REVIEW ARTICLE

Impact of various factors on the stability of biodiesel – a review

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Biodiesel is a class of biofuels as an alternative to petroleum diesel (PD). It is gaining importance as it is environment friendly, renewable, and locally available. The main drawback of biodiesel is its poor storage stability comparing to PD. Many factors including feedstock, temperature, contact with oxygen, water, residual catalyst, alcohol due to incomplete transesterification, the fatty acid profile of biodiesel, and contaminants are related to the instability of biodiesel. Instability occurs in the form of oxidation. Along with elevated temperature, biodiesel oxidation reaches its peak. Identification of the insoluble formed in biodiesel is possible by distortion and absorption of ultrasonic waves. The biodiesel oxidation analysis is taken place by using tools such as Fourier Transform Infrared (FTIR) spectroscopy and Nuclear Magnetic Resonance (NMR) method. The fatty acid profile of biodiesel plays a key role in biodiesel stability together with oxygen and temperature.

Keywords: biodiesel stability; oxidation; fatty acid profile; contaminants; temperature; ultrasonic; analytical tools.

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Introduction

Energy is the primary need of a country for its socio-economic growth. Now, fossil fuels are declining at a drastic rate [1]. Biodiesel is a better substitution for petroleum diesel (PD). Biodiesel is a renewable fuel [2]. It is environment friendly and biodegradable. The main drawback of biodiesel is its poor storage stability that is more susceptible to degradation than it of PD and is a crucial factor to commercialize biodiesel [3].

Biodiesel feedstock

Biodiesel is also a part of biofuels. Biodiesel feedstock is categorized into four generations. The 1st generation biodiesels were produced from oil crops. Most of the biodiesel production cost is due to its feedstock cost. About 350 different oil crops that belong to edible and non-edible are available as feedstocks. The common sources of edible crops include peanut, safflower, corn, rice bran, coconut, olive, castor, milkweed seed, linseed, rapeseed, soybean, palm, and sunflower. The non-edible sources include *Jatropha curcas*, *Pongamia glabra*, *Madhuca indica*, *Salvadora oleoides*, cottonseed oil, Tobacco, *Calophyllum Eruca Sativa Gars*, *inophyllum, terebinth*, fish oil, desert date, Jojoba, neem oil, leather pre-fleshings, apricot seed, *Pistacia chinensis* bunge seed, and rubber seed. The 2nd generation feedstocks belong to energy crops, agricultural remains, and wood residual wastage. Common energy crops for this purpose are *Jatropha*, *Aleurites moluccana*,

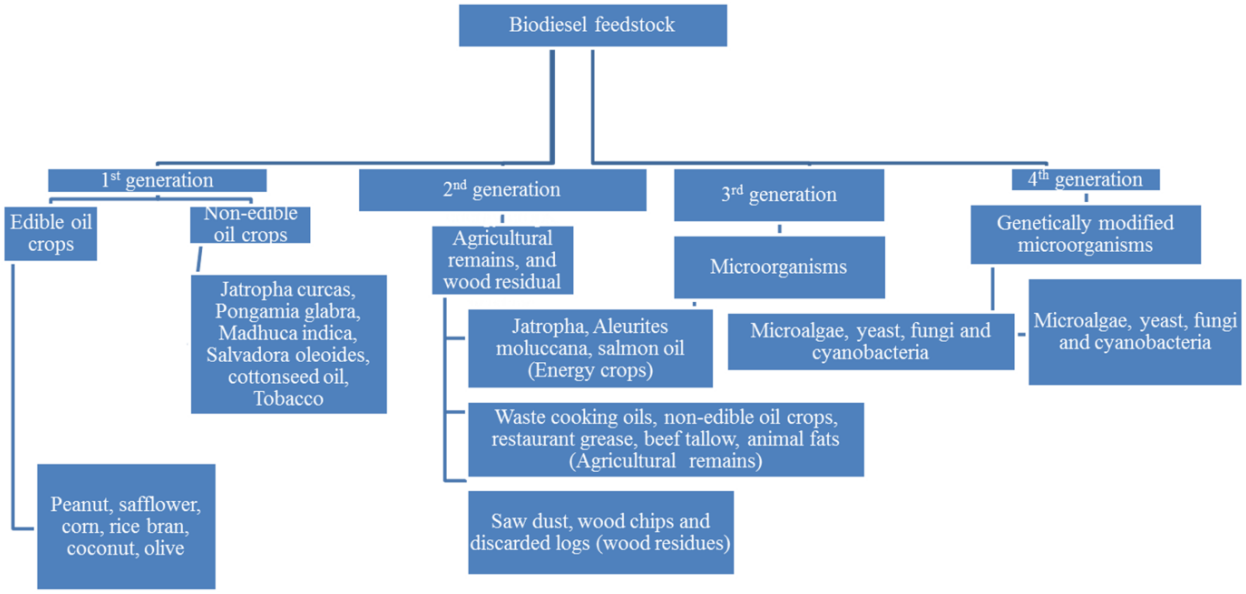

Figure 1. Classification of biodiesel feedstock.

salmon oil, Rubber tree *Madhuca longifolia*, tobacco seed, sea mango, and jojoba oil. In addition, waste cooking oils, non-edible oil crops, restaurant grease, beef tallow, animal fats, and pork lard are also used as biodiesel feedstocks. Wood wastes such as sawdust, wood chips, and discarded logs are also potential feedstocks for biodiesel production [4]. Animal fats are encouraged over 1st generation feedstocks due to properties of higher-octane numbers and non-corrosiveness. The main problem with these feedstocks is the increase in production cost as they have a high fraction of saturated fatty acid methyl esters (FAME) which require a long transesterification process. Another hurdle of this feedstock is poor cold flow properties again because of the high content of saturated FAME. Production of biodiesel from microalgae is considered as the 3rd generation biodiesel. Various other microorganisms are also used for this purpose such as microalgae autotrophs and heterotrophs. Oil yield is different for various microalgae. Some microalgal species possess a high triacylglycerol content of up to 80% of their dry mass. However, there are production difficulties that must get rid of for the commercialization of these species. The 4th generation biodiesel is produced from genetically modified microorganisms such as microalgae, yeast, fungi, and cyanobacteria. The benefits of using microalgae include high growth rate, high oil content, and low structural complexity, which increase their commercial applications [5]. The classification of biodiesel feedstock is shown in Figure 1.

The latest trends of feedstock for biodiesel production have been investigated [6]. To avoid conflict with food in using edible oils as feedstock, the researchers suggested non-edible sources, like animal fat, waste oil, insect oil, or single cell oil. Various feedstocks for biodiesel production were reviewed with a major focus on non-edible plant sources and algal sources [7]. There are 75 different plant sources which have 29% of oil in their seed/kernel. Major European countries use rapeseed oil for biodiesel production. Reports showed that biodiesel produced from palm and *Jatropha* has physical properties in the optimal balance of proper oxidation stability and cold flow properties. Concerning soybean and canola oil as quality-standard, suggested sources are non-edible animal fat-based beef tallow, pork lard and yellow grease, which are cheaper than plant-based feedstock. However, they need more

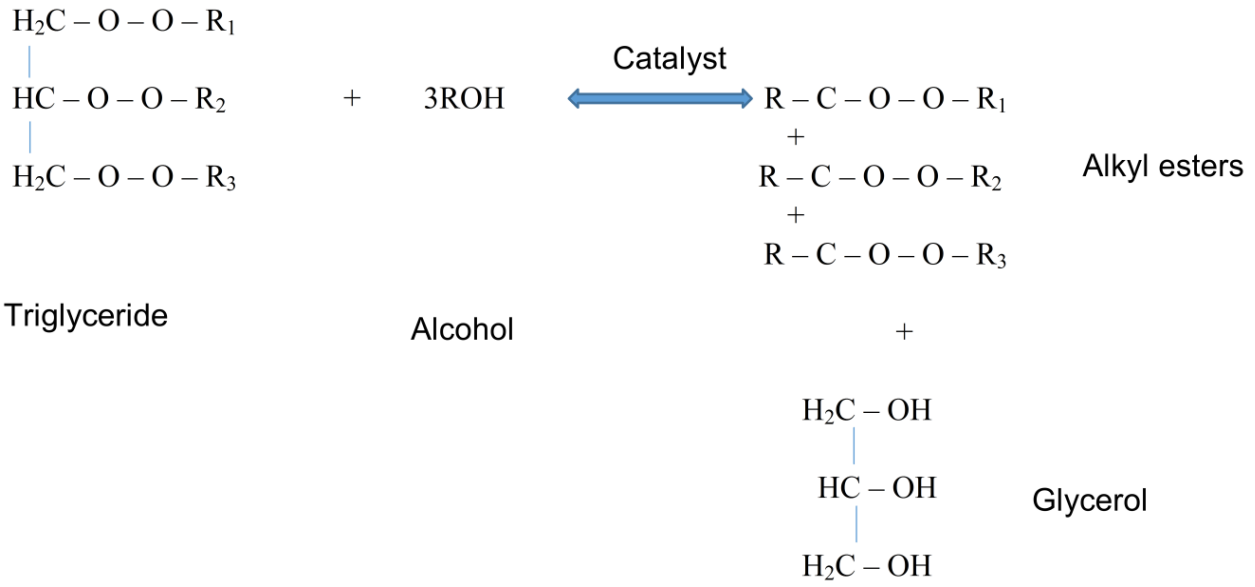

Figure 2. Transesterification reaction for the production of biodiesel.

processing than plant-based feedstocks as they contain saturated fatty acids [8]. As the fatty acid profile of biodiesel is the same as that of feedstock, the choice of the feedstock will be mostly based on that factor only [9].

Biodiesel production

There are 4 major procedures to produce biodiesel. The purpose of these techniques is to reduce the high viscosity. They are direct use and blending, micro emulsification, thermal cracking, and transesterification. The common method used is the transesterification process [10].

Biodiesel is produced from oil or fat by transesterification with methanol. In the process triglycerides present in oil or fat are converted to monoalkyl esters in the presence of a catalyst. Chemically these are fatty acid methyl esters (FAME) [11]. Transesterification intends to decrease the viscosity of oil or fat so that it uses directly in PD engines [12]. The produced esters have fuel properties close to that of PD [13]. Biodiesel is used as a blend part with PD in any percentage [14]. The general transesterification process is as shown in Figure 2. In the transesterification process, short-chain alcohol in the presence of a catalyst [15] will replace the glycerol present in the triglycerides of oil or fat. For obtaining high yields of biodiesel in a short span, the transesterification process accelerates by the ultrasonic irradiation process [16]. There are studies where the transesterification reaction intensifies with the help of ultrasound [17-19]. Biodiesel also produces by the enzyme catalyzed transesterification procedure [20]. There are distinct types of transesterification processes available [21]. They are classified into homogeneous, heterogeneous, enzyme catalysis, and supercritical methanol.

Now, the 4th generation biodiesels gained importance as a biodiesel feedstock because of the light sensitivity and quick growth of the algae. In general, fast growing algae have low oil content and slow growing algae have high oil content. Genetic modification or metabolic engineering are the good alternatives to increase the oil levels in algae [22]. Biodiesel production from algae involves culturing algae, harvesting algae, extraction of oil, purification of oil, and conversion of oil into biodiesel. The synthesis of biodiesel from algal oil is again from transesterification process. Algal oils show

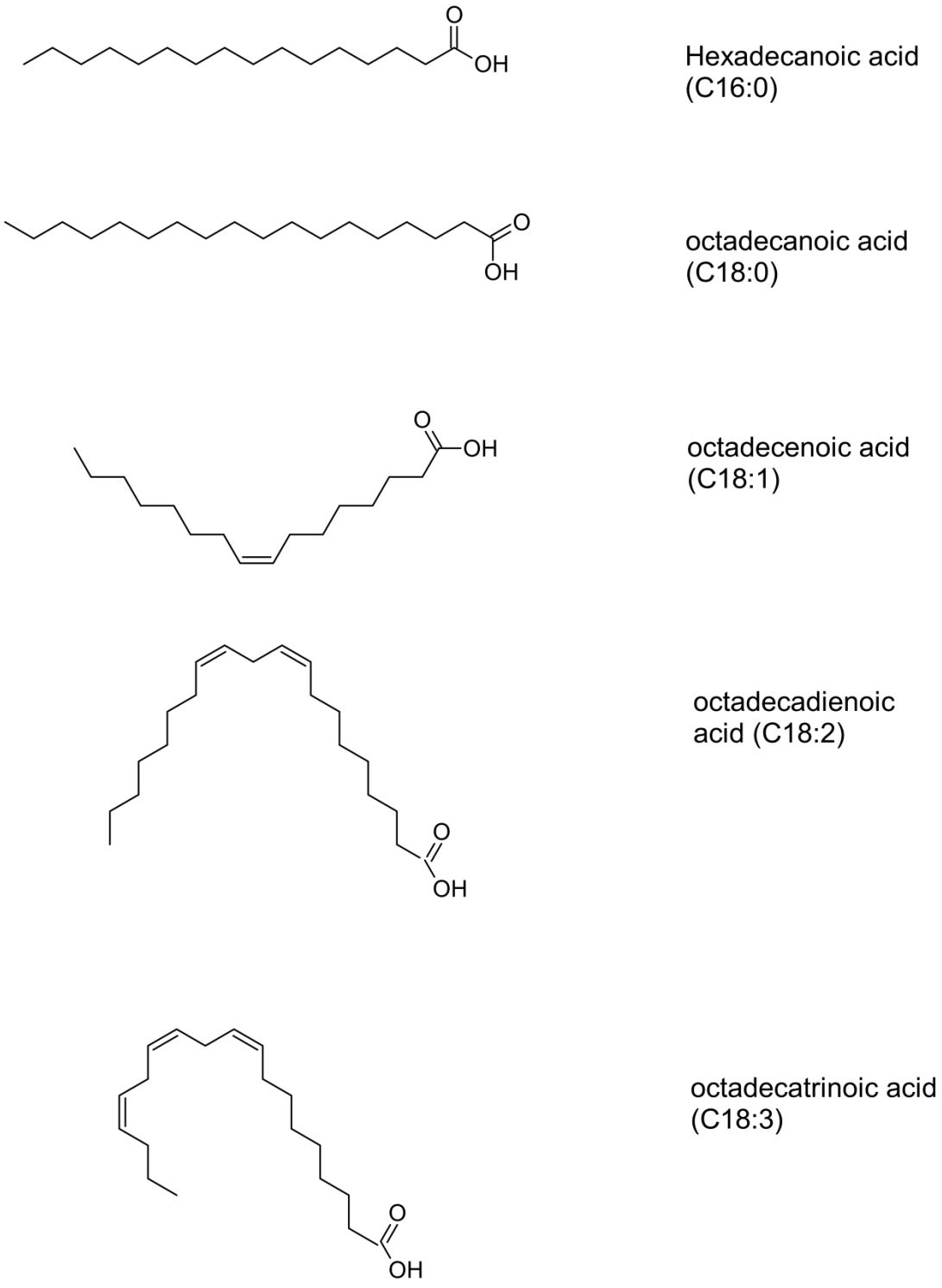

Figure 3. Structure of some common saturated and unsaturated fatty acids.

excellent tendency of converting into biodiesel. In this context, the catalysts used in the process play vital role. Porous catalyst Hβ and mixed oxide of Nickel and Molybdenum give almost 100% yield of biodiesel [23].

Types of FAME present in the biodiesel

Broadly, two types of FAME are present in biodiesel, saturated FAME and unsaturated FAME. Hexadecanoic acid methyl ester (C16:0) and octadecanoic acid methyl ester (C18:0) are examples of saturated FAME and unsaturated FAME, respectively. The unsaturated FAME can be further subclassified into mono and polyunsaturated FAME [24]. The structure of the various fatty acids is shown in Figure 3. The fuel properties of biodiesel not only depend on the type of the FAME but also the structure of the FAME. The physical features that affect the fuel properties are chain length, linearity, branching of the chain, and degree of unsaturation [9].

Alcohols used in biodiesel production

Transesterification reaction performs to produce biodiesel with alcohols such as methanol, ethanol, 2-propanol, and 1-butanol. The results showed that suitable alcohol is methanol. Other alcohols used with an acid catalyst for long–time reactions of around 48 h. Among the used plant oils to produce biodiesel, sunflower oil produced reliable results. Another important factor is the recovery of methanol which is easy when comparing to ethanol as it has low molecular weight, and it is cheaper [25]. When the transesterification of waste oil with high content of free fatty acids was performed with methanol, ethanol, and 1-propanol at the greatest temperature of 100^{o}C, 1-propanol reduced the energy requirement by 36.3% and 34.4 % comparing to methanol and ethanol, respectively [26]. The yield of biodiesel in the transesterification process also depends on the methanol oil molar ratio. A best yield of 98% biodiesel occurred for the 8:1 ratio of methanol palm kernel and coconut oils [27]. It is against to common 6:1 molar ratio [25].

Catalysts used in biodiesel production

Catalysts make the transesterification process complete. In general, either chemical or biological catalysts are used in transesterification reactions. The catalysts used in the transesterification process are classified as homogeneous acid or base catalysts, heterogeneous solid acid or alkali catalysts, heterogeneous nano-catalysts, and supercritical fluids [28]. The regularly using homogeneous catalysts are base catalysts such as NaOH, KOH, CH_3ONa, and CH_3OK. If the oil has free fatty acids (FFA) greater than 1%, product recovery becomes tough in an alkali-catalyzed transesterification reaction. In such cases, first, the oil is treated with acid-based esterification which reduces the FFA content of the oil, and then, the oil allowed for alkali catalysis. The commonly used acid catalysts for esterification and transesterification are sulphuric, phosphoric, hydrochloric, and sulphonic acids [28]. Heterogeneous catalysts have advantages such as reusability, fast reaction rate, easy product and catalyst separation, and low cost. The commonly used heterogeneous catalysts are alkaline metal oxides such as CaO and MgO [29].

Researchers now started investigating the use of metal oxides for solid acid catalyst development. Among these, ferric compounds are more suitable to develop various non-acid solid catalysts such as α-Fe_2O_3, $CaFe_2O_4$–$Ca_2Fe_2O_5$ [30]. Nano-catalysts used recently because they are highly reactive and generate useful product yield [28]. Supercritical fluids are preferred when biodiesel must produce without a catalyst [31]. Diverse types of catalysts used in different transesterification reactions are listed in Table 1. Based on the type of catalyst used, there will be quality production of biodiesel, which affects the stability of the biodiesel [32].

Characteristic properties of biodiesel

The biodiesel and blends are characterized by kinematic viscosity, density, surface tension, flash point, cetane number, cloud point, acid value, iodine value, and peroxide value. The deviation in the measurement of these values as per the global standards of American Society for Testing Materials (ASTM) and European Nation (EN) are referred to as the level of instability of biodiesel [11]. The viscosity of fuel is resistance offered to its flow and is a temperature-dependent parameter. Excess fuel viscosity leads to poor atomization which increases engine

Table 1. Distinct types of catalysts used in the transesterification process for biodiesel production.

S No	Type of transesterification	Catalysts used	Reference
1	Homogeneous	Alkaline catalysts NaOH, CH_3ONa, KOH; acid catalysts H_2SO_4, HCl, H_3PO_4	28, 77, 78
2	Heterogeneous	Alkaline earth metal oxides such as BeO, MgO, CaO, SrO, BaO, and RaO. MgO and SrO	79
		mixed metal oxide catalysts $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, $CaO–CeO_2$	80, 81
3	Heterogeneous nano catalysts	Li-doped CaO nanocatalyst	28
		Nanostructured mixed-metal oxides of CaO–MgO	
		nano-solid base catalyst, $K2O/\gamma–Al_2O_3$	
		solid acid of an aluminum dodecatungstophosphate (Al0.9H0.3PW12O40, AlPW)	
4	Supercritical fluids	supercritical methanol	31
		supercritical methanol in the presence of propane	82, 83
		supercritical methanol in the presence of hexane and supercritical CO_2	84

Table 2. American standard specification (ASTM D6751) for biodiesel [11].

S No	Parameter	Test method	Limitations	Units
1	Flash point	D93	130	°C
2	Kinematic viscosity, 40°C	D445	1.9-6.0	mm^2/s
3	Cetane number	D613	47	min
4	Cloud point	D2500	Report	°C
5	Acid number, max	D664	0.8	mg KOH/g
6	Water and sediment, max	D2709	0.05	% volume
7	Free glycerin, max	ASTM D6584	0.02	% mass
8	Total glycerin, max	ASTM D6584	0.24	% mass
9	Phosphorous content	ASTM D4951	0.001 max	% mass
10	Carbon residue	ASTM D4530	0.050 max	% mass
11	Sulfur	ASTM D5453	0.0015 max (S15), 0.05 max (S500)	% mass (ppm)

deposits, excessive fuel pressure, and incomplete fuel combustion [33]. Density is an important fuel property that influences engine performance. The fuel properties such as cetane number and heating value are directly linked to density. Change in the fuel density affects the mass of the fuel entering engine and this in turn influences engine output power [34]. The surface tension of the fuel is crucial in understanding the spray behavior of the fuel in an engine [28]. Flashpoint (FP) is the minimum temperature at which sufficient vapor of the fuel takes place for the ignition [35]. Cloud point (CP) is the temperature at which fuel starts showing haze that says the formation of crystals. It is a useful parameter in cold countries [36]. Cetane number (CN) is a measure of fuel ignition quality. Shorter is the ignition delay, the time gap between fuel injection and beginning of combustion, better is the fuel ignition quality [37]. Acid value (AV), iodine value (IV), and peroxide value (PV) decide the presence of FFA, the degree of unsaturation, and the level of degradation of biodiesel [38]. Some of the important parameters including kinematic viscosity, FP, CP, AV, CN, water content standard specifications are mentioned in ASTM

Table 3. European biodiesel standard specification (EN14214) [11].

S No	Parameter	Test method	Limitations	Units
1	Flash point, °C, min	ISO/CD 3679	120.0 min	°C
2	Kinematic viscosity, mm^2/s, 40°C	EN ISO 3104	3.5–5.0	mm^2/s
3	Cetane number, min	EN ISO 5165	51 min	min
4	Acid number, mg KOH/g, max	Pr EN 14104	0.5 max	mg KOH/g
5	Water and sediment, % volume, max	EN ISO 12937	500 max	mg/kg
6	density	EN ISO 3675/EN ISO 12185	860–900	kg/m^3
7	Iodine number	Pr EN 14111	120 max	
8	Carbon residue	EN ISO 10370	0.30 max	% (mol/mol)
9	Oxidation stability, 110°C	EN 14112	6.0 min	
10	MAG content	EN 14105	0.80 max	% (mol/mol)
11	DAG content	EN 14105	0.20 max	% (mol/mol)
12	TAG content	EN 14105	0.20 max	% (mol/mol)
13	Free glycerol	EN 14105	0.020 max	% (mol/mol)
14	Methanol content	EN 14110	0.20 max	% (mol/mol)
15	Group I metals (Na, K)	EN 14108, EN 14109	5.0 max	mg/kg
16	Group II metals (Ca, Mg)	EN 14538	5.0 max	mg/kg
17	Phosphorous content	EN 14107	10.0 max	mg/kg
18	Sulfur content	EN ISO 20846, EN ISO 20884	10.0 max	mg/kg

Table 4. American standard specifications for biodiesel blends (ASTM D7467 B6-B20) [11].

S No	Parameter	Test method	Limitations	Units
1	Biodiesel content	D7371	6–20	% volume
2	Acid number, max	D664	0.3	mg KOH/g
3	Kinematic viscosity, 40°C	D445	1.9-4.1a	mm^2/s
4	Flash point	D93	52b	°C
5	Cloud point	D2500, D4539, D6371	only guidance provided	°C
6	Cetane number	D613	40	min
7	Ash content	D482	0.01 max	% mass
8	Water and Sediment, max	D2709	0.05	% volume
9	Sulfur content	D5453, D2622	15 max (S15) 500 max (S500)	ppm

biodiesel standards (ASTM D6751) [11]. Density is not included in ASTM, however, included in the EN standard (EN 14214). Similarly, IV is included in the EN 14214, while not in ASTM D6751 specifications [11]. The ASTM and EN specifications for some key fuel properties of biodiesel are listed in Table 2 and Table 3, while ASTM specifications for biodiesel blends is listed in Table 4.

Storage stability of biodiesel

The stability of the fuel is the resistance of a fuel to degradation process that changes fuel properties and forms undesirable matter. Biodiesel fuel properties deteriorate by oxidation or auto-oxidation due to the contact with oxygen present in the air, thermal-oxidative decomposition due to excess heat, and hydrolysis because of the interaction with water or moisture and microbial contamination that takes place due to the transfer of dust particles or water droplets that have bacteria into water [39]. Storage stability refers to the general stability of the fuel in its long–term storage. Oxidative

degradation is the main important concern of storage stability. Stability is also linked with water contamination and microbial growth. Oxidation stability is the general parameter to stand for storage stability [39]. The poor thermal and oxidative stability of biodiesel leads to gum formation that results in storage problems over an extended period [40]. The oxidation of biodiesel shows a considerable effect on fuel properties such as kinematic viscosity, acid value, and cetane number [41].

Basic oxidation reactions

In contrary to PD components such as paraffin and aromatic hydrocarbons, biodiesel contains unsaturated FAME. The allylic carbons in mono-unsaturated FAME and bis-allylic carbons in poly-unsaturated FAME are more prone to radical attack that leads to the formation of hydroperoxides [42]. For the octadecenoic acid methyl ester (C18:1), octadecadienoic acid methyl ester (C18:2), and octadecatrienoic acid methyl ester (C18:3), the allylic and bis-allylic sites are shown in Figure 4. In the case of the auto-oxidation process, the mono-unsaturated FAMEs are reactive at elevated temperatures and poly-unsaturated FAME are reactive at room temperature [43]. With increasing blend level of biodiesel in PD, the blend leads to instability. The nature of the instability depends on numerous factors such as biodiesel quality, biodiesel type, time of storage, and storage conditions like humidity, temperature, *etc*. [44]. The oxidation of unsaturated FAME is made up of two types of reactions as primary oxidation and secondary oxidation reactions. The primary oxidation reaction is classified into a set of radical reactions as initiation, propagation, and termination as follows:

Initiation

$RH + I \longrightarrow R^{\cdot}$ **(free radical)** + IH (Abstraction of hydrogen)

Propagation

$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot}$ **(peroxy radical)**

$ROO^{\cdot} + ROO^{\cdot} \longrightarrow$ ROOH (Hydrogen peroxide) + $R^{\cdot}$

Termination

$R^{\cdot} + R^{\cdot} \longrightarrow R - R$

$ROO^{\cdot} + ROO^{\cdot} \longrightarrow$ Stable products

In the first step, the removal of hydrogen from the carbon atom takes place to produce a free radical. This can happen either by photo-oxidation or existing peroxide. During the second step, the oxygen present will react with radical to generate peroxyl radical which removes hydrogen from another carbon that produces hydrogen peroxide and carbon-free radical. At the last step, termination, the reaction stops with the combination of two radicals in the form of stable products [45]. The hydrogen peroxides formed are very unstable and can continue in different secondary oxidation reactions that lead to a variety of products. One that kind of reaction is β cleavage. This division leads to the formation of aldehydes and radicals [42]. The other possible products are ketones, alcohols, olefins, and alkanes [13].

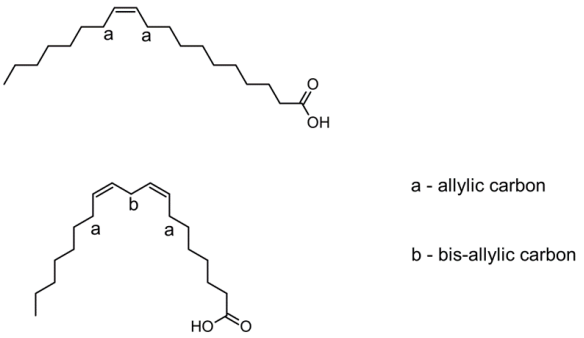

Figure 4. Positions of allylic and bis-allylic carbons.

Effect of fatty acid profile on biodiesel stability

The fatty acid profile of biodiesel is the same as that of feedstock. Most feedstocks contain C16 (hexadecenoic acid) and C18 (octadecanoic acid, 9(Z)-octadecenoic, (9(Z),12(Z)-octadecadienoic and 9(Z),12(Z),15(Z)-octadecatrienoic) fatty acids, except oils such as coconut oil, which contains high amounts of saturated acids in the C12–C16 range and other fatty acids [24]. Further, oxidative stability depends on the degree of unsaturation, location, and number of double bonds present in the fatty acid [46]. The determination of iodine value and peroxide value is a measure of the degree of unsaturation and level of peroxides formed in biodiesel [38]. Most

of the biodiesels were produced from edible feedstocks such as soybean, rapeseed, sunflower, and palm oils. However, extensive use of the edible feedstock may create scarcity for edible oils on the long-term basis. Hence, no-edible sources can be the potential feedstocks such as *Jatropa*, *Karanja*, Mahua, and castor oils for biodiesel production. *Jatropa* oil contains saturated fatty acids (palmitic acid (14.2%) and stearic acid (7%)) and unsaturated fatty acids (oleic acid (44.7%) and linoleic acid (32.8%)). *Karanja* oil contains saturated fatty acids (palmitic acid (10.7%) and stearic acid (7%)) and unsaturated fatty acids (oleic acid (51.8%) and linoleic acid (10.7%)). Mahua oil contains high level of FFA (20%). Therefore, it requires much more refining of oil for the production of biodiesel. The main content of the castor oil is ricinoleic acid (90%) [47].

Effect of free fatty acids on biodiesel stability

The free fatty acids (FFA) present in biodiesel affect the fuel properties such as oxidative stability, kinematic viscosity, flash point, and cold flow properties. The acid value is a measure of it [38]. That is why these are impurities in biodiesel [48]. Unsaturated FFAs are also oxidized on par with FAME. The main challenge with the presence of FFAs is the formation of soap in the transesterification reaction with alkali catalyst that leads to the low speed of reaction and biodiesel yield [49]. The fatty acid profile affects fuel properties such as cloud point [36]. The amount of FFA present in the feedstock depends on the soil and environment of cultivation [50].

Effect of residual catalyst on biodiesel stability

Biodiesel production takes place by transesterification in the presence of alkaline catalysts such as NaOH and KOH. After the reaction, the presence of the residual alkaline metals in biodiesel fuel can cause problems in the fuel injection system components due to the formation of carbon residue, even they promote oxidation [51].

Effect of alcohol on biodiesel stability

The type of alcohol used in the production of biodiesel can affect oxidation stability by changing the molecular weight of the alkyl esters [39]. When pentanol mix with pure biodiesel in the 10% and 15% volume concentrations to B20 blend, the 10% mixture of pentanol increased the oxidative stability of B20 by 44.57% while the 15% mixture decreased the oxidative stability of B20 by 19.48% [52]. The residual alcohol in the biodiesel because of incomplete transesterification affects its flash point (FP). The presence of alcohol decreases the FP and *vice versa* [53]. Hence, the determination of FP is the way to check the presence of residual alcohol.

Effect of temperature on biodiesel stability

The mixed effect of air and temperature has a profound effect on the stability of biodiesel [54]. Due to the accelerated temperature, the density, viscosity, and acid value increase, and the amount of unsaturated FAME decrease [55]. The fuel property, kinematic viscosity (KV), is more affected by temperature than by the presence of oxygen [56].

Effect of contamination on the biodiesel stability

The biodiesel performance depends on the purity of the final product. Impurities may present in biodiesel in the form of contamination as a by-product or coming from any other sources. These impurities affect the stability of biodiesel, which include glycerol, metals, alcohol, FFAs, water, and bacteria [32]. The presence of metals in the biodiesel happens due to corrosion of the container. Metals can catalyze the oxidation and polymerization of hydrocarbons [32]. Some metals are effective in accelerating biodiesel oxidation. It shows that Copper (Cu) metal promotes biodiesel oxidation effectively. The metals Molybdenum (Mo) and Rhenium (Re) have shown a restrictive effect on biodiesel oxidation. The corresponding metal oxides have shown a similar effect [57]. Glycerol affects biodiesel stability effectively. Glycerol can oxidize to form diols or acids that make biodiesel unstable. These degraded by-products may catalyze the polymerization of unsaturated fatty acids [32]. Water content in the feedstock oils

Table 5. FTIR spectral responses by biodiesel functional groups [68].

S No	Wave number (cm^{-1})	Type of vibration	Functional group
1	3,000 – 2,500	Hydrogen bonded O-H stretch	carboxylic acid
2	2,925	C-H asymmetrical stretch	Alkanes
3	2,850	C-H symmetrical stretch	Methelene
4	1,745	C=O stretch	Functional group of FAME
5	1,377 – 1,465	C-H bending and rocking	End methyl group ($-CH_3$)
6	1,300 – 1,500	C=C bending	Aromatics
7	900 – 1,200	C-O stretch	Aromatics
8	860 - 680	C-H bending	Aromatics
9	850	C-H out of plane bending	Alkenes
10	721	CH_2 rocking vibration	Methelene groups in alkenes and aromatics

should be less than 0.06% (wt) to support the quality. The presence of excess water may lead to FAME hydrolysis, oxidative degradation, and rapid growth of microorganisms [58].

Effect of storage time on the stability

The effect of storage time majorly depends on the fatty acid profile of biodiesel. The presence of unsaturated FAME makes the biodiesel deteriorate more with time as they are more prone to oxidation [59]. In the biodiesel blends that are rich in unsaturated FAME, sediment formation takes place while in the biodiesel blends rich in saturated FAME, there is no sediment formation for a storage period of two years [60].

Effect of storage light on the stability

The degradation rate of biodiesel is considerably higher for the biodiesel stored in light than in the dark conditions [61].

Tools for characterization of biodiesel

Various ultrasonic, chromatographic, and spectroscopic tools are available for the characterization of biodiesel. Ultrasonic velocity measurements are useful tools for finding the adiabatic compressibility thereby fuel injection time [62]. Measurement of ultrasonic absorption supplies information related to shear and volume viscosities, even it predicts that ultrasonic absorption in biodiesel depends on the fatty acid profile of biodiesel [63]. Ultrasonic measurements are also helpful in understanding the molecular interactions with which the stability of the biodiesel assessed [60]. The viscosity and related parameters including relaxation time, ultrasonic absorption, change in Gibb's free energy also estimated on the measurement of ultrasonic velocity [64]. With the help of distortions in ultrasonic waves, it is possible to find biodiesel degradation [65].

Chromatographic and spectroscopic methods were used to assess the fatty acid profile of the biodiesel [66]. A small deviation in the fatty acid profile tremendously changes the fuel properties of biodiesel [46]. Chromatographic methods such as Gas Chromatography - Flame Ionization Detector (GC-FID) and Gas Chromatography - Mass Spectrometer (GC-MS) for qualification and quantification of biodiesel composition, High Performance Liquid Chromatography (HPLC) and Liquid Chromatography (LC) for purity check are available [67]. Analytical tools such as Ultraviolet-Visible Spectroscopy (UV-VIS), Fourier Transform Infrared (FTIR), and Nuclear Magnetic Resonance (NMR) are available for the qualification of biodiesel components [66]. FTIR spectroscopic method is also efficiently used to detect biodiesel components on finding OH, C=O, $-CH_3$ functional groups [64]. The wavenumbers of response by various functional groups present in biodiesel are listed in Table 5. Apart from these regular groups, the peaks such as at 3,700 – 4,500 cm^{-1}, 3,550 – 3,200 cm^{-1} and 2,200 – 2,000 cm^{-1} indicate the

Table 6. NMR spectral response of pure biodiesel [75, 85].

S No	Chemical shift (ppm)	Responding protons
1	5.2 – 5.3	-CH=CH- (olefinic protons)
2	3.6 – 3.7	-CO-CH_3 (methyl protons adjacent to carboxyl)
3	2.6 – 2.8	-CH=CH-CH_2-CH=CH- (bis-allylic carbons)
4	2.1 – 2.2	CH_3-O_2C-CH_2-
5	1.9 – 2.0	-CH_2-CH_2-CH=CH- (allylic carbon)
6	1.1 – 1.3	-CH_2- (methylene protons)
7	0.7 – 0.9	-CH_3 (terminal methyl group protons)

presence of amides, phenols, and ketones that form due to the degradation of biodiesel [68]. Based on the UV absorbance, it is possible to find a blend mixture level of biodiesel in petroleum diesel (PD). The UV absorbance decreases as the blend level of biodiesel in PD increases [69]. Biodiesel presence in the PD in the form of adulterants is also identified by UV - VIS method [70]. The oxidative degradation of biodiesel is also estimated with UV - VIS method because the oxidative products with conjugated double bonds can absorb UV - VIS regions [71]. The specialty of the NMR technique is to find vegetable oil components that are not detected by FTIR [72]. NMR method is also useful in finding the molecular structure, moieties of the molecules, and even to evaluate the transesterification process [73]. The blend level of biodiesel in PD was also identified with Time Domain NMR methods [74, 75]. The oxidized biodiesel was also showed by NMR spectroscopy [76]. The typical regions of various proton responses for the normal ^{1}H NMR spectrum of biodiesel are listed in Table 6. This is for the identification of functional groups present and the structure of the molecules present in biodiesel. The oxidation of biodiesel was seen in the NMR spectrum by seeing the decrease in strong single peak for methyl ester moiety which can be due to the formation of FFA [76].

Conclusions

From all the reviews it is worth saying that storage stability is sensitive to the fatty acid profile of biodiesel and contaminants such as metals, water, and glycerol. The nature and number of contaminants depend on the factors such as feedstock, the efficiency of the transesterification process, and the purification of the final product. The presence of unsaturated FAME along with oxygen and elevated temperature will be more effective in disrupting the stability of biodiesel. Distortion of ultrasonic waves and absorption are useful tools to detect insoluble formed in biodiesel. There are analytical tools such as FTIR and NMR spectroscopic methods to show degradation thereby the stability of the biodiesel.

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