectors. Hydrodesulfurization reduces not only the sulfur content of diesel fuel but also removes oxygen- and nitrogen-containing compounds which were responsible for its inherent lubricity [311,312]. The effect of heteroatoms on lubricity was confirmed by an investigation of neat C₃ compounds with OH, NH₂, and SH groups leading to the sequence of lubricity improvement OH > NH₂ > SH [313].

The commonly applied procedure for lubricity testing of petrodiesel and biodiesel is the high-frequency reciprocating rig (HFRR) in which a vibrator arm holding a steel ball slides back and forth over a steel disk immersed in the sample to be tested as described in standards such as ASTM D6079 [314] or ISO 12156 [315]. During this test, wear scars are generated on both the steel ball and disk. The dimensions of the wear scars are proportional to the lubricating properties of the sample, with smaller wear scars indicating better lubricating properties. The wear scar on the ball is used for assessing the lubricating properties of the sample. The wear scar on the disk is also suitable, however, with the advantages of easier handling of the disk and a more recognizable wear scar [316].

Table 9

Oxidative stability (induction times) of unsaturated fatty acid methyl esters [229,243]. Induction times of saturated fatty acid methyl esters are all >24 h [243].

Fatty acid methyl ester	Oxidative stability (h)
16:1 Δ9c	2.11
18:1 Δ9c	2.79
18:2 Δ9c, Δ12c	0.94
18:3 Δ9c, Δ12c, Δ15c	0
20:4 Δ5c, Δ8c, Δ11c, Δ14c	0.09
22:6 Δ4c, Δ7c, Δ10c, Δ13c, Δ16c, Δ19c	0.07
18:1 Δ9c 12-OH	0.67

Lubricity has not been included in biodiesel standards despite the favorable behavior of biodiesel vs. petrodiesel with respect to this fuel property. Thus the maximum wear scars prescribed in petrodiesel standards are used as guidelines for lubricity imparted by biodiesel. These maximum wear scars are 520 μm in the American petrodiesel standard ASTM D975 [17] and 460 μm in the European petrodiesel standard EN 590 [233]. The maximum values are averages of the major and minor axes of the wear scar on the ball assessed using a metallurgical microscope.

Numerous studies on the lubricity of biodiesel or fatty compounds have shown the beneficial effect of these materials on the lubricity of petrodiesel, particularly low-sulfur petrodiesel fuel with poor lubricity. An advantage of biodiesel compared to lubricity-enhancing additives is that biodiesel inherently possesses fuel properties competitive and compatible with petrodiesel, which those additives usually do not possess. Thus, adding biodiesel at low levels (1–2%) restores the lubricity to low-sulfur petrodiesel. On the other hand, neat free fatty acids, monoacylglycerols, and glycerol possess better lubricity than neat esters [313,317] because of their free OH groups as OH groups also enhance lubricity in fatty acid chains [313,318], with lubricity also improving slightly with chain length and the presence of double bonds. Overall, an order of oxygenated moieties enhancing lubricity ($\text{COOH} > \text{CHO} > \text{OH} > \text{COOCH}_3 > \text{C}=\text{O} > \text{C}-\text{O}-\text{C}$) was obtained from studying various oxygenated C_{10} compounds [313]. This sequence resembles those established for other physical properties such as melting point, boiling point, viscosity, etc.

Adding commercial biodiesel at low levels improves the lubricity of low-sulfur petrodiesel more than the addition of neat fatty esters. This indicates that biodiesel components other than methyl esters are largely responsible for improving the lubricity of low-level blends of biodiesel in petrodiesel. Thus, some materials, namely free fatty acids and monoacylglycerols, usually considered undesirable constituents because of their impairment of low-temperature or other properties of biodiesel, are largely responsible for the lubricity of low-level blends of biodiesel in (ultra-)low-sulfur petrodiesel [313]. Table 10 contains some results on the lubricity of biodiesel with the aforementioned HFRR test, underscoring the effects discussed here. Thus, commercial biodiesel is required at a level of 1–2% in low-lubricity petrodiesel, which exceeds the typical additive level, to attain the lubricity-imparting additive level of biodiesel contaminants in petrodiesel.

The above results are underscored by other studies [319,320] discussing the lubricity-enhancing effects of minor components of biodiesel. While all studies agree on the effect of the minor components, the order of reported effectiveness varies from study to study. It was stated [317] that methyl esters and monoacylglycerols mainly affect lubricity while free fatty acids and diacylglycerols have less effect. On the other hand, a sequence of lubricity enhancement $\text{FFA} > \text{soy biodiesel} > \text{phospholipids} > \text{antioxidant} > \text{glycerol} > \text{distilled soy biodiesel} > \text{individual FAME}$ was established [320], although it is not clear why glycerol should enhance lubricity more than individual fatty acid methyl esters because of the poor solubility of glycerol in petrodiesel [313]. Also, phospholipids are generally not observed as biodiesel components. Furthermore, moisture in biodiesel negatively affects its lubricity [321], an issue related to the increased tendency of biodiesel to take up water as discussed above. Therefore, care needs to be taken to avoid this issue.

Thus, although in contrast to oxidative stability and cold flow lubricity is not a problematic issue with biodiesel, it resembles those issues in the aspect of minor components having more influence than their minor amounts indicate.

2.5.6. Density

Density is only specified in EN 14214 with a range of 860–900 kg/m^3 . While density affects combustion, the major reason for

Table 10
Lubricity (HFRR) of fatty acid methyl esters. Data from Ref. [313].

Saturated fatty acid methyl esters		Unsaturated fatty acid methyl esters	
Neat fatty acid methyl ester	HFRR wear scar (60 °C; μm)	Comparison materials	HFRR wear scar (60 °C; μm)
12:0	416, 408	ULSD (ultra low sulfur diesel fuel)	651, 623
16:0	357, 362	Commercial biodiesel	129, 134
18:0	322, 277	Prepared mixtures in ULSD	
18:1 $\Delta 9c$	290, 342	1% Biodiesel	292, 292
18:2 $\Delta 9c, \Delta 12c$	236, 219	2% Biodiesel	281, 258
18:3 $\Delta 9c, \Delta 12c, \Delta 15c$	183, 185	1% Methyl oleate	597, 515
18:1 $\Delta 9c$ 12-OH	191, 174	2% Methyl oleate	384, 368
Other fatty compounds		5% Methyl oleate	365, 359
Monolein	139, 123	10% Methyl oleate	289, 298
Di olein	186, 183	1% Methyl linoleate	579, 574
Tri olein	143, 154	0.01% Oleic acid	234, 233
Oleic acid	0, 0	1% Oleic acid	178, 188
Linoleic acid	0, 0	1% Monolein	134, 161
Glycerol	88, 83	1% Di olein	237, 251
		1% Tri olein	385, 370
		1% Glycerol	641, 649
		1% Methyl oleate w. 1% oleic acid ^a	356, 344
		2% Methyl oleate w. 1% oleic acid ^a	273, 236
		1% Methyl oleate w. 1% monoolein ^a	335, 303
		1% Methyl oleate w. 1% di olein ^a	533, 485
		1% Methyl oleate w. 1% glycerol ^a	444, 441

^a Samples described in this fashion contain 1% of the second-named material in the first-named material. This mixture was then added to the petrodiesel fuel. Thus, the second- and third-named materials are present at 0.01% (100 ppm) levels in the petrodiesel fuel.

the existence of this specification is likely to have another factor distinguishing biodiesel from the parent oil and to exclude some biodiesel fuels containing significant amounts of polyunsaturated fatty esters.

Density increases with increasing unsaturation and content of heavier atoms. Density values of some neat fatty acid alkyl esters are given in Table 11. Similar to CN and viscosity it is possible to calculate the density of mixtures of fatty acid methyl esters (biodiesel) itself using the equation

$$\rho_{\text{mix}} = \sum A_c \times \rho_c \quad (6)$$

Table 11
Density (15 °C) of fatty acid methyl esters. Data from Ref. [322].

Saturated fatty acid methyl esters		Unsaturated fatty acid methyl esters	
Fatty acid methyl ester	Density (g/cm^3)	Fatty acid methyl ester	Density (g/cm^3)
8:0	0.8802	16:1 $\Delta 9c$	0.8810
10:0	0.8764	18:1 $\Delta 9c$	0.8775
12:0	0.8730	18:1 $\Delta 9t$	0.8748
14:0	ND ^a	18:2 $\Delta 9c, \Delta 12c$	0.8902
16:0	ND ^a	18:3 $\Delta 9c, \Delta 12c, \Delta 15c$	0.9017
18:0	ND ^a	20:1 $\Delta 11c$	0.8766
		20:4 $\Delta 5c, \Delta 8c, \Delta 11c, \Delta 14c$	0.9064
		22:1 $\Delta 13c$	0.8744
		22:6 $\Delta 4c, \Delta 7c, \Delta 10c, \Delta 13c, \Delta 16c, \Delta 19c$	0.9236
		18:1 $\Delta 9c$ 12-OH	0.9295

^a Melting point >15 °C.

Table 12
Properties of some biodiesel fuels.

Methyl esters	Major fatty acids (%)	Kinematic viscosity (40 °C; mm ² /s)	Cetane number	Oxidation stability (110 °C; h)	Cloud point (°C)	Density (15 °C; kg/m ³)	Reference
Camelina	C16:0 – 6.8 C18:0 – 2.7 C18:1 Δ9c – 18.6 C18:2 Δ9c,12c – 19.6 C18:3 Δ9c,12c,15c – 32.6 C20:0 – 1.5 C20:1 Δ11c – 12.4 C22:1 Δ13c – 2.3	4.15	52.8	2.5	3	ND	[150]
Castor	C16:0 – 1.0 C18:0 – 1.8 C18:1 Δ9c – 3.6 C18:2 Δ9c,12c – 5.4 C18:1 Δ9c, 12-OH – 85.5	14.82	37.5	5.87		92.770	[117]
Cuphea	C10:0 – 64.7 C12:0 – 3.0 C14:0 – 4.5 C18:1 Δ9c – 12.2 C18:2 Δ9c,12c – 6.7	2.38, 2.40 ^a	56.1, 55.1	3.09, 3.57	–9.1, –10.1	ND	[102]
Palm	C16:0 – 40–46% C18:0 – 3–5% C18:1 Δ9c – 35–40% C18:2 Δ9c,12c – 10–12% C18:3 Δ9c,12c,15c – 0–1%				16	864.42 (25 °C)	[309]
Pennycress	C18:1 Δ9c – 11.1 C18:2 Δ9c,12c – 22.4 C18:3 Δ9c,12c,15c – 11.8 C20:1 Δ11c – 8.6 C22:1 Δ13c – 32.8 C24:1 Δ15c – 2.9	5.24	59.8	4.4	–10	ND	[105]
Rapeseed (canola)	C16:0 – C18:0 – C18:1 Δ9c – C18:2 Δ9c,12c – C18:3 Δ9c,12c,15c – C20:0 – 0.7 C22:0 – 0.3	4.42	50–55		–2		[150]
Soy	C16:0 – 9–12 C18:0 – 3–5 C18:1 Δ9c – 20–25 C18:2 Δ9c,12c – 48–55 C18:3 Δ9c,12c,15c – 6–9	3.95–4.1	48–51		0		[150]
Tallow	C16:0 – C18:0 – C18:1 Δ9c – C18:2 Δ9c,12c – C18:3 Δ9c,12c,15c –				17		[195]
From algae <i>Isochrysis</i> sp.	C14:0 – 11.3–16.7 C16:0 – 9.4–12.9 C16:1 Δ9c – 5.3–6.9 C18:1 Δ9c – 10.5–11.8 C18:2 Δ9c,12c – 6.4–8.0 C18:3 Δ9c,12c,15c – 5.2–8.0 C18:4 – 18.2–22.2 C20:5 – 0.8–2.9 C22:6 – 7.9–11.65	2.46	36.5	0.06	ND	934.92	[293]

^a Duplicate determination.

in which ρ_{mix} is the density of the biodiesel sample (mixture of fatty acid alkyl esters) and ρ_c is the density of the individual compounds in the mixture [322] and, again, A_c = the relative amount (vol.-%). Overall, density is of less operational significance for biodiesel than other properties.

2.5.7. Fuel properties of some biodiesel fuels: “Designer” biodiesel, feedstock optimization and fuel property improvement

The various fuel properties (except solvent properties, of course) discussed above largely for individual fatty acid methyl esters can be applied to assess the properties of the mixtures that comprise biodiesel from different feedstocks and to formulate what can be

termed “designer” biodiesel, i.e., a fuel with optimized fatty acid composition. Table 12 lists the fatty acid profiles and properties of some selected biodiesel fuels. The biodiesel fuels listed there are derived from a variety of feedstocks, including plant oils with differing fatty acid profiles and also algae. Note that the fatty acid profiles of algae usually contain elevated amounts of myristic and palmitic acids, leading to problematic cold flow properties, as well as elevated amounts of highly polyunsaturated fatty acids, leading to reduced oxidative stability.

A review of data in Table 12 underscores the effect of the individual fatty acid methyl esters on the overall properties of biodiesel fuels from different feedstocks. These effects include, as discussed

above, the presence of high-melting saturated FAMES increasing cloud point and polyunsaturated FAMES decreasing oxidative stability.

Beyond the above evaluations, the information on properties of individual fatty acid alkyl esters can be used to formulate what can be termed “designer” biodiesel, i.e., a fuel with optimized fatty acid composition [243,323]. Five approaches exist for improving overall biodiesel fuel properties [323]. These approaches are (a) the use of additives, (b) the use of esters other than methyl, and changing the fatty acid profile by (c) either physical procedures, (d) genetic modification, or (e) utilizing feedstocks with inherently different fatty acid profiles. Regarding approach (b), the properties of esters other than methyl are given in Table 13. The data in Table 13 show that the major advantage is the reduced melting point of these esters (also see discussion above on cold flow properties) compared to methyl esters while the other properties remain similar or, at least, within biodiesel standard specifications. An approach based on blending of feedstocks and neat methyl esters to achieve a desired fatty acid profiles has been discussed taking into account the fuel properties [324] as well as economic and political considerations [325]. Engine tests have been conducted to test the concept of improving fuel performance through blending [326,327]. Some properties improved and some showed negative effects which suggests that the overall “desirability” of a fuel may indeed need to be determined by assigning weights to different aspects of performance, economic and social impact. Algae can be modified to increase lipid production [328,329] and the fatty acid profile of algae can apparently be tailored depending on various parameters employed for their cultivation. Microbiological approaches to biodiesel fuels with modified fatty ester profiles have been reported that do not use classical lipid feedstocks, using carbohydrates instead [330–334].

Relating to the approaches (d) and (e), oleic acid enrichment with linoleic acid as the secondary fatty acid was suggested with the additional aspect that such a fatty acid composition has useful organoleptic properties [335]. An overall evaluation of the properties suggests that, when using methyl esters, methyl palmitoleate or methyl decanoate would be compounds to target for enrichment in biodiesel [243]. Accordingly, an oil moderately enriched in palmitoleic acid, macadamia nut oil, was investigated for its fuel properties but the moderate level of palmitoleic acid and the presence of some high-melting C20 and C22 esters led to properties typical for biodiesel from other oils [336]. Biodiesel derived from a variety of cuphea oil highly enriched in decanoic acid (approximately 65%) possesses improved properties including a low CP of -9 to -10 °C [102], besides showing a distillation curve resembling more closely that of petrodiesel than that of biodiesel derived from vegetable oils [337,338]. The genetic engineering of crops to enrich medium-chain fatty acids such as decanoic acid in oils has been discussed [339]. Additionally, biodiesel from field pennycress oil with a fatty acid profile consisting mainly of erucic acid and C18:1 unsaturated fatty acids also exhibited a lower CP of -10 °C [105].

2.5.8. Solvent properties of fatty acid alkyl esters

Besides application as fuel, solvent use is probably the most common use of biodiesel (fatty acid alkyl esters). As indicated above, early documentation of this was the utilization of biodiesel as agent for shoreline remediation after petroleum spills [27,28]. Biodiesel is sold as solvent as it has been employed for various cleaning and degreasing purposes [340]. The solvent use of fatty acid alkyl esters also takes advantage of the high flash point of biodiesel and its low levels of volatile organic compounds (VOC). Other applications of biodiesel in the area of solvents include use as a polymerization solvent [341,342] and as alternative for organic solvents in liquid–liquid extraction [343,344] but a detailed discussion of these is beyond the scope of this article. While the use of biodiesel as solvent

Table 13
Properties of fatty acid alkyl esters other than methyl.

Fatty acid ester ^a	m.p. ^b (°C)	Oxidative stability ^c (h)	Cetane no. ^d	Kinematic viscosity ^e (40 °C; mm ² /s)
8:0				
Ethyl ester	−44.7	> 24	42.2	
Propyl ester	−45.7			
Butyl ester	−43.3		39.6 (98.7)	
10:0				
Ethyl ester	−20.4	> 24	54.5; 51.2(99.4)	1.87
Propyl ester	−21.8		52.9 (98.0)	2.30
Butyl ester	−23		54.6 (98.6)	2.60
12:0				
Ethyl ester	−1.8			2.63
Propyl ester	−4.35			3.04
Butyl ester	−6.5			3.39
<i>Iso</i> -butyl ester				3.48
14:0				
Ethyl ester	12.5		66.9 (99.3)	3.52
Propyl ester	9.2			4.05
<i>Iso</i> -propyl ester				3.91
Butyl ester	5.6			4.47
<i>Iso</i> -butyl ester				4.65
16:0				
Ethyl ester	23.2		93.1	4.57
Propyl ester	20.3		85.0	5.30
<i>Iso</i> -propyl ester	13–4		82.6	5.20
Butyl ester	16.1		91.9	6.49
2-Butyl ester			84.8	
<i>Iso</i> -butyl ester	22.5,28.9		83.6	6.02
18:0				
Ethyl ester	33.0		76.8; 97.7	5.92
Propyl ester	28.1		69.9; 90.9	6.78
<i>Iso</i> -propyl ester			96.5	
Butyl ester	25.6		80.1; 92.5	7.59
2-Butyl ester			97.5	
<i>Iso</i> -butyl ester			99.3	
16:1 Δ9c				
Ethyl ester	−36.65			
Propyl ester	−52.6			
Butyl ester	−54.1			
18:1 Δ9c				
Ethyl ester	−20.3	2.68	53.9; 67.8	4.78
Propyl ester	−30.5		55.7; 58.8	5.44
<i>Iso</i> -propyl ester			86.6	
Butyl ester	−34.8		59.8; 61.6	5.69
2-Butyl ester			71.9	
<i>Iso</i> -butyl ester			59.6	
18:2 Δ9c, Δ12c				
Ethyl ester	−56.7		37.1; 39.6	4.25
Propyl ester			40.6; 44.0	4.39
Butyl ester	−51.5		41.6; 53.5	4.80
18:3 Δ9c, Δ12c, Δ15c				
Ethyl ester				
Propyl ester	−61.7		26.8	3.42
Butyl ester			28.6	
22:1 Δ13c				
Ethyl ester	−10.5			

^a For definition of fatty acid acronyms, see Table 1.

^b Melting point data from Ref. [270].

^c Oxidative stability data from Ref. [243].

^d Cetane numbers from Refs. [237,240,243]; CN with numbers in parentheses indicates purity (%) of the material used for CN determinations as given in Ref. [240].

^e Kinematic viscosity data from Ref. [227].

may appear somewhat removed from a discussion on fuel (and lubricant) use such as the present one, it may be noted that, according to numerous anecdotal reports, the solvent properties of biodiesel have caused sediments or sludge formed in fuel tanks by petrodiesel to (partially) dissolve and move down the fuel line, causing problems similar to poor cold flow. This issue has not been investigated in the literature so it remains largely anecdotal but appears worthy of study in connection with solvent properties.

Table 14

Solvent-related properties of fatty acid methyl esters. Hansen solubility parameters from Ref. [347] and Kauri-butanol values from Ref. [346].

Compound/material	Hansen solubility parameters ^a			Kauri-butanol value
	δ_D	δ_P	δ_H	
C8:0	15.4	2.7	5.9	122.6
C10:0	15.9	2.4	5.7	96.1
C12:0	16.0	2.1	5.2	77.0
C14:0	16.0	1.9	4.2	63.5
C16:0	16.0	1.6	3.6	nd ^b
C18:0	15.9	1.4	3.2	nd
C18:1 $\Delta 9c$	16.1	1.5	3.5	52.1
C18:2 $\Delta 9c, \Delta 12c$	16.2	1.6	3.9	58.2
C18:3 $\Delta 9c, \Delta 12c, \Delta 15c$	16.2	1.7	4.2	nd
C18:1 $\Delta 9c, 12-OH$	16.4	3.5	9.3	nd
Soybean methyl esters	15.03	3.69	8.92	59.3
Coconut methyl esters	15.12	3.99	9.25	
Palm methyl esters	15.43	5.28	6.61	
Castor methyl esters	16.10	6.72	9.11	
Soybean oil				19.1

^a Hansen solubility parameters are the mean of two approaches described in Ref. [339].

^b Not determined.

The Kauri-butanol (KB) value is a descriptor for solvent strength with a higher KB value indicating stronger solvency. A standard method for determining the KB value is ASTM D1133 [345] in which the sample is “titrated” with KB solution until it becomes turbid. While the KB value of straight-chain hydrocarbons is in the range from approximately 25 to low 30s decreasing with chain length, the KB value of neat fatty acid methyl esters increases from C1 to C4/C5 and then decreases with increasing chain length [346]. The KB values of free fatty acids, octanoic acid and oleic acid were found to be significantly higher [346]. The KB value of soybean methyl esters was determined as 59.6 [346], coinciding with a previous report of around 58 [340]. Vegetable oils, on the other hand, appear to have low KB values, for example, the KB value of neat soybean oil has been given as 19.1 [346]. Some KB values as determined in the literature are given in Table 14.

Hansen solubility parameters (HSPs) [348] are more elaborate and reliable predictors of solubility but a discussion of which is beyond the scope of this article. Briefly, the HSPs are used to predict if one material will dissolve another and form a solution. For the prediction, each material possesses three Hansen parameters and the closer these parameters are for two given materials, the more likely they will form a solution. The three HSP parameters are δ_d (energy from dispersion forces between molecules), δ_p (energy from dipolar intermolecular force between molecules) and δ_h (energy from hydrogen bonds between molecules). HSPs can be applied to neat individual compounds as well as to mixtures and innumerable other materials, including of biological or other nature. The HSPs of methyl soyate [347,349,350] and some other vegetable oil esters as well as individual fatty acid methyl esters [347,349] have been reported. Recent literature data for HSPs of for some vegetable oil esters and individual fatty acid methyl esters [347,350] are also listed in Table 14.

3. Summary

Significant research progress has been made in recent years regarding plant oil alkyl esters, commonly referred to as biodiesel. It has come to be accepted as an environmentally friendly fuel alternative and it is now used in blends with petrodiesel in many countries. Numerous feedstocks have been studied and several have been developed for commercial use. To potentially improve process efficiency, many variations of biodiesel production have been investigated, although the “conventional” process preferably using alkoxide (methoxide) remains well-established. Most fuel properties

have been shown to correlate directly with the fatty acid profile, and thus the source feedstock. With this knowledge, pathways toward improved biodiesel fuel compositions have been elucidated.

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