

A comprehensive review on biodiesel as an alternative energy resource and its characteristics

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ABSTRACT

As the fossil fuels are depleting day by day, there is a need to find out an alternative fuel to fulfill the energy demand of the world. Biodiesel is one of the best available resources that have come to the forefront recently. In this paper, a detailed review has been conducted to highlight different related aspects to biodiesel industry. These aspects include, biodiesel feedstocks, extraction and production methods, properties and qualities of biodiesel, problems and potential solutions of using vegetable oil, advantages and disadvantages of biodiesel, the economical viability and finally the future of biodiesel. The literature reviewed was selective and critical. Highly rated journals in scientific indexes were the preferred choice, although other non-indexed publications, such as Scientific Research and Essays or some internal reports from highly reputed organizations such as International Energy Agency (IEA), Energy Information Administration (EIA) and British Petroleum (BP) have also been cited. Based on the overview presented, it is clear that the search for beneficial biodiesel sources should focus on feedstocks that do not compete with food crops, do not lead to land-clearing and provide greenhouse-gas reductions. These feedstocks include non-edible oils such as *Jatropha curcas* and *Calophyllum inophyllum*, and more recently microalgae and genetically engineered plants such as poplar and switchgrass have emerged to be very promising feedstocks for biodiesel production.

It has been found that feedstock alone represents more than 75% of the overall biodiesel production cost. Therefore, selecting the best feedstock is vital to ensure low production cost. It has also been found that the continuity in transesterification process is another choice to minimize the production cost. Biodiesel is currently not economically feasible, and more research and technological development are needed. Thus supporting policies are important to promote biodiesel research and make their prices competitive with other conventional sources of energy. Currently, biodiesel can be more effective if used as a complement to other energy sources.

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Contents

1. Overview of global transportation sector consumption and emissions production	2071
1.1. Global transportation sector energy consumption	2071
1.2. Global transportation sector emissions production	2071
2. Biodiesel as an emerging energy resource	2073
3. Biodiesel feedstock	2074
4. Oil extraction methods	2077
4.1. Mechanical extraction	2077
4.2. Solvent extraction (chemical extraction)	2077
4.3. Enzymatic oil extraction	2077
5. Biodiesel production technologies	2078

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5.1.	Pyrolysis (thermal cracking)	2078
5.2.	Dilution	2078
5.3.	Micro-emulsion	2078
5.4.	Transesterification (alcoholysis)	2079
5.4.1.	Variables affecting the transesterification reaction	2081
6.	Properties and qualities of biodiesel	2081
6.1.	Kinematic viscosity	2081
6.2.	Density and relative density	2081
6.3.	Flash point (FP)	2081
6.4.	Cloud point (CP) pour point (PP) and cold filter plugging point (CFPP)	2081
6.5.	Titer	2082
6.6.	Cetane number (CN)	2082
6.7.	Oxidation stability (OS)	2082
6.8.	Lubrication properties	2082
6.9.	Acid value	2082
6.10.	Heating value, heat of combustion	2082
6.11.	Free glycerin	2082
6.12.	Total glycerol	2087
6.13.	Water content and sediment	2087
6.14.	Sulfated ash	2087
6.15.	Carbon residue	2088
6.16.	Copper strip corrosion	2088
6.17.	Cold soak filtration	2088
6.18.	Visual inspection	2088
6.19.	Phosphorous, calcium, and magnesium	2088
6.20.	Moisture contents	2088
7.	Problems and potential solutions of using vegetable oils	2089
8.	Advantages and disadvantages of biodiesel	2089
9.	Economical viability of biodiesel	2089
10.	Future of biodiesel	2090
11.	Conclusion	2090
	Acknowledgment	2090
	References	2090

1. Overview of global transportation sector consumption and emissions production

1.1. Global transportation sector energy consumption

Energy has become a crucial factor for humanity to continue the economic growth and maintain high standard of living especially after the inauguration of the industrial revolution in the late 18th and early 19th century. According to the International Energy Agency (IEA) report [1] and Shahid and Jamal [2], the world will need 50% more energy in 2030 than today, of which 45% will be accounted for by China and India. In the past 30 years, the transportation sector has experienced a steady growth especially due to the increasing numbers of cars around the world. It has been estimated that the global transportation energy use is expected to increase by an average of 1.8% per year from 2005 to 2035. Fig. 1 shows the total world, OECD (Organization for Economic Cooperation and Development) and non-OECD (Countries outside the Organization for Economic Cooperation and Development) transportation sector energy consumption between 2005 and 2035 [3]. Globally, the transportation sector is the second largest energy consuming sector after the industrial sector and accounts for 30% of the world's total delivered energy, of which 80% is road transport. It is believed that this sector is currently responsible for nearly 60% of world oil demand and will be the strongest growing energy demand sector in the future. Nearly all fossil fuel energy consumption in the transportation sector is from oil (97.6%), with a small amount from natural gas. Between 2006 and 2030, around three quarters of the projected increase in oil demand is expected to come from this sector [3–5]. Fig. 2 shows total world, transportation and other sectors oil consumption by end-use sector between 2007 and 2035 [3].

Fig. 3 shows the history of oil proved reserves between 1980 and 2009. Fig. 4 presents the trends of oil production and

consumption between 1965 and 2009. Although oil is expected to remain the largest source of energy, the oil share of world marketed energy consumption is expected to decline from 35% in 2007 to 30% in 2035 as can be seen in Fig. 5 [3]. There is speculation about the peak oil production. A 2005 French Economics, Industry and Finance Ministry report suggested it may occur in 2013. However, few models predicted the peak year has already taken place in 2010, while other models predicted that it was in 2005. There are few other studies that reported the peak extraction will be occurred in 2020. The World Energy Forum has predicted that reserves will be exhausted in less than another 10 decades. Other believes that it will be depleted in fewer than 45 years if consumed at an increasing rate of 3% per annum [7–10].

1.2. Global transportation sector emissions production

It is believed that climate change is currently the most pressing global environmental problem. If the average global temperature increases by more than 2 °C, up to one million species could become extinct and hundreds of millions of people could lose their lives [9,11].

It is expected that about 4.1 billion metric tons of carbon dioxide will be released to the atmosphere from 2007 to 2020. Moreover, it is estimated that another additional 8.6 billion metric tons carbon dioxide will be released to the atmosphere from 2020 to 2035. This is estimated to be about 43% increase for the aforementioned projected period [3,12]. Fig. 6 shows the carbon dioxide emission trends for OECD, non-OECD countries and total world until 2035.

Globally, transportation sector accounted for about 23% and 22% of total world CO₂ emissions in 2007 and 2008 respectively [13,14]. Within this sector, road transport, accounting for 10% of global GHG emissions [15]. According to the United Nations'

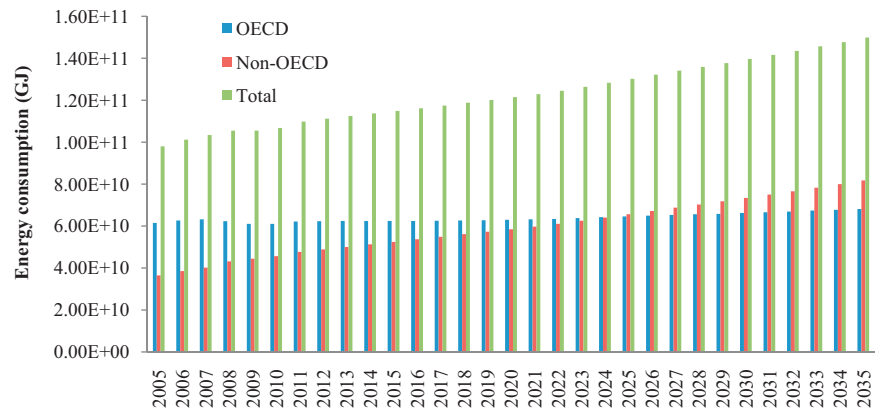


Fig. 1. Total world, OECD and non-OECD transportation sector energy consumption (GJ) between 2005 and 2035 [3,6].

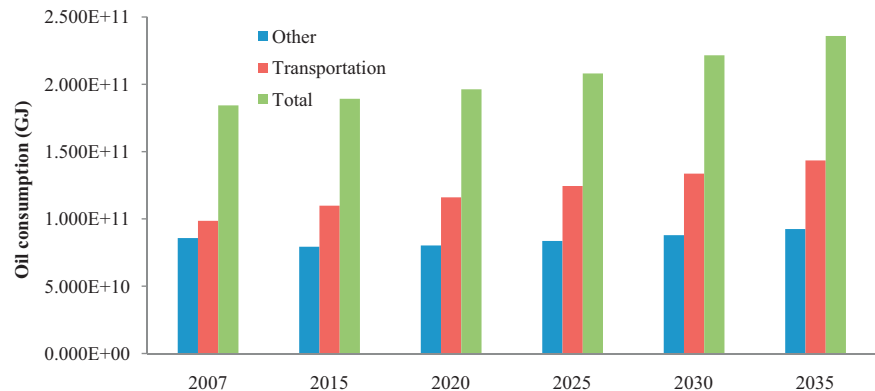


Fig. 2. Total world oil consumption, transportation oil consumption and other sectors oil consumption (GJ) between 2007 and 2035 [3,6].

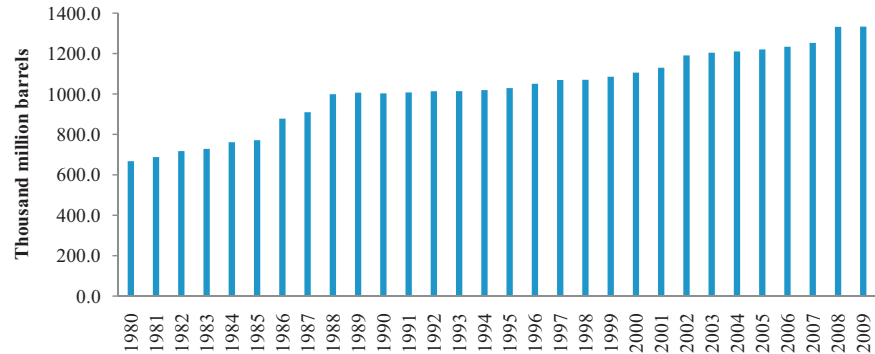


Fig. 3. Total oil proved reserves between 1980 and 2009 (thousand million barrels) [7].

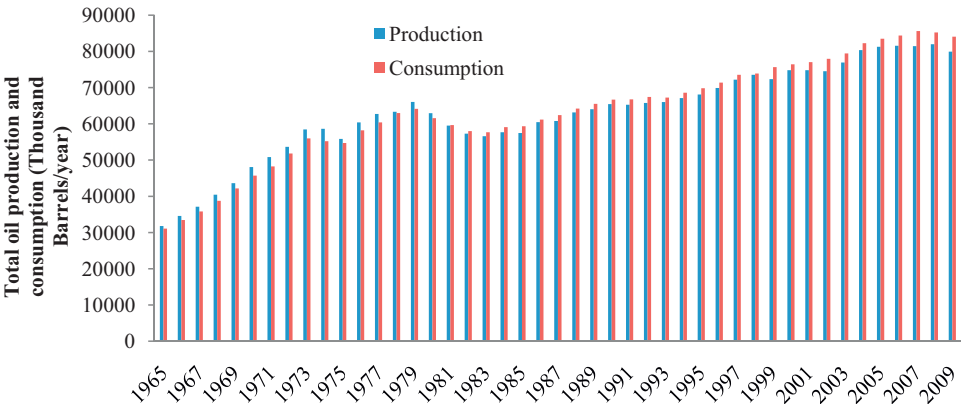


Fig. 4. Total oil production and consumption between 1965 and 2009 (thousand barrels per year) [7].

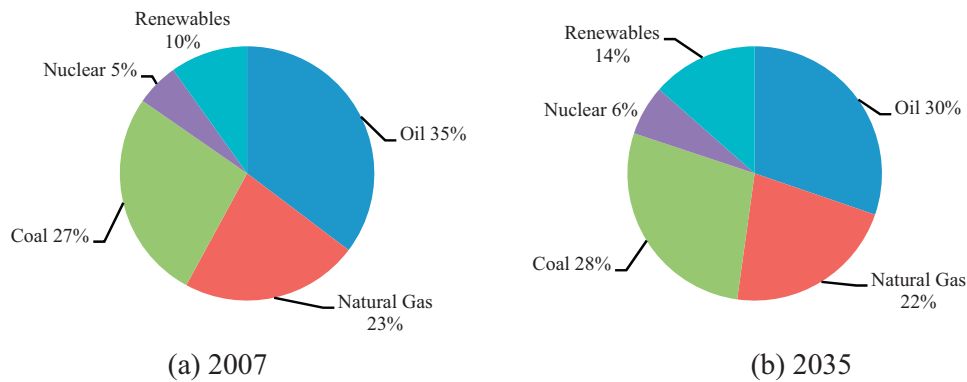


Fig. 5. Breakdown of world marketed energy consumption by fuel in 2007 and 2035 [3].

Intergovernmental Panel on Climate Change, the transportation sector was responsible for about 23% of energy-related greenhouse gas emissions in 2004. Passenger vehicles account for about 45% of this total [16]. In Europe, transportation sector accounts for more than a fifth of greenhouse gas emissions. Between 1990 and 2001, emissions of greenhouse gases (GHGs) from transport (excluding international transport) increased by 20% [17,18]. In Australia, The transport sector contributed to 13.7% of Australia's net emissions in 2006. Road transport was responsible for 87% of these emissions or 12% of Australia's total emissions [19]. In 2008, Almost 30% of total U.S. greenhouse gas (GHG) emissions come from the transportation sector, making transportation the second largest source of GHG emissions in the United States after the electric power sector (35%) [20].

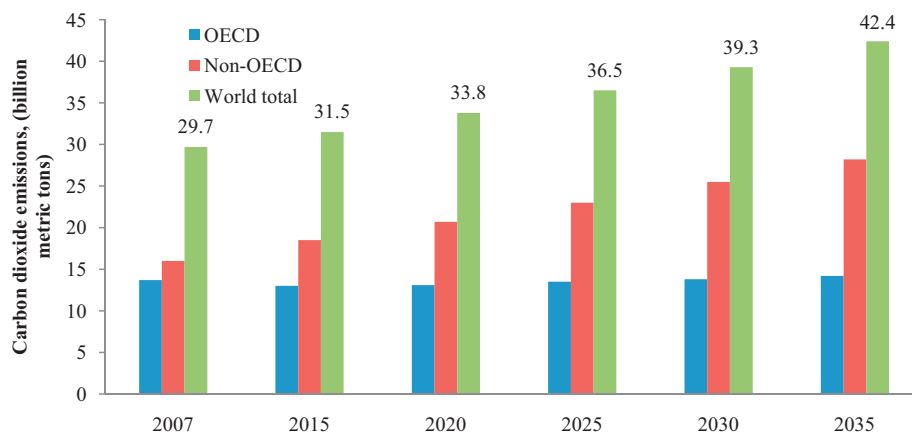
The majority of transportation GHG emissions (95%) are composed of carbon dioxide (CO_2). An additional one percent comes from methane (CH_4) and nitrous oxides (N_2O). The leakage of hydro fluorocarbons (HFCs) from vehicle air conditioning systems is responsible for the remaining three percent of GHG emissions. Transportation sources also emit ozone, carbon monoxide (CO), and aerosols. These substances are not counted as greenhouse gases but are believed to have an indirect effect on global warming, although their impact has not been quantified with certainty [20].

2. Biodiesel as an emerging energy resource

Globally, the awareness of energy issues and environmental problems associated with burning fossil fuels has encouraged

many researchers to investigate the possibility of using alternative sources of energy instead of oil and its derivatives. Among them, biodiesel seems very interesting for several reasons: it is highly biodegradable and has minimal toxicity, it can replace diesel fuel in many different applications such as in boilers and internal combustion engines without major modifications and small decrease in performances is reported, almost zero emissions of sulfates, aromatic compounds and other chemical substances that are destructive to the environment, a small net contribution of carbon dioxide (CO_2) when the whole life-cycle is considered (including cultivation, production of oil and conversion to biodiesel), it appears to cause significant improvement of rural economic potential [9,21,22]. The invention of the vegetable oil fuelled engine by Sir Rudolf Diesel dated back in the 1900s. However, full exploration of biodiesel only came into light in the 1980s as a result of renewed interest in renewable energy sources for reducing greenhouse gas (GHG) emissions, and alleviating the depletion of fossil fuel reserves. Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats and alcohol with or without a catalyst [2,9,10,23–26]. Compared to diesel fuel, biodiesel produces no sulfur, no net carbon dioxide, less carbon monoxide, particulate matters, smoke and hydrocarbons emission and more oxygen. More free oxygen leads to the complete combustion and reduced emission [27,28].

Biodiesel has been in use in many countries such as United States of America, Malaysia, Indonesia, Brazil, Germany, France, Italy and other European countries. However, the potential for its production and application is much more. Table 1 shows the list of the top 10



OECD (Organization for Economic Cooperation and Development)

Non-OECD (Countries outside the Organization for Economic Cooperation and Development)

Fig. 6. World, OECD and non-OECD carbon dioxide emissions from 2007 to 2035 [3].

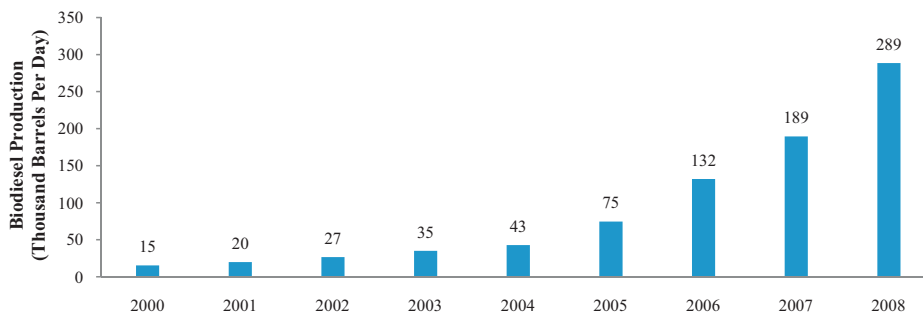


Fig. 7. Total world biodiesel productions (thousand barrels per day) between 2000 and 2008 [27,33].

Table 1

Top 10 countries in terms of biodiesel potential [8,29–31].

Rank	Country	Biodiesel potential (ML)	Production (\$/L)
1	Malaysia	14,540	0.53
2	Indonesia	7595	0.49
3	Argentina	5255	0.62
4	USA	3212	0.70
5	Brazil	2567	0.62
6	Netherlands	2496	0.75
7	Germany	2024	0.79
8	Philippines	1234	0.53
9	Belgium	1213	0.78
10	Spain	1073	1.71

biodiesel producing countries. From this table, it can be seen that Malaysia is far ahead among the rest [8,29–31].

Biodiesel has a massive potentiality to be a part of a sustainable energy mix in the future [32]. Globally, annual biodiesel production increased from 15 thousand barrel per day in 2000 to 289 thousand barrel per day in 2008 as shown in Fig. 7 [27,33]. It is believed that, 85% of biodiesel production comes from the European Union [9]. The demand for biodiesel in European countries is expected to be up to 10.5 billion liters by 2010 [34].

3. Biodiesel feedstock

Globally, there are more than 350 oil-bearing crops identified as potential sources for biodiesel production. Table 2 shows main feedstocks of biodiesel. The wide range of available feedstocks for biodiesel production represents one of the most significant factors of producing biodiesel [2,23,35]. As much as possible the feedstock should fulfill two main requirements: low production costs and large production scale. The availability of feedstock for producing biodiesel depends on the regional climate, geographical locations, local soil conditions and agricultural practices of any country. From the literature, it has been found that feedstock alone represents 75% of the overall biodiesel production cost as shown in Fig. 8. Therefore, selecting the cheapest feedstock is vital to ensure low

production cost of biodiesel. Fig. 9 shows pictures of some biodiesel feedstocks. In general, biodiesel feedstock can be divided into four main categories as below [9,10,27,36–44]:

1. Edible vegetable oil: rapeseed, soybean, peanut, sunflower, palm and coconut oil.
2. Non-edible vegetable oil: *jatropha*, *karanja*, sea mango, algae and halophytes.
3. Waste or recycled oil.
4. Animal fats: tallow, yellow grease, chicken fat and by-products from fish oil.

Table 3 shows primary biodiesel feedstock for some selected countries around the world [9,45].

It is very important to consider some factors when comparing between different feedstocks. Each feedstock should be evaluated based on a full life-cycle analysis. This analysis includes: (1) availability of land, (2) cultivation practices, (3) energy supply and balance, (4) emission of greenhouse gases, (5) injection of pesticides, (6) soil erosion and fertility, (7) contribution to biodiversity value losses, (8) logistic cost (transport and storage), (9) direct economic value of the feedstocks taking into account the co-products, (10) creation or maintain of employment, (11) water requirements and water availability, (12) effects of feedstock on air quality [9,53,54].

To consider any feedstock as a biodiesel source, the oil percentage and the yield per hectare are important parameters. Table 4 shows the estimated oil content and yields of different biodiesel feedstocks.

Edible oils resources such as soybeans, palm oil, sunflower, safflower, rapeseed, coconut and peanut are considered as the first generation of biodiesel feedstock because they were the first crops to be used for biodiesel production. Their plantations have been well established in many countries around the world such as Malaysia, USA and Germany. Currently, more than 95% of the world biodiesel is produced from edible oils such as rapeseed (84%), sunflower oil (13%), palm oil (1%), soybean oil and others (2%). However, their use raises many concerns such as food versus fuel crisis and major environmental problems such as serious destruction of vital soil resources, deforestation and usage of much of the available arable land. Moreover, in the last 10 years the prices of vegetable oil plants have increased dramatically which will affect the economical viability of biodiesel industry [29,53,61]. Furthermore, the use of such edible oils to produce biodiesel is not feasible in the long-term because of the growing gap between demand and supply of such oils in many countries. For instance, dedicating all US soybean to biodiesel production would meet only 6% of diesel demands [62].

One of the possible solutions to reduce the utilization of the edible oil for biodiesel production is by exploiting non-edible oils. Non-edible oils resources are gaining worldwide attention because they are easily available in many parts of the world especially

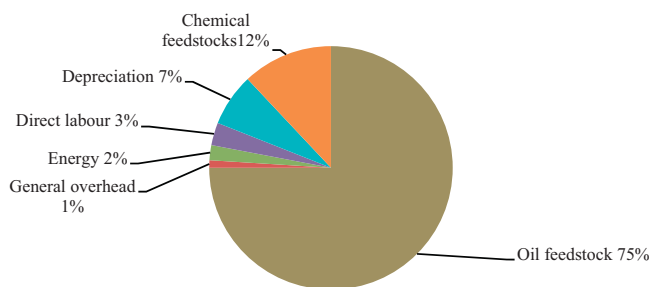


Fig. 8. General cost breakdown for production of biodiesel [9,27,40,46,47].

Table 2

Main feedstocks of biodiesel [2,10,43,45,46,48].

Edible oils	Non-edible oils	Animal fats	Other sources
Soybeans (<i>Glycine max</i>)	<i>Jatropha curcas</i>	Pork lard	Bacteria
Rapeseed (<i>Brassica napus</i> L.)	Mahua (<i>Madhuca indica</i>)	Beef tallow	Algae (Cyanobacteria)
Safflower	Pongamia (<i>Pongamia pinnata</i>)	Poultry fat	Microalgae (<i>Chlorellavulgaris</i>)
Rice bran oil (<i>Oryza sativum</i>)	Camelina (<i>Camelina Sativa</i>)	Fish oil	Tarpenes
Barley	Cotton seed (<i>Gossypium hirsutum</i>)	Chicken fat	Poplar
Sesame (<i>Sesamum indicum</i> L.)	Karanja or honge (<i>Pongamia pinnata</i>)		Switchgrass
Groundnut	Cumaru		Miscanthus
Sorghum	<i>Cynara cardunculus</i>		Latexes
Wheat	<i>Abutilon muticum</i>		Fungi
Corn	Neem (<i>Azadirachta indica</i>)		
Coconut	Jojoba (<i>Simmondsia chinensis</i>)		
Canola	Passion seed (<i>Passiflora edulis</i>)		
Peanut	Moringa (<i>Moringa oleifera</i>)		
Palm and palm kernel (<i>Elaeis guineensis</i>)	Tobacco seed		
Sunflower (<i>Helianthus annuus</i>)	Rubber seed tree (<i>Hevea brasiliensis</i>)		
	Salmon oil		
	Tall (<i>Carnegiea gigantea</i>)		
	Coffee ground (<i>Coffea arabica</i>)		
	Nagchampa (<i>Calophyllum inophyllum</i>)		
	<i>Croton megalocarpus</i>		
	<i>Pachira glabra</i>		
	<i>Aleurites moluccana</i>		
	<i>Terminalia belerica</i>		

wastelands that are not suitable for food crops, eliminate competition for food, reduce deforestation rate, more efficient, more environmentally friendly, produce useful by-products and they are very economical comparable to edible oils. The main sources for biodiesel production from non-edible oils are jatropha or ratanjyote or seemaikattamankku (*Jatropha curcas*), karanja or honge (*Pongamia pinnata*), *Aleurites moluccana*, *Pachira glabra* nagchampa (*Calophyllum inophyllum*), rubber seed tree (*Hevea brasiliensis*), Desert date (*Balanites aegyptiaca*), *Croton megalocarpus*, Rice bran, Sea mango (*Cerbera odollam*), *Terminalia belerica*, neem (*Azadirachta indica*), Koroch seed oil (*Pongamia glabra* vent.), mahua (*Madhuca indica* and *Madhuca longifolia*), Tobacco seed (*Nicotiana tabacum* L.), Chinese tallow, silk cotton tree (*Ceiba pentandra*), jojoba (*Simmondsia chinensis*), babassu tree and *Euphorbia tirucalli*. Non-edible oils are regarded as the second generation of biodiesel feedstocks. Animal fats such as beef tallow, poultry fat and pork lard,

waste oils and grease are also considered second generation feedstocks. The use of these types of feedstock eliminates the need to dispose them. However, it has been reported that second generation feedstocks may not be plentiful enough to satisfy the global energy demand. Moreover, biodiesel derived from vegetable oils and animal fats has a relatively poor performance in cold weather. Furthermore, for many types of animal fats the transesterification process is difficult because they contain high amount of saturated fatty acids. In case of waste cooking oil, collection infrastructure

Table 3

Current potential feedstocks for biodiesel worldwide [2,8,9,29,45,46,50–52].

Country	Feedstock
USA	Soybeans/waste oil/peanut
Canada	Rapeseed/animal fat/soybeans/yellow grease and tallow/mustard/flax
Mexico	Animal fat/waste oil
Germany	Rapeseed
Italy	Rapeseed/sunflower
France	Rapeseed/sunflower
Spain	Linseed oil/sunflower
Greece	Cottonseed
UK	Rapeseed/waste cooking oil
Sweden	Rapeseed
Ireland	Frying oil/animal fats
India	<i>Jatropha/Pongamia pinnata</i> (karanja)/soybean/rapeseed/sunflower/peanut
Malaysia	Palm oil
Indonesia	Palm oil/jatropha/coconut
Singapore	Palm oil
Philippines	Coconut/jatropha
Thailand	Palm/jatropha/coconut
China	<i>Jatropha</i> /waste cooking oil/rapeseed
Brazil	Soybeans/palm oil/castor/cotton oil
Argentina	Soybeans
Japan	Waste cooking oil
New Zealand	Waste cooking oil/tallow

Table 4

Estimated oil content and yields of different biodiesel feedstocks [9,23,29,45,48,49,52–60].

Feedstocks	Oil content (%)	Oil yield (L/ha/year)
Castor	53	1413
<i>Jatropha</i>	Seed: 35–40, kernel: 50–60	1892
Linseed	40–44	–
Neem	20–30	–
<i>Pongamia pinnata</i> (karanja)	27–39	225–2250 ^a
Soybean	15–20	446
Sunflower	25–35	952
<i>Calophyllum inophyllum</i> L.	65	4680
<i>Moringa oleifera</i>	40	–
<i>Euphorbia lathyris</i> L.	48	1500–2500 ^a
<i>Sapium sebiferum</i> L.	Kernel 12–29	–
Rapeseed	38–46	1190
Tung	16–18	940
<i>Pachira glabra</i>	40–50	–
Palm oil	30–60	5950
Peanut oil	45–55	1059
Olive oil	45–70	1212
Corn (Germ)	48	172
Coconut	63–65	2689
Cottonseed	18–25	325
Rice bran	15–23	828
Sesame	–	696
Jojoba	45–50	1818
Rubber seed	40–50	80–120 ^a
Sea mango	54	–
Microalgae (low oil content)	30	58,700
Microalgae (medium oil content)	50	97,800
Microalgae (high oil content)	70	136,900

^a (kg oil/ha).

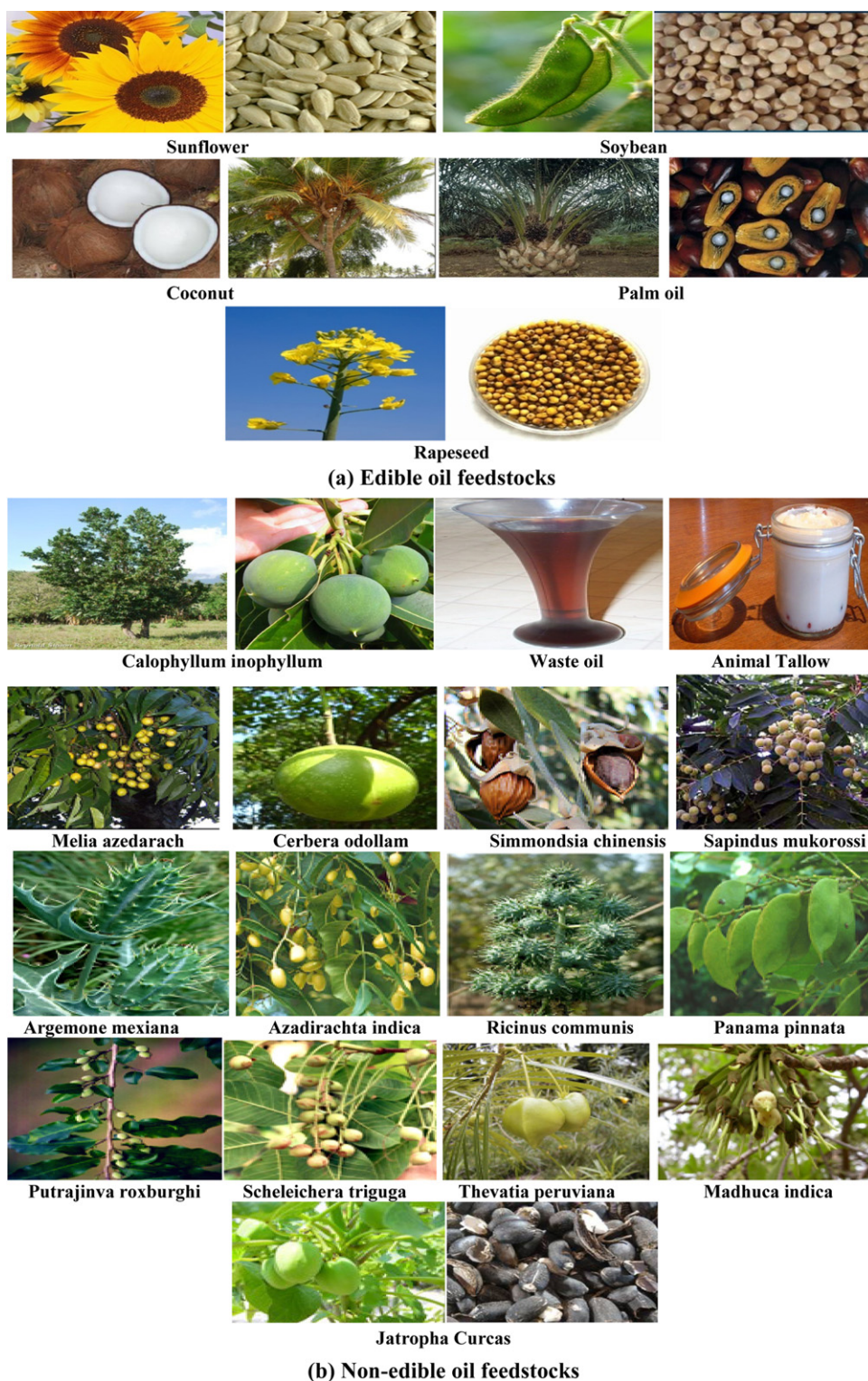


Fig. 9. Main biodiesel feedstocks: (a) edible and (b) non-edible [27,37,41,49].

and logistics could be hurdle as the sources are generally scattered [8–10,23,36,43,46,48,49,53,60–73].

More recently, microalgae have emerged to be the third generation of biodiesel feedstock. Microalgae are photosynthetic microorganisms that convert sunlight, water and CO₂ to algal biomass but they do it more efficiently than conventional crop plants. It represents a very promising feedstock because of its high photosynthetic efficiency to produce biomass, higher growth

rates and productivity and high oil content compared to edible and non-edible feedstocks (Table 5). Microalgae have the potential to produce an oil yield that is up to 25 times higher than the yield of oil palm and 250 times the amount of soybeans as can be seen in Table 4. This is because microalgae can be grown in farm or bioreactor. Moreover, they are easier to cultivate than many other plants. It is believed that microalgae can play an important role in solving the problem between the production of food

Table 5
Comparison of biodiesel production from algae and oil plants [23,57].

	Biodiesel produced from algae	Biodiesel produced from plants
Technology	Cell bioengineering, automatically produced in pilot plant	Agriculture in farm
Production period	5–7 days for a batch cultivation	Several months or years
Oil content	30% (low oil content), 50% (medium oil content), 70% (high oil content)	Less than 20% in seeds or fruits
Land occupied	0.010–0.013 hectare for producing 1×10^3 L oil ^a	2.24 ha for producing 1×10^3 L oil ^b
Cost performance	\$2.4 per liter microalgal oil	\$0.6–0.8 per liter plant oil
Development potential	Unlimited (work just beginning)	Limited (many works have been done)

^a Based on soybean cultivation in farmland.^b Based on projected area of bioreactor in pilot plant.

and that of biodiesel in the near future. Moreover, among other generations of biodiesel feedstocks, microalgae appear to be the only source of renewable biodiesel that is capable of meeting the global demand for transport fuels and can be sustainably developed in the future. The main obstacle for the commercialization of microalgae is its high production cost from requiring high-oil-yielding algae strains and effective large-scale bioreactors. Recent studies indicate that algae for biodiesel production can grow on flue gas, giving opportunities in consuming greenhouse gas as feedstock [8,9,23,36,39,43,46,49,53,63–65,74,75]. Table 5 shows the comparison of biodiesel production from algae and oil plants.

Knothe [76] reported that the use of the terms first, second and third generation are sometimes misleading and should not be used to imply that biodiesel derived from second or third generation feedstock may have superior fuel properties over first generation. For instance, biodiesel from *Jatropha* oil possesses poorer cold flow properties than biodiesel derived from soybean, palm or rapeseed oil. Recently, there have been several publications which highlighted the positive effects of blending different oils on the basic properties of biodiesel [77–79].

Janaun and Ellis [23] and Lin et al. [46] show that genetically engineered plants such as poplar, switchgrass, miscanthus and big bluestem can be considered new feedstocks for biodiesel production. These feedstocks will create new bioenergy crops that are not associated with food crops. Therefore, they are expected to represent a sustainable biodiesel feedstock in the future. However, precaution on biosafety must be considered for these feedstocks.

4. Oil extraction methods

The second step in the production of biodiesel is oil extraction. In this process, the oil contained in the seeds has to be extracted. The main products are the crude oil and the important by-products such as seeds or kernel cakes. There are three main methods that have been identified for extraction of the oil: (i) Mechanical extraction, (ii) solvent extraction and (iii) enzymatic extraction. Before the oil extraction takes place, seeds have to be dried. Seed can be either dried in the oven (105 °C) or sun dried (3 weeks). Mechanical expellers or presses can be fed with either whole seeds or kernels or a mix of both, but common practice is to use whole seeds. However, for chemical extraction only kernels are used as feed [80].

Table 6
Calculated oil yields (% of contained oil) of mechanical extraction methods [5,80,82–84].

Press	Oil yield (%)	Necessary treatment
Engine driven screw press	68.0	Filterization and degumming
	80.0	
	79.0	
Ram press	62.5	
	62.5	

4.1. Mechanical extraction

The technique of oil extraction by mechanical presses is the most conventional one among other methods. In this type, either a manual ram press or an engine driven screw press can be used. It has been found that, engine driven screw press can extract 68–80% of the available oil while the ram presses only achieved 60–65% (Table 6). This broader range is due to the fact that seeds can be subjected to a different number of extractions through the expeller. The oil extracted by mechanical presses needs further treatment of filterization and degumming. One more problems associated with conventional mechanical presses are, their design is suited for some particular seeds, and therefore the yield is affected if used for other seeds. It has been found that, pretreatment of the seeds, such as cooking, can increase the oil yield of screw pressing up to 89% after single pass and 91% after dual pass [80,81].

4.2. Solvent extraction (chemical extraction)

Solvent extraction is the technique of removing one constituent from a solid by means of a liquid solvent. It is also called leaching. There are many factors influencing the rate of extraction such as particle size, the type of liquid chosen, temperature and agitation of the solvent. The small particle size is preferable because it allows for a greater interfacial area between the solid and liquid. The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low to circulate freely. Temperature also affects the extraction rate. The solubility of the material will increase with the increasing temperature. Agitation of the solvent also affects, it increases the eddy diffusion and therefore increases the transfer of material from the surface of the particles. Solvent extraction is only economical at a large-scale production of more than 50 ton biodiesel per day. There are three methods that are used in this type as follow [80,81]:

- (1) Hot water extraction.
- (2) Soxhlet extraction.
- (3) Ultrasonication technique.

4.3. Enzymatic oil extraction

Enzymatic oil extraction technique has emerged as a promising technique for extraction of oil. In this process suitable enzymes are used to extract oil from crushed seeds. Its main advantages are that it is environment friendly and does not produce volatile organic compounds. However, the long process time is the main disadvantage associated with this technique [81].

Table 7 shows the reaction temperature, reaction pH, time consumption and oil yield of different chemical and enzymatic extraction methods. It has been found that the chemical extraction using n-hexane method results in the highest oil yield which makes it the most common type. However, this type consumes much more time compared to other types. Furthermore n-hexane solvent extraction has a negative environmental impacts as a result

Table 7
Reported oil yields percentage for different chemical and enzymatic extraction methods and different reaction parameters [80].

Extraction method	Reaction temperature (°C)	Reaction pH	Time consumption (h)	Oil yield (%)
n-Hexane oil extraction (Soxhelt) apparatus	–	–	24	95–99
1st acetone	–	–	48	
2nd n-hexane	–	–		
Aqueous oil extraction (AOE)	50	9	2	38
AOE with 10 min of ultrasonication as pretreatment	50	9	6	38
Aqueous enzymatic oil extraction (AEOE) (hemicellulase or cellulase)	60	4.5	2	67
AEOE (alkaline protease)	60	7	2	73
AEOE (alkaline protease) with 5 min of ultrasonic as pretreatment	50	9	6	86
Three-phase partitioning	25	9	6	64
			2	74
				94

of the waste water generation, higher specific energy consumption and higher emissions of volatile organic compounds and human health impacts (working with hazardous and inflammable chemicals). Using aqueous enzymatic oil extractions greatly reduces these problems. In aqueous enzymatic oil extraction the use of alkaline protease gave better results. Furthermore, ultrasonication pretreatment is a more useful step in aqueous oil extraction [80,81].

5. Biodiesel production technologies

Globally, there are many efforts to develop and improve vegetable oil properties in order to approximate the properties of diesel fuels. It has been remarked that high viscosity, low volatility and polyunsaturated characters are the mostly associated problems with crude vegetable oils. These problems can be overcome by four methods; pyrolysis, dilution with hydrocarbons blending, Micro-emulsion, and transesterification [29,36,46,51,85–88]. Lin et al. [46] conduct a comparison between different biodiesel production technologies. This comparison is given in Table 8.

5.1. Pyrolysis (thermal cracking)

Pyrolysis is the thermal decomposition of the organic matters in the absence of oxygen and in the presence of a catalyst. The paralyzed material can be vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids. Many investigators have studied the pyrolysis of triglycerides to obtain suitable fuels for diesel engine. Thermal decomposition of triglycerides produces alkanes, alkenes, alkanes, aromatics and carboxylic acids [29,51,58,65,68,81,89–93]. It has been observed that pyrolysis process is effective, simple, wasteless and pollution free [43]. According to Sharma et al. [75], pyrolysis of the vegetable oil can produce a product that has high cetane number, low viscosity, acceptable amounts of sulfur, water and sediments contents, acceptable copper corrosion values. However, ash contents, carbon residues, and pour points were unacceptable.

5.2. Dilution

Mainly, vegetable oils are diluted with diesel to reduce the viscosity and improve the performance of the engine. This method does not require any chemical process [29,88]. Singh and Singh [43]

Table 8
Comparison of main biodiesel production technologies [46].

Technologies	Advantage	Disadvantage
Dilution (direct blending or micro-emulsion)	• Simple process	• High viscosity • Bad volatility • Bad stability
Pyrolysis	• Simple process • No-polluting	• High temperature is required • Equipment is expensive • Low purity
Transesterification	• Fuel properties is closer to diesel • High conversion efficiency • Low cost • It is suitable for industrialized production	• Low free fatty acid and water content are required (for base catalyst) • Pollutants will be produced because products must be neutralized and washed • Accompanied by side reactions • Difficult reaction products separation
Supercritical methanol	• No catalyst • Short reaction Time • High conversion • Good adaptability	• High temperature and pressure are required • Equipment cost is high • High energy consumption

reported that substitution of 100% vegetable oil for diesel fuel is not practical. However a blend of 20% vegetable oil and 80% diesel fuel was successful. The use of blends of diesel fuel with sunflower oil, coconut oil, African pear seed, rice bran oil, PP (Pistachia Palestine), waste cooking oil, palm oil, soybean oil, cottonseed oil, rubber seed oil, rapeseed oil, *J. curcas* oil, *P. pinnata* oil has been described in the literature [29,58,65,88,89,91,94,95]. For instance, Ziejewski et al. [95] investigated the effects of the fuel blend of 25% sunflower oil with 75% diesel fuel (25/75 fuel) in a direct injection diesel engine. The authors found that this blend is not suitable for long-term use in direct injection engines. This is because the viscosity at 313 K was 4.88cSt (maximum specified ASTM value is 4.0cSt at 313 K). Generally, direct use of vegetable oils and their blends have been considered to be difficult to use in both direct and indirect diesel engines [58,65].

5.3. Micro-emulsion

A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions generally into 1–150 nm range formed spontaneously from two normally immiscible liquids and one and more ionic or more ionic amphiphiles. Micro-emulsions using solvents such as methanol, ethanol, hexanol, butanol and 1-butanol have been investigated by many researchers. Micro-emulsion with these solvents has met the maximum viscosity requirement for diesel fuel. It has been demonstrated that short-term performances of both ionic and non-ionic micro-emulsions of aqueous ethanol in soybean oil are nearly as well as that of No. 2 diesel fuel [29,43,65,68,81,89,91].

The fuel properties of the liquid product fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. Soybean oil pyrolyzed distillate had a cetane number of 43, exceeding that of soybean oil (37.9) and the ASTM minimum value of 40. However, the viscosity of the distillate was 10.2 mm²/s at 311 K, which is higher than the ASTM specification for No. 2 diesel fuel (1.9–4.1 mm²/s) but considerably below that of soybean oil (32.6 mm²/s) [29].

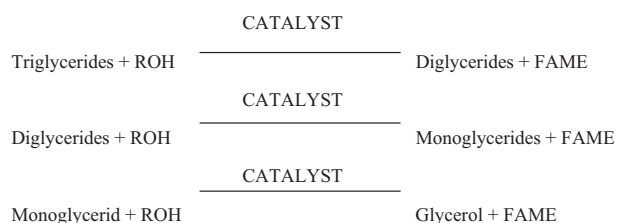


Fig. 10. Equation of transesterification reaction [2,29,43,51,75,87,96].

5.4. Transesterification (alcoholysis)

Transesterification is regarded as the best method among other approaches due to its low cost and simplicity [2,8,29,65,93]. Biodiesel is the main product of this process. Transesterification consists of a number of consecutive, reversible reactions. In these reactions, the triglycerides are converted step wise to diglycerides, monoglyceride and finally glycerol which sinks to the bottom and biodiesel which floats on top and can be siphoned off as shown in Fig. 10. Glycerol is an important by-product and can be burned for heat or be used as feedstock in the cosmetic industry. In this reaction, methanol and ethanol are the two main light alcohols used for transesterification process due to their relatively low cost. However, propanol, isopropanol, tert-butanol, branched alcohols and octanol and butanol can also be employed but the cost is much higher [2,29,43,45,58,75,87,96].

In this reaction, 100 lb of fat or oil are reacted with 10 lb of a short chain alcohol in the presence of a catalyst to produce 10 lb of glycerin and 100 lb of biodiesel. As per the transesterification reaction, 3 moles of methanol were required to react with the vegetable oil [54]. Generally, transesterification process includes two main processes; catalytic and non-catalytic method. A catalyst is used to commence the reaction. The catalyst is vital as alcohol is barely soluble in oil or fat. The catalyst enhances the solubility of alcohol and thus increases the reaction rate. The most frequently used process is the catalytic transesterification process. Fig. 11 shows the detailed classification of transesterification processes [41,45].

Alkaline catalysts include catalysts such as NaOH, NaOCH₃, KOCH₃, KOH, NaMeO and K₂CO₃. Most of the biodiesel producers use sodium hydroxide or potassium hydroxide. Even though some authors reported that sodium hydroxide is better than potassium hydroxide and some are of the view that potassium hydroxide is better than sodium hydroxide. However, most of the researchers reported that both sodium and potassium hydroxide perform equally well. Sodium and potassium methoxides return better yield than all catalysts but they are costly, so they are not very frequently used. Many researchers have found that alkaline catalytic method is the fastest and most economical catalyst than other catalysts. An alkaline catalyst proceeds at around 4000 times faster than with the same amount of acid catalyst. Moreover, this method can achieve high purity and yield of biodiesel product in a short time (30–60 min). Therefore, it dominates the current biodiesel production methods. However, to use alkaline catalysts, free fatty acid (FFA) level should be below a desired limit (ranging from less than 0.5% to less than 3%). Beyond this limit the reaction will not take place and the product formed will be soap and water instead of esters and the yield of esters will be too less. In addition to, this reaction has several drawbacks; it is energy intensive; recovery of glycerol is difficult; the catalyst has to be removed from the product; alkaline wastewater requires treatment and the level of free fatty acids and water greatly interfere with the reaction [2,8,23,29,31,36,43,45,54,61,75,81,85,89,91,93,98–100].

Acid catalysts include sulfuric, hydrochloric, ferric sulfate, phosphoric and organic sulfonic acid. Some researchers have claimed that acid catalysts are more tolerant than alkaline catalysts for vegetable oils having high free fatty acids and water. Therefore, acid catalyst is used to reduce the free fatty acids contents to a level safe enough for alkaline transesterification which is preferred over the acid catalyst after the acid value is reduced to the desired limit. It has been reported that acid-catalyzed reaction gives very high yield in esters. However, the reaction is slow (3–48 h). It has been reported that the homogeneous transesterification consumes large amount of water for wet washing to remove the salt produced from the neutralization process, and the residual acid or base catalyst. Nevertheless, there are many companies around the world commercializing this technology because of its relatively lower energy

Table 9
Enzymatic transesterification reactions using various types of alcohols and lipases [43].

No.	Oil	Alcohol	Lipase	Conversion (%)	Solvent
1	Rapeseed	2-Ethyl-1-hexanol	<i>C. rugosa</i>	97	None
2	Palm oil	Methanol	<i>Rhizopus oryzae</i>	55 (w/w)	Water
3	Sunflower	Ethanol	<i>M. meihei</i> (Lypozyme)	83	None
4	Soybean oil	Methanol	<i>C. antarctica</i> lipase	93.80	>1/2 molar equivalent MeOH
5	Fish	Ethanol	<i>C. anturctica</i>	100	None
6	Palm kernel	Methanol	<i>I. cepuciu</i>	15	None
7	Recycled restaurant grease	Ethanol	<i>J. cepacia</i> (Lipase PS-30) + <i>C. anturctica</i> (Lipase SP435)	85.4	None

Table 10
Summary of transesterification method [43,75].

No.	Sample	Catalyst	Alcohol	Temperature (°C)	Ration of alcohol to oil	Yields (%)
1	Microalgae	Sulfuric acid	Methanol	30	56:1	60
2	<i>Pongamia pinnata</i>	KOH (1%, w/w)	Methanol	105	10:1	92
3	Soybean oil	Absence of catalyst	Supercritical methanol	280	24 and CO ₂ /methanol = 0.1	98
4	Sunflower oil	No catalyst	Supercritical methanol and ethanol	200–400 (pressure 200 bar)	40:1	78–96
5	Rice bran	Sulfuric acid	Methanol	60	10:1	<96
6	<i>Madhuca indica</i>	H ₂ SO ₄ (1%, v/v)	Methanol	60	0.3–0.35 (v/v)	98
7	Peanut oil	NaOH	Methanol	50	–	90
8	Rubber seed oil	H ₂ SO ₄ (0.5%, v/v)	Methanol	45	6:1	–
9	Canola oil	NaOH (1%, w/w)	Methanol	45	6:1	98

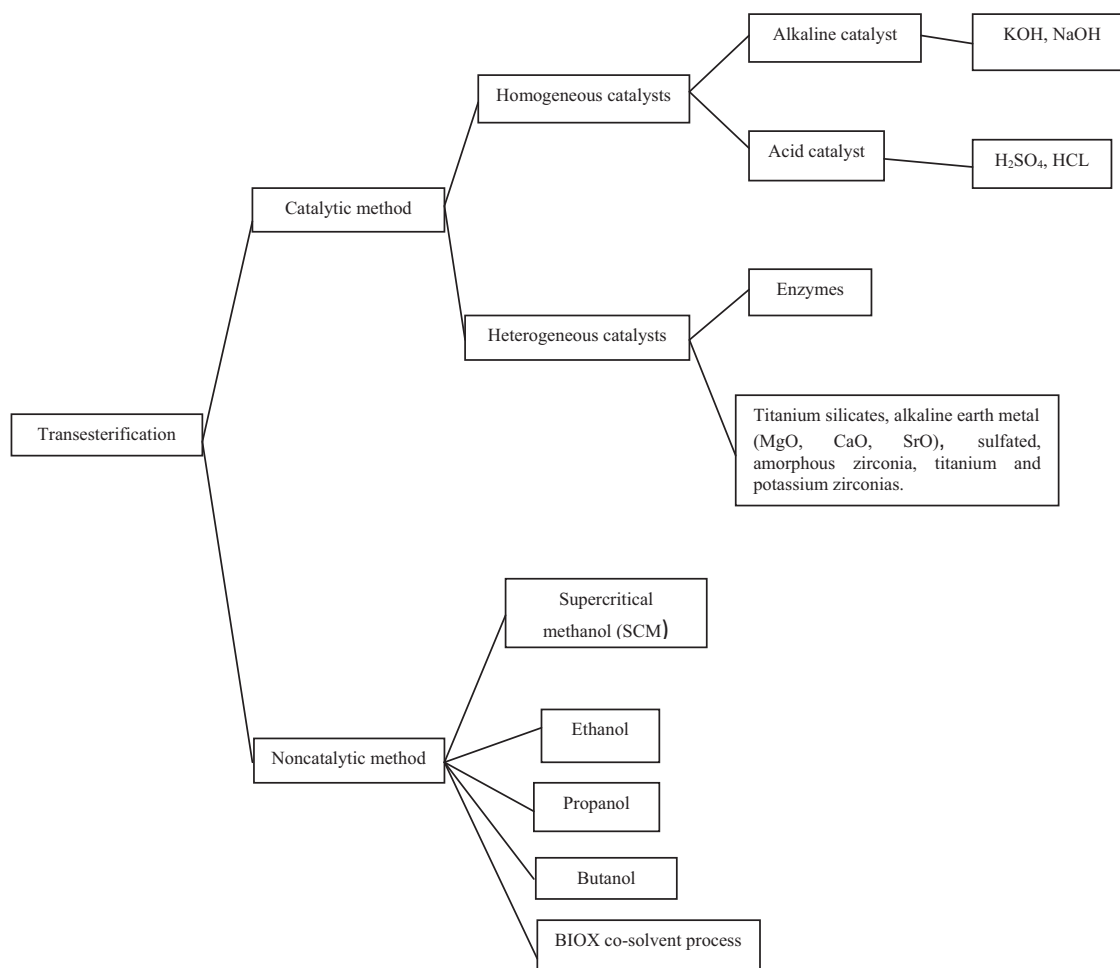


Fig. 11. Classification of transesterification processes [29,41,65,97].

use, high conversion efficiency and cost effective reactants and catalyst [2,8,23,29,36,43,45,81,85,91,98,99].

Lipase catalysts such as Diazomethane CH_2N_2 have shown good tolerance for the free fatty acid level of the feedstock. Moreover, they are known to have a propensity to act on long-chain fatty alcohols better than on short-chain ones. Therefore, the efficiency of the transesterification of triglycerides with ethanol is higher compared to that with methanol in systems with or without a solvent (Table 9). In this reaction, there is no need for complex operations for the recovery of glycerol and the elimination of catalyst and soap. However, the reaction yields and the reaction times are still unfavorable compared to the alkaline catalysts. Moreover, lipases are very expensive for large scale industrial production and they are unable to provide the degree of reaction completion required to meet ASTM fuel specifications. Recently, it has been found that the use of solvent-tolerant lipases, multiple enzymes and immobilized lipases-making catalysts can be developed as cost-effective enzymes [2,29,43,45,65,96]. In general, chemically catalyzed processes, including alkali catalyzed and acid catalyzed ones have been proved to be more practical than the enzyme catalyzed process [100].

The catalytic transesterification has some problems such as: high time consumption, lag of reaction time caused by the extremely low solubility of the alcohol in the triglyceride phase and the need for separation of the catalyst and saponified impurities from biodiesel. These problems are not faced in the non-catalytic transesterification methods. For instance, supercritical methanol method uses lower energy and completes in a very short time

(2–4 min) compared to catalytic transesterification. Further, since no catalyst is used, the purification of biodiesel and the recovery of glycerol are much easier, trouble free and environment friendly [2,45,81,87]. However, the method has a high cost in reactor and operation (due to high pressures and high temperatures), and high methanol consumption (e.g., high methanol/crude-oil molar ratio of 40/1) [2,61].

There are a variety of studies have been conducted for transesterification reaction for different catalysts, alcohols and molar ratios at different temperatures. The summary of these studies is given in Table 10. Table 11 presents a comparison between

Table 11

Comparisons between chemically catalytic processes and supercritical methanol method for biodiesel production from vegetable oils by transesterification [2,101].

	Alkali catalytic method	Acid catalytic method	Supercritical method
Reaction temperature (K)	303–338	338	523–573
Reaction pressure (MPa)	0.1	0.1	10–25
Reaction time (min)	60–360	4140	7–15
Methyl ester yield (wt%)	96	90	98
Removal of	Methanol, catalyst	Methanol, catalyst	Methanol
Purification	Glycerol, soaps	Glycerol	
Free fatty acids	Saponified products	Methyl esters, water	Methyl esters, water
Process	Complicated	Complicated	Simple
Yield	Normal	Normal	High

chemically catalyzed processes and a non-catalytic supercritical methanol method for biodiesel production.

5.4.1. Variables affecting the transesterification reaction

Transesterification reaction is affected by various parameters depending upon the reaction conditions. The reaction is either incomplete or the yield is reduced to a significant extent if the parameters are not optimized. Each parameter is equally important to achieve a high quality biodiesel which meets the regulatory standards. The most important parameters that affect the transesterification process are mentioned below [2,8,29,51,68,75,89,91,93,96,99,102–109]:

1. Free fatty acids, moisture and water content.
2. Type of alcohol and molar ratio employed.
3. Type and concentration of catalysts.
4. Reaction temperature and time.
5. Rate and mode of stirring.
6. Purification of the final product.
7. Mixing intensity.
8. Effect of using organic co-solvents.
9. Specific gravity.

6. Properties and qualities of biodiesel

The advancements of biodiesel quality are being developed globally to maintain the quality of the end product and to ensure better criteria of biodiesel storage and feedstock for consumers' confidence and successful commercialization of biodiesel. Since biodiesel is produced from quite differently scaled plants of varying origins and qualities, it is necessary to install a standardization of fuel quality to guarantee an engine performance without any difficulties [29,46]. Austria was the first country in the world to define and approve the standards for rapeseed oil methyl esters as a diesel fuel. The guidelines for standards and the quality of biodiesel have also been defined in other countries such as in Germany, Italy, France, the Czech Republic and the United States [99]. Currently, the properties and qualities of biodiesel must adhere with the international biodiesel standard specifications. These specifications include the American Standards for Testing Materials (ASTM 6751-3) or the European Union (EN 14214) Standards for biodiesel fuel [35]. However, there are some other standards available globally such as in Germany (DIN 51606), Austria (ON) and Czech republic (CSN) [46]. The properties of biodiesel are characterized by physicochemical properties. Some of these properties include; caloric value (MJ/kg), cetane number, density (kg/m^3), viscosity (mm^2/s), cloud and pour points ($^{\circ}\text{C}$), flash point ($^{\circ}\text{C}$), acid value (mg KOH/g-oil), ash content (%), copper corrosion, carbon residue, water content and sediment, distillation range, sulfur content, glycerine (% m/m), phosphorus (mg/kg) and oxidation stability. The physical and chemical fuel properties of biodiesel basically depend on the type of feedstock and their fatty acids composition [35,41,46,50,79,108,110–114]. Table 12 shows the general parameters for the quality of biodiesel in different countries. A summary of physicochemical properties of diesel and biodiesel produced from different feedstocks, ASTM 6751-3 and EN 14214 specifications are shown in Table 13.

The following section gives explanations of some general properties of biodiesel.

6.1. Kinematic viscosity

Viscosity is the most important property of any fuel as it indicates the ability of a material to flow. It therefore affects the

operation of the fuel injection equipment and spray automation, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. The kinematic viscosity of biodiesel is 10–15 times greater than that of diesel fossil fuels. This is because of its large molecular mass and large chemical structure. In some cases at low temperatures biodiesel can become very viscous or even solidified. Some literatures thought that higher viscosity of biodiesel can affect the volume flow and injection spray characteristics in the engine. At low temperature it may even compromise the mechanical integrity of the injection pump drive systems. The maximum allowable limit according to ASTM D445 ranges are (1.9–6.0 mm^2/s) and (3.5–5.0 mm^2/s) in EN ISO 3104 [5,29,41,53,87,108,112,116–120].

6.2. Density and relative density

Density is the weight per unit volume. Oils that are denser contain more energy [111]. Density is measured according to EN ISO 3675/12185 and ASTM D1298. Following this standard, density should be tested at the temperature reference of 15 or 20 $^{\circ}\text{C}$ [113,120].

Relative density is the density of the component compared to the density of water. The relative density of biodiesel is needed to make mass to volume conversions, calculate flow and viscosity properties, and is used to judge the homogeneity of biodiesel tanks [121].

6.3. Flash point (FP)

Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or a spark. Flash point varies inversely with the fuel's volatility. The flash point of biodiesel is higher than the prescribed limit of diesel fossil fuel, which is safe for transport, handling and storage purpose [35,99,108,111]. Usually biodiesel has a flash point more than 150 $^{\circ}\text{C}$, while conventional diesel fuel has a flash point of 55–66 $^{\circ}\text{C}$ [121]. Demirbas [122] stated that the flash point values of fatty acid methyl esters are significantly lower than those of vegetable oils. The limit of flash point ranges in ASTM D93 is 93 $^{\circ}\text{C}$ and in EN ISO 3679 is 120 $^{\circ}\text{C}$ [41,116,120,123].

6.4. Cloud point (CP) pour point (PP) and cold filter plugging point (CFPP)

The behavior of biodiesel at low temperature is an important quality criterion. This is because partial or full solidification of the fuel may cause blockage of the fuel lines and filters, leading to fuel starvation, problems of starting, driving and engine damage due to inadequate lubrication. The cloud point is the temperature at which wax crystals first becomes visible when the fuel is cooled. Pour point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. Cloud and pour points are measured using ASTM D2500 EN ISO 23015 and D97 procedures. Generally, biodiesel has higher CP and PP compared to conventional diesel [37,41,116,120,121,124].

Cold filter plugging point (CFPP) refers to the temperature at which the test filter starts to plug due to fuel components that have started to gel or crystallize. It is a commonly used as indicator of low temperature operability of fuels and reflects their cold weather performance. At low operating temperature fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. CFPP defines the fuels limit of filterability, having a better correlation than cloud point for biodiesel as well as diesel. CFPP is measured using ASTM D6371 [41,99,108,121,125].

Table 12
General parameters of the quality of biodiesel [68,93,115].

Parameters	Austria (ON)	Czech republic (CSN)	India (BIS)	France (general official)	Germany (DIN)	Italy (UNI)	USA (ASTM)
Density at 15 °C/g/cm ³	0.85–0.89	0.87–0.89	0.87–0.89	0.87–0.89	0.875–0.89	0.86–0.90	–
Viscosity at 40 mm ² /s	3.5–5.0	3.5–5.0		3.5–5.0	3.5–5.0	3.5–5.0	1.9–6.0
Flash point (°C)	100	110		100	110	100	130
Pour point (°C)	–	–		–10	–	0/–5	–
Cetane number	≥49	≥48		≥49	≥49	–	≥47
Conradson carbon residue (%)	0.05	0.05		–	0.05	–	0.05
Iodine number	≤120	–		≤115	≤115	–	–
Methanol/ethanol (mass%)	≤0.2	–		≤0.1	≤0.3	≤0.2	–
Ester content (mass%)	–	–		≥96.5	–	≥98	–
Monoglyceride (mass%)	–	–		≤0.8	≤0.8	≤0.8	–
Diglyceride (mass%)	–	–		≤0.2	≤0.4	≤0.2	–
Triglyceride (mass%)	–	–		≤0.2	≤0.4	≤0.1	–
Free glyceride (mass%)	≤0.02	≤0.02		≤0.02	≤0.02	≤0.05	≤0.02
Total glycerol (mass%)	≤0.24	≤0.24		≤0.25	≤0.25	–	≤0.24

6.5. Titer

Titer is the temperature at which oil changes from solid to liquid. Titer is important because the transesterification process is fundamentally a liquid process, and oils with high titer may require heating, which increase the energy requirements and production costs for a biodiesel plant [45].

6.6. Cetane number (CN)

The cetane number (CN) is the indication of ignition characteristics or ability of fuel to auto-ignite quickly after being injected. Better ignition quality of the fuel is always associated with higher CN value. It is one of the most important parameters, which is considered during the selection procedure of methyl esters for using as biodiesel [29,53,99,108,116,126]. Cetane number increases with increasing chain length of fatty acids and increasing saturation. A higher CN indicates shorter time between the ignition and the initiation of fuel injection into the combustion chamber [45,127]. Biodiesel has higher cetane number than conventional diesel fuel, which results in higher combustion efficiency [124,127]. The CN of diesel, specified by ASTM D613 is 47 min and EN ISO 5165 is 51.0 min [15,120,127].

6.7. Oxidation stability (OS)

The oxidation of biodiesel fuel is one of the major factors that helps assess the quality of biodiesel. Oxidation stability is an indication of the degree of oxidation, potential reactivity with air, and can determine the need for antioxidants. Oxidation occurs due to the presence of unsaturated fatty acid chains and the double bond in the parent molecule, which immediately react with the oxygen as soon as it is being exposed to air [35,121]. The chemical composition of biodiesel fuels makes it more susceptible to oxidative degradation than fossil diesel fuel [41]. The Rancimat method (EN ISO 14112) is listed as the oxidative stability specification in ASTM D6751 and EN 14214. A minimum IP (110 °C) of 3 h is required for ASTM D6751, whereas a more stringent limit of 6 h or greater is specified in EN 14214 [125].

6.8. Lubrication properties

Atadashi et al. [35] stated that the lubrication properties of the biodiesel are better than diesel, which can help to increase the engine life. Lapuerta et al. [127] reported that fatty acid alkyl esters (biodiesel) have improved lubrication characteristics, but they can contribute to the formation of deposits, plugging of filters, depending mainly on degradability, glycerol (and other

impurities) content, cold flow properties, etc. Demirbas [110] stated that biodiesel provides significant lubricity improvement over diesel fuel. Xue et al. [119] shows that high lubricity of biodiesel might result in the reduced friction loss and thus improve the brake effective power.

6.9. Acid value

Acid number or neutralization number is a measure of free fatty acids contained in a fresh fuel sample. Free fatty acids (FFAs) are the saturated or unsaturated monocarboxylic acids that occur naturally in fats, oils or greases but are not attached to glycerol backbones. Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). The structures of common fatty acids are given in Table 14. Higher amount of free fatty acids leads to higher acid value. Acid value is expressed as mg KOH required for neutralizing 1 g of FAME. Higher acid content can cause severe corrosion in fuel supply system of an engine. The acid value is determined using the ASTM D664 and EN 14104. Both standards approved a maximum acid value for biodiesel of 0.50 mg KOH/g [8,41,79,89,116,128]. Fig. 12 shows fatty acid profile of some selected biodiesel feedstocks.

6.10. Heating value, heat of combustion

Heating value, heat of combustion is the amount of heating energy released by the combustion of a unit value of fuels. One of the most important determinants of heating value is the moisture content of the feedstock oil [45,111]. The heating value is not specified in the biodiesel standards ASTM D6751 and EN 14214 but is prescribed in EN 14213 (biodiesel for heating purpose) with a minimum of 35 MJ/kg [128].

6.11. Free glycerin

Free glycerol refers to the amount of glycerol that is left in the finished biodiesel. The content of free glycerol in biodiesel is dependent on the production process. The high yield of glycerol in biodiesel may be resulted from insufficient separation during washing of the ester product. Glycerol is essentially insoluble in biodiesel so almost all of the glycerol is easily removed by settling or centrifugation. Free glycerol may remain either as suspended droplets or as the very small amount that is dissolved in the biodiesel. High free glycerol can cause injector coking and damage to the fuel injection. The ASTM specification requires that the total glycerol be less than 0.24% of the final biodiesel product as measured using a gas chromatographic method described in ASTM D6584 and EN 14105/14106 has limit max. 0.02% [41,116,131,132].

Table 13

Properties and qualities of biodiesel produced from different feedstocks in comparison with diesel [5,9,10,26,29,35,40,44,45,47,51,53,56,59,65,78,89,94,99,101,108,110,112,114,119,121,125–129,132–134,136–178].

Fuel properties	Diesel fuel		Biodiesel		Test method	
	ASTM D975		ASTM D6751	DIN 14214	ASTM	DIN
Density 15 °C (kg/m ³)	850		880	860–900	D1298	EN ISO 3675/12185
Viscosity at 40 °C (cSt)	2.6		1.9–6.0	3.5–5.0	D-445	EN ISO 3104
Cetane number	40–55		Min. 47	Min. 51	D-613	EN ISO 5165
Iodine number	38.3		–	Max. 120	–	EN 14111
Calorific value (MJ/kg)	42–46		–	35	–	EN 14214
Acid (neutralization) value (mg KOH/g)	0.062		Max.0.50	Max.0.5	D-664	EN 14104
Pour point (°C)	–35		–15 to –16	–	D-97	–
Flash point (°C)	60–80		Min. 100–170	>120	D-93	ISO DIS 3679
Cloud point (°C)	–20		–3 to –12	–	D-2500	–
Cold filter plugging point (°C)	–25		19	Max. +5	D-6371	EN 14214
Copper strip corrosion (3 h at 50 °C)	1		Max. 3	Min.1	D-130	EN ISO 2160
Carbon (wt%)	84–87		77	–	–	–
Hydrogen (wt%)	12–16		12	–	–	–
Oxygen (wt%)	0–0.31		11	–	–	–
Methanol content % (m/m)	–		–	Max. 0.20	–	EN 14110
Water and sediment content (vol%)	0.05		Max. 0.05	Max. 500 ^b	D2709	EN ISO 12937
Ash content % (w/w)	0.01		0.02	0.02	–	EN 14214
Sulfur % (m/m)	0.05		Max. 0.05	10 ^b	D 5453	EN ISO 20846
Sulfated ash % (m/m)	–		Max. 0.02	Max. 0.02	D-874	EN ISO 3987
Phosphorus content	–		Max. 0.001	10 ^b	D-4951	EN 14107
Free glycerin % (m/m)	–		Max. 0.02	Max.0.02	D-6584	EN 14105/14106
Total glycerin % (m/m)	–		Max. 0.24	0.25	D-6584	EN 14105
Monoglyceride % (m/m)	–		0.52	0.8	–	EN 14105
Diglyceride % (m/m)	–		–	0.2	–	EN 14105
Triglyceride % (m/m)	–		–	0.2	–	EN 14105
CCR 100% (mass%)	0.17 (0.1) ^d		Max. 0.05	Max. 0.03	D-4530	EN ISO10370
Distillation temperature (%)	–		Max. 360 °C	–	D-1160	–
Oxidation stability (h, 110 °C)	–		3 min	6 min	D-675	EN 14112
Lubricity (HFRR; μm)	685		314	–	–	–

Fuel properties	Jatropha FAME	<i>Callophyllum inaphyllum</i> FAME	Madhuca FAME	Mesua FAME	Rubber FAME	<i>Camelina sativa</i> FAME	<i>Canola sativa</i> FAME	<i>Idesia polycarpa</i> var. vestita fruit FAME
Density 15 °C (kg/m ³)	879.5	888.6	874	898	–	–	–	886.2
Viscosity at 40 °C (cSt)	4.8 ^g	7.724	3.98	6.2	5.81	4.15	4.42	4.12
Cetane number	51.6	51.9	65	54	–	52.8	–	47
Iodine number	104	85	–	–	–	–	–	–
Calorific value (MJ/kg)	39.23	–	36.8	42.23	36.5	–	–	–
Acid (Neutralization) value (mg KOH/g)	0.4	0.76	0.41	0.01	–	0.31	0.01	0.27
Pour point (°C)	2	–	6	3	–8	–4	–9	–
Flash point (°C)	135	151	208	112	130	>160	>160	>174
Cloud point (°C)	2.7	38	–	–	4	3	–3.3	–4
Cold filter plugging point (°C)	0	–	–	–	–	–3	–7	–2
Copper strip corrosion (3 h at 50 °C)	1a	1b	–	–	–	1a	1a	1a
Carbon (wt%)	–	–	–	–	–	–	–	–
Hydrogen (wt%)	–	–	–	–	–	–	–	–
Oxygen (wt%)	–	–	–	–	–	–	–	–
Methanol content % (m/m)	–	–	–	–	–	–	–	–
Water and sediment content (vol%)	<0.005	–	–	0.035 ^b	–	<0.005	<0.005	–
Ash content % (m/m)	0.012	0.026	0.01	0.01	–	–	–	–
Sulfur % (m/m)	1.2 ^a	16 ^a	164.8 ^a	70 ^a	–	3 ^a	2 ^a	–
Sulfated ash % (m/m)	0.009	–	–	–	–	<0.005	<0.005	–
Phosphorus content	<0.1	0.223 ^a	–	–	–	<0.1 ^a	<0.1	–
Free glycerin % (m/m)	0.006	–	–	–	–	0.002	0.006	–
Total glycerin % (m/m)	0.1	0.232	–	–	–	0.08	0.114	–
Monoglyceride % (m/m)	0.291	–	–	–	–	0.222	0.363	–
Diglyceride % (m/m)	0.104	–	–	–	–	0.125	0.127	–
Triglyceride % (m/m)	0.022	–	–	–	–	0.022	0	–
CCR 100% (mass%)	0.025	0.434	0.02	0.25	–	0.075	0.03	–
Oxidation stability (h, 110 °C)	2.3	–	–	–	–	2.5	6.4	–
Lubricity (HFRR; μm)	–	–	–	–	–	–	–	–

Table 13 (Continued)

Fuel properties	Peanut (<i>Arachis hypogaea</i> L.) FAME	Coriander (<i>Coriandrum sativum</i> L.) FAME	Maclura FAME	Okra (<i>Hibiscus esculentus</i>) FAME	<i>Terminalia catappa</i> L. FAME	<i>Terminalia belerica</i> roxb FAME	Pumpkin (<i>Cucurbita pepo</i> L.) FAME	Tung (<i>Vernicia fordii</i>) FAME
Density 15 °C (kg/m ³)	0.8485 ^h	–	0.889 ^h	876 ± 14.9	873 ^f	882.8	883.7	901 ^f
Viscosity at 40 °C (cSt)	4.42	4.21	4.66	4.01 ± 0.10	4.3	5.17	4.41	7.07
Cetane number	53.59	53.3	48	55.2 ± 2.00	–	53	–	–
Iodine number	67.45	89	125	–	83.2	–	115	–
Calorific value (MJ/kg)	40.1	–	–	–	36.97	39.22	38.08	–
Acid (neutralization) value (mg KOH/g)	0.28	0.10	0.4	0.39 ± 0.05	–	0.23	0.48	0.11
Pour point (°C)	–8	–19	–9	2.00 ± 0.12	–	6	–	–
Flash point (°C)	166	–	180	156 ± 3.80	–	90	>120	167
Cloud point (°C)	0	–	–5	1.00 ± 0.10	–	–	–	–
Cold filter plugging point (°C)	–	–15	–	1.00 ± 0.10	–	–	–9	–19
Copper strip corrosion (3 h at 50 °C)	–	–	1a	1a	–	–	–	–
Carbon (wt%)	62.1	–	–	–	–	–	–	–
Hydrogen (wt%)	–	–	–	–	–	–	–	–
Oxygen (wt%)	–	–	–	–	–	–	–	–
Methanol content % (m/m)	–	–	–	0.181 ± 0.004	–	–	–	–
Water and sediment content (vol%)	–	–	–	–	–	0.126 ^b	490 ^k	–
Ash content % (w/w)	–	–	–	0.010 ± 0.001	–	–	–	–
Sulfur % (m/m)	0	4 ^a	–	0.012 ± 0.001	–	96 ^a	2 ^k	0.002
Sulfated ash % (m/m)	–	–	–	–	–	–	–	–
Phosphorus content	–	0	–	–	–	–	3 ^k	–
Free glycerin % (m/m)	–	0.005	–	0.012 ± 0.001	–	–	0	–
Total glycerin % (m/m)	–	0.119	–	0.220 ± 0.020	–	–	0.16	–
Monoglyceride % (m/m)	–	–	–	0.38 ± 0.05	–	–	0.47	–
Diglyceride % (m/m)	–	–	–	0.13 ± 0.02	–	–	0.15	–
Triglyceride % (m/m)	–	–	–	0.07 ± 0.01	–	–	0.14	0
CCR 100% (mass%)	–	–	–	–	–	0.0085	–	–
Oxidation stability (h, 110 °C)	–	14.6	–	1.71 ± 0.15	–	–	–	–
Lubricity (HFRR; μm)	–	–	–	138 ± 3.50	–	–	–	–
Fuel properties	Perilla seed FAME	Stillingia FAME	Poultry fat FAME	Choice white grease FAME	Hemp FAME	Hepar, high IV FAME	Hepar, low IV FAME	Corn, distiller's FAME
Density 15 °C (kg/m ³)	–	0.900 ^h	–	–	–	–	–	–
Viscosity at 40 °C (cSt)	3.937 ^g	4.81 ^g	4.496 ^g	4.536 ^g	3.874 ^g	4.422 ^g	4.643 ^g	4.382 ^g
Cetane number	–	50	–	–	–	–	–	–
Iodine number	–	–	–	–	–	–	–	–
Calorific value (MJ/kg)	–	–	–	–	–	–	–	–
Acid (neutralization) value (mg KOH/g)	0.293	0.007	0.044	0.021	0.097	0.062	0.165	0.283
Pour point (°C)	–	–	–	–	–	–	–	–
Flash point (°C)	>160	137	>160	>160	>160	>160	>160	>160
Cloud point (°C)	–8.5	–13	6.1	7	–1.3	16	6.7	–2.8
Cold filter plugging point (°C)	–11	–10	2	6	–6	13	6	–3
Copper strip corrosion (3 h at 50 °C)	1a	–	1a	1a	1a	1a	1a	1a
Carbon (wt%)	–	–	–	–	–	–	–	–
Hydrogen (wt%)	–	–	–	–	–	–	–	–
Oxygen (wt%)	–	–	–	–	–	–	–	–
Methanol content % (m/m)	–	–	–	–	–	–	–	–
Water and sediment content (vol%)	<0.005	–	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Ash content % (w/w)	–	0.037	–	–	–	–	–	–
Sulfur % (m/m)	1.5 ^a	1.5 ^a	21.1 ^a	5.4 ^a	0.4 ^a	3.4 ^a	3.1 ^a	4.6 ^a
Sulfated ash % (m/m)	<0.005	–	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Phosphorus content	<0.1 ^a	<0.1 ^a	<0.1 ^a	<0.1 ^a	<0.1 ^a	<0.1 ^a	<0.1 ^a	<0.1 ^a
Free glycerin % (m/m)	0	0	0.002	0.012	0.001	0.002	0.002	0.001
Total glycerin % (m/m)	0.091	0.156	0.079	0.095	0.151	0.070	0.088	0.66
Monoglyceride % (m/m)	0.308	0.359	0.244	0.265	0.513	0.227	0.282	0.197
Diglyceride % (m/m)	0.075	0.423	0.079	0.089	0.101	0.065	0.072	0.080
Triglyceride % (m/m)	0	0	0.02	0.019	0.022	0	0.022	0.021
CCR 100% (mass%)	0.037	0.26 (10%)	0.025	0.034	0.019	0.041	0.025	0.02
Oxidation stability (h, 110 °C)	0.2	0.6	11	0.2	0.9	1.4	1.2	2.2
Lubricity (HFRR; μm)	–	–	–	–	–	–	–	–

Table 13 (Continued)

Fuel properties	Rapeseed FAME	Sunflower FAME	Tobacco FAME	Safflower FAME	<i>Cynara cardunculus</i> L. FAME	Rice bran FAME	Microalgal 1 FAME	<i>Vernicia forii</i> FAME	
Density 15 °C (kg/m ³)	882	880.0	888.5	888.5	0.889 ^b	0.872 ^{c,h}	–	864	
Viscosity at 40 °C (cSt)	4.439 ^g	4.439	4.23 ^g	5.8 ^g	5.101 ^g	4.811 ^{g,i}	4.519	2.5	
Cetane number	54.4	49	51.6	56	59	51.6	–	53	
Iodine number	–	–	136	–	117	–	–	–	
Calorific value (MJ/kg)	37	–	–	38.122	–	41.38	–	–	
Acid (neutralization) value (mg KOH/g)	–	0.027	0.3	–	–	0.48	0.022	0.19	
Pour point (°C)	–12	–	–	–	–	269 ^j	–	–	
Flash point (°C)	170	>160	165.4	148	182	430 ^j	>160	185	
Cloud point (°C)	–3.3	3.4	–	–5	–4	–	–5.2	–	
Cold filter plugging point (°C)	–13	–3	–5	–	–10	–	–7	–	
Copper strip corrosion (3 h at 50 °C)	–	1a	1a	–	–	–	1a	–	
Carbon (wt%)	81	–	–	59.5	–	–	–	–	
Hydrogen (wt%)	12	–	–	–	–	–	–	–	
Oxygen (wt%)	7	–	–	–	–	–	–	–	
Methanol content % (m/m)	–	–	<0.01	–	–	–	–	–	
Water and sediment content (vol%)	–	<0.005	354.09 ^b	–	–	–	<0.005	–	
Ash content % (w/w)	–	–	–	–	–	–	–	–	
Sulfur % (m/m)	–	0.2 ^a	–	–	<0.02	11 ^a	5.1 ^a	–	
Sulfated ash % (m/m)	–	<0.005	0.0004	–	–	–	<0.005	–	
Phosphorus content	–	<0.1 ^a	4 ^b	–	<5	–	<0.1 ^a	–	
Free glycerin % (m/m)	–	0.007	0.002	–	–	–	0.009	0.01	
Total glycerin % (m/m)	–	0.121	0.23	–	–	–	0.091	0.04	
Monoglyceride % (m/m)	–	0.387	0.54	–	–	–	0.265	–	
Diglyceride % (m/m)	–	0.092	0.13	–	–	–	0.078	–	
Triglyceride % (m/m)	–	0.0	0.17	–	–	0	0.02	–	
CCR 100% (mass%)	–	0.035	0.29	–	0.36	0.023	0.007	0.02	
Oxidation stability (h, 110 °C)	7.6	0.9	0.8	–	–	–	8.5	–	
Lubricity (HFRR; μm)	–	–	–	–	–	280	–	–	
Fuel properties	<i>Syagrus coronata</i> FAME	Babasu FAME	Cottonseed FAME	Linseed FAME	Mustard FAME	Coconut FAME	<i>Eruca Sativa</i> Gars FAME	<i>Cammelia Japonica</i> FAME	
Density 15 °C (kg/m ³)	876 ^f	–	(875 ± 15.7) ^c	874	–	807.3	–	877	
Viscosity at 40 °C (cSt)	3.8	3.239	4.07 ± 0.04	3.752	–	2.726 ^g	5 ^g	4.7	
Cetane number	–	–	54.13 ± 1.52	52	–	–	49	54	
Iodine number	–	–	–	–	–	–	–	–	
Calorific value (MJ/kg)	37.86	–	40,430 ^e	–	–	–	38.67	–	
Acid (neutralization) value (mg KOH/g)	–	0.431	0.16 ± 0.03	0.058	0.037	0.106	0.09	0.16	
Pour point (°C)	–	–	6.00 ± 0.15	–15	–	–	–10	–	
Flash point (°C)	–	135	150 ± 3.00	<160	–	114.8	127	193	
Cloud point (°C)	–	4	7.00 ± 0.11	–3.8	3.2	0	–	–	
Cold filter plugging point (°C)	–11	10	1.00 ± 0.12	–8	–5	–4	–	–	
Copper strip corrosion (3 h at 50 °C)	1a	1a	1a	1a	1a	1b	–	–	
Carbon (wt%)	–	–	77	–	–	–	–	–	
Hydrogen (wt%)	–	–	12.5	–	–	–	–	–	
Oxygen (wt%)	–	–	10.49	–	–	–	–	–	
Methanol content % (m/m)	–	–	0.175 ± 0.002	–	–	–	–	–	
Water and sediment content (vol%)	–	<0.005	–	<0.005	–	<0.005	–	–	
Ash content % (w/w)	–	–	0.013 ± 0.001	–	–	–	–	–	
Sulfur % (m/m)	–	5.3 ^a	0.011 ± 0.001	1.9 ^a	0.9 ^a	3.2 ^a	–	–	
Sulfated ash % (m/m)	–	<0.005	–	<0.005	–	0.006	–	–	
Phosphorus content	–	<0.1	–	<0.1	<0.1	<0.1 ^a	–	–	
Free glycerin % (m/m)	–	0.008	0.015 ± 0.001	0.001	0.004	0.025	–	0.01	
Total glycerin % (m/m)	–	0.135	0.229 ± 0.015	0.12	0.062	0.065	–	0.04	
Monoglyceride % (m/m)	–	0.341	–	0.392	0.195	0.13	–	–	
Diglyceride % (m/m)	–	0.231	–	0.112	0.04	0.04	–	–	
Triglyceride % (m/m)	–	0.038	–	0	0.019	0	–	–	
CCR 100% (mass%)	–	0.05	–	0.035	–	0.01	–	0.02	
Oxidation stability (h, 110 °C)	8	15.7	1.83 ± 0.12	0.2	1.1	35.5	–	–	
Lubricity (HFRR; μm)	–	–	139.5 ± 2.6	–	–	–	–	–	
Fuel properties	Pongamia (karanja) FAME	Palm FAME	Soybean FAME	Neem FAME	<i>Hibiscus sabdariffa</i> LFAME (Rossele)	Microalgal 2 FAME	Beef tallow FAME	Borage FAME	Evening primrose FAME
Density 15 °C (kg/m ³)	931	864.42 ^c	913.8	868	880.1	–	–	–	–
Viscosity at 40 °C (cSt)	6.13	4.5	4.039	5.213 ^g	4.588 ^g	4.624 ^g	4.824 ^g	4.083 ^g	4.112 ^g
Cetane number	55	54.6	37.9	–	–	–	–	–	–
Iodine number	–	54	128–143	–	62	–	–	–	–

Table 13 (Continued)

Fuel properties	Pongamia (karanja) FAME	Palm FAME	Soybean FAME	Neem FAME	Hibiscus sabdariffa LFAME (Rossele)	Microalgal 2 FAME	Beef tallow FAME	Borage FAME	Evening primrose FAME	
Calorific value (MJ/kg)	43.42	–	39.76	39.81	–	–	–	–	–	
Acid (neutralization) value (mg KOH/g)	0.42	0.24	0.266	0.649	0.43	0.003	0.147	0.138	0.37	
Pour point (°C)	3	15	–	2	–1	–	–	–	–	
Flash point (°C)	95	135	254	76	>130	>160	>160	>160	>160	
Cloud point (°C)	7	16	0.9	9	–	3.9	16	–1.3	–7.5	
Cold filter plugging point (°C)	–	12	–4	11	–	2	14	–4	–10	
Copper strip corrosion (3 h at 50 °C)	–	1a	1a	1b	1a	1a	1a	1a	1a	
Carbon (wt%)	–	–	–	–	–	–	–	–	–	
Hydrogen (wt%)	–	–	–	–	–	–	–	–	–	
Oxygen (wt%)	–	–	–	–	–	–	–	–	–	
Methanol content % (m/m)	–	–	–	–	–	–	–	–	–	
Water and sediment content (vol%)	–	–	<0.005	<0.005	450 ^b	<0.005	<0.005	<0.005	<0.005	
Ash content % (w/w)	0.001	–	–	–	–	–	–	–	–	
Sulfur % (m/m)	50 ^a	0.003	0.8	473.8 ^a	0.00021	0.6 ^a	7.0 ^a	1.3 ^a	1.1 ^a	
Sulfated ash % (m/m)	–	0.002	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.038	
Phosphorus content	–	<0.001	<0.1 ^a	<0.1 ^a	–	<0.1 ^a	<0.1 ^a	<0.1 ^a	<0.1 ^a	
Free glycerin % (m/m)	0.015	0.01	0.012	0	0	0.014	0.008	0.001	0.005	
Total glycerin % (m/m)	0.0797	0.01	0.149	0.158	0.11	0.102	0.076	0.076	0.128	
Monoglyceride % (m/m)	–	–	0.473	0.338	0.5733	0.292	0.223	0.250	0.386	
Diglyceride % (m/m)	–	–	0.088	0.474	0.0163	0.07	0.063	0.066	0.134	
Triglyceride % (m/m)	–	–	0.019	0	0	0.019	0	0	0.035	
CCR 100% (mass%)	0.781	<0.01	0.038	0.105	0.84	0.042	0.028	0.008	0.051	
Oxidation stability (h, 110 °C)	–	10.3	2.1	7.1	2.58	11	1.6	1.8	0.2	
Lubricity (HFRR; μm)	–	172	–	–	–	–	–	–	–	
Fuel properties	Coffee FAME	Lesquerella fendleri FAME	Guizotia abyssinica L. FAME	Moringa oleifera FAME	Camellia oleifera abel FAME	Euphorbia lathyrus L. FAME	Croton megalocarpus FAME	Palm Kernel FAME	Taramira FAME	Babassu FAME
Density 15 °C (kg/m ³)	–	–	–	883 ^f	–	876.1 ^f	889.9	–	881.1	879
Viscosity at 40 °C (cSt)	4.852 ^g	10.020 ^g	4.30	5.008 ^g	4.54 ^g	4.637	4.56	8.85	5.9	3.6
Cetane number	–	–	57	67.07	–	59.6	–	–	48	63
Iodine number	–	–	–	74	–	–	–	–	–	–
Calorific value (MJ/kg)	–	–	–	–	–	–	–	34.75	–	31.8
Acid (neutralization) value (mg KOH/g)	0.076	0.63	0.15	0.185	0.22	0.19	0.16	–	0.4	–
Pour point (°C)	–	–	–	17	–	–	–9	10	–	–
Flash point (°C)	>160	>160	157	>160	150	181	189	167	52	127
Cloud point (°C)	0.2	–11.6	4	13.3	–	–	–4	13	–	4
Cold filter plugging point (°C)	–4	–6	–	13	–	–11	–	–	–	–
Copper strip corrosion (3 h at 50 °C)	1a	1a	1	1a	–	1a	–	–	1	–
Carbon (wt%)	–	–	–	–	–	–	–	–	–	–
Hydrogen (wt%)	–	–	–	–	–	–	–	–	–	–
Oxygen (wt%)	–	–	–	–	–	–	–	–	–	–
Methanol content % (m/m)	–	–	0.003	–	–	–	–	–	–	–
Water and sediment content (vol%)	<0.005	0.075	0.03	<0.005	–	400 ^b	–	–	0.05	–
Ash content % (w/w)	–	–	–	–	–	–	–	–	–	–
Sulfur % (m/m)	9.7 ^a	180.0 ^a	0.003	9.9 ^a	–	–	–	–	0.02	–
Sulfated ash % (m/m)	<0.005	0.01	0.0016	<0.005	–	–	–	–	–	–
Phosphorus content	<0.1 ^a	<0.1 ^a	<0.001	<0.1	–	–	–	–	–	–
Free glycerin % (m/m)	0.001	0.055	0.002	0.001	–	0.01	–	–	–	–
Total glycerin % (m/m)	0.178	0.307	0.017	0.067	–	0.09	–	–	–	–
Monoglyceride % (m/m)	0.575	0.559	–	0.208	–	–	–	–	–	–
Diglyceride % (m/m)	0.175	0.71	–	0.070	–	–	–	–	–	–
Triglyceride % (m/m)	0.022	0.023	–	0.021	–	–	–	–	–	–
CCR 100% (mass%)	0.004	0.109	0.018	0.033	0.038	–	–	–	0.04	–
Oxidation stability (h, 110 °C)	8.1	10.5	1.02	2.3	–	10.4	–	–	6	–
Lubricity (HFRR; μm)	–	–	–	135	–	–	–	–	–	–

^a ppm.^b mg/kg.^c Determined at 25 °C.^d wt.%.^e kJ/kg.^f Determined at 20 °C.^g mm²/s.^h g/cm³.ⁱ Determined at 313 K.^j K.^k μg g^{–1}.

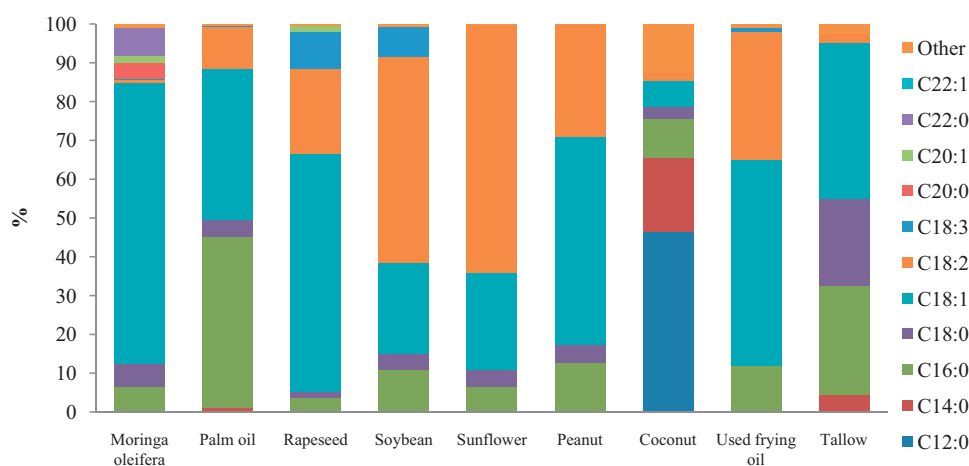


Fig. 12. Fatty acid profile of some biodiesel feedstocks [44,46,130].

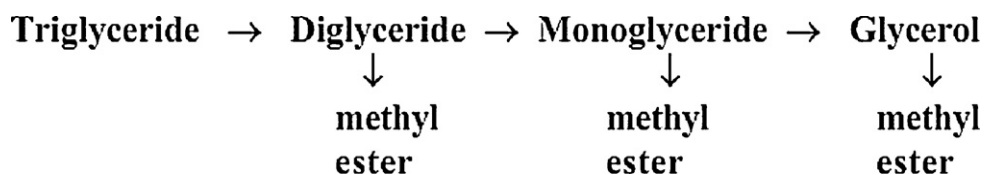
Table 14

The chemical structures of common fatty acids [38,46,51,75,89,129].

Fatty acid	Structure	Systematic name	Chemical structure
Lauric	(12:0)	Dodecanoic	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
Myristic	(14:0)	Tetradecanoic	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
Palmitic	(16:0)	Hexadecanoic	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
Stearic	(18:0)	Octadecanoic	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Oleic	(18:1)	cis-9-Octadecenoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Linoleic	(18:2)	cis-9-cis-12-Octadecadienoic	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Linolenic	(18:3)	cis-9-cis-12	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Arachidic	(20:0)	Eicosanoic	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$
Behenic	(22:0)	Docosanoic	$\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$
Erucic	(22:1)	cis-13-Docosenoic	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$
Lignoceric	(24:0)	Tetracosanoic	$\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$

6.12. Total glycerol

Total glycerin is a measurement of how much triglyceride remains unconverted into methyl esters. Total glycerin is calculated from the amount of free glycerin, monoglycerides, diglycerides, and triglycerides [133]. The reactions are shown below:



Each reaction step produces a molecule of a methyl ester of a fatty acid. If the reaction is incomplete, then there will be triglycerides, diglycerides, and monoglycerides left in the reaction mixture. Each of these compounds still contains a glycerol molecule that has not been released. The glycerol portion of these compounds is referred to as bound glycerol. When the bound glycerol is added to the free glycerol, the sum is known as the total glycerol. The ASTM specification requires that the total glycerol be less than 0.24% of the final biodiesel product as measured using a gas chromatographic method described in ASTM D 6584 and 0.25% in EN 14105. Fuels that do not meet these specifications are prone to coking; thus, may cause the formation of deposits on the injector nozzles, pistons and valves [41,116,131].

6.13. Water content and sediment

Water and sediment contamination are basically housekeeping issues for biodiesel. Water can present in two forms, either as dissolved water or as suspended water droplets. While biodiesel is generally considered to be insoluble in water, it actually takes up considerably more water than diesel fuel. Biodiesel can contain as much as 1500 ppm of dissolved water while diesel fuel usually only takes up about 50 ppm. Sediment may consist of suspended rust and dirt particles or it may originate from the fuel as insoluble compounds formed during fuel oxidation [116,131,132]. Water and sediment testing is done using 100 mL of biodiesel and centrifuging it at 1870 rpm for 11 min. If the water and sediment level is below 0.005 vol% (vol), the result is reported as <0.005 vol% [121]. Water in the fuel generally causes two problems. First, it can cause corrosion of engine fuel system components. The most direct form of corrosion is rust, but water can become acidic with time and the resulting acid corrosion can attack fuel storage tanks. Water contamination can contribute to microbial growth. The species of yeast, fungi, and bacteria can grow at the interface between the fuel and water at the bottom of a storage tank. The organisms produce sludges and slimes that can cause filter plugging. Some of the organisms can convert the sulfur in the fuel to sulfuric acid which can corrode metal fuel tanks. Moreover, high water contents can

also contribute to hydrolysis reaction that is responsible for converting biodiesel to free fatty acids which is also linked to fuel filter blockage. The standard of water content and sediment for biodiesel in ASTM D2709 and EN ISO 12937 specifications is 0.05 (vol%) max. [41,116,131,134,135].

6.14. Sulfated ash

The ash content describes the amount of inorganic contaminants such as abrasive solids, catalyst residues and the concentration of soluble metal soaps contained in a fuel sample. The biodiesel is ignited and burned and then treated with sulfuric acid to determine

Table 15

Known problems, probable cause and potential solutions for using straight vegetable oil in diesel engines [58,81,89,91,179].

Problem	Probable cause	Potential solution
Short-term		
1. Cold weather starting	<ul style="list-style-type: none"> • High viscosity, low cetane number and low flash point of vegetable oils 	<ul style="list-style-type: none"> • Preheat fuel prior to injection
2. Plugging and gumming of filters, lines and injectors	<ul style="list-style-type: none"> • Natural gums (phosphatides) in vegetable oil. • Other ash 	<ul style="list-style-type: none"> • Refine the oil partially to remove gums
3. Engine knocking	<ul style="list-style-type: none"> • Low cetane numbers. Improper injection timing 	<ul style="list-style-type: none"> • Adjust injection timing • Use higher compression engines. Preheat fuel prior to injection. Chemically alter fuel to an ester
Long term		
4. Cooking of injector on piston and engine head	<ul style="list-style-type: none"> • High viscosity of vegetable oil • Incomplete combustion of fuel 	<ul style="list-style-type: none"> • Heat fuel prior to injection • Switch engine to diesel fuel when operation at part loads • Chemically alter the vegetable oil to an ester
5. Carbon deposits on piston and head of engine	<ul style="list-style-type: none"> • Poor combustion at part load with vegetable oils • High viscosity of vegetable oil • Incomplete combustion of fuel • Poor combustion at part load with vegetable oils • High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil 	<ul style="list-style-type: none"> • Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester
6. Excessive engine wear	<ul style="list-style-type: none"> • High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil 	<ul style="list-style-type: none"> • Heat fuel prior to injection • Switch engine to diesel fuel when operation at part loads • Chemically alter the vegetable oil to an ester. Increase motor oil changes • Motor oil additives to inhibit oxidation • Heat fuel prior to injection • Switch engine to diesel fuel when operation at part loads • Chemically alter the vegetable oil to an ester • Increase motor oil changes • Motor oil additives to inhibit oxidation
7. Failure of engine lubricating oil due to polymerization	<ul style="list-style-type: none"> • Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs 	<ul style="list-style-type: none"> • Heat fuel prior to injection • Switch engine to diesel fuel when operation at part loads • Chemically alter the vegetable oil to an ester • Increase motor oil changes • Motor oil additives to inhibit oxidation

the percentage of sulfated ash present in the biodiesel. The ASTM D874 standard mentions that the samples can have a maximum 0.02% of sulfated ash [116,121].

6.15. Carbon residue

Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel after combustion. Canradsons carbon residue for biodiesel is more important than that in diesel fuel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities. Although this residue is not solely composed of carbon, the term carbon residue is found in all standards because it has long been commonly used. The range of limit standard ASTM D4530 is max. 0.050% (m/m) and EN ISO10370 is max. 0.30% (m/m) [41,99,108,116,121].

6.16. Copper strip corrosion

The copper corrosion test measures the corrosion tendency of fuel when used with copper, brass, or bronze parts. A copper strip is heated to 50 °C in a fuel bath for 3 h followed by comparison with a standard strips to determine the degree of corrosion. Corrosion resulting from biodiesel might be induced by some sulfur compounds by acids; hence this parameter is correlated with acid number. The ASTM D130 standard mentions that the samples can have class 3 and EN ISO 2160 has class 1 [41,116,121].

6.17. Cold soak filtration

Cold soak filtration is the newest biodiesel requirement set in ASTM D6751. The cold soak filtration test is done to determine if crystals form at low temperatures and do not redissolve when the biodiesel returns to a higher temperature. The ASTM D6751 procedure involves chilling 300 mL of biodiesel for 16 h at 40 °F, removing

the sample and letting the sample warm back up to room temperature. When the sample has warmed back up to 20–22 °C, it is filtered through a 0.7 µm filter paper. The sample is timed as it passes through the filter paper and when all 300 mL passes through the paper, the result is reported (in seconds). The maximum allowable test result for cold soak filtration is 360 s [121].

6.18. Visual inspection

The visual inspection test is used to determine the presence of water and particulates in biodiesel. It is measured as a haze value by placing a line chart behind a clear jar of biodiesel and referencing how the lines compare to six different pictures with haze ratings from 1 to 6, with 1 being the least amount of particulates and 6 being the highest. A haze rating of 1 is the clearest; while a haze rating of 6 means that the biodiesel is very cloudy. Visual inspection of biodiesel is determined by ASTM D4176, Standard Test. Method for Free Water and Particulate Contamination in Distillate Fuels (Visual Inspection Procedures), Procedure 2 [121].

6.19. Phosphorous, calcium, and magnesium

The specifications from ASTM D6751 state that phosphorous content in biodiesel must be less than 10 ppm, and calcium and magnesium combined must be less than 5 ppm. Phosphorous was determined using ASTM D4951, calcium and magnesium were determined using EN Standard 14538 [121].

6.20. Moisture contents

Moisture is the amount of water which cannot be converted to biodiesel. Moisture can react with the catalyst during transesterification which can lead to soap formation and emulsions. The moisture in the biodiesels is measured in accordance with ASTM E203 standard test method for water (up to 1500 ppm). In Europe,

Table 16

Advantages and disadvantages of biodiesel.

	Reference
Advantages of biodiesel	
Biodiesel has 10–11% of oxygen; this makes biodiesel a fuel with high combustion characteristics	[29,35,53,64,75,76,79,114,122,126,149,154,157,176]
Biodiesel reduces net carbon-dioxide emissions by 78% on a lifecycle basis when compared to conventional diesel fuel and reduces smoke due to free soot	[35,131,154]
Biodiesel is renewable, non-toxic, non-flammable, portable, readily available, biodegradable, sustainable, eco-friendly and free from sulfur and aromatic content, this makes it an ideal fuel for heavily polluted cities. Biodiesel also reduces particular matter content in the ambient air and hence reduces air toxicity. It provides a 90% reduction in cancer risks and neonatal defects due to its less polluting combustion	[2,10,27,29,35,53,58,64,76,115,123,154,179–182]
Biodiesel helps rural development to restore degraded lands over a period. Moreover, it has good potential for rural employment generation	[76]
Biodiesel serves as climatic neutral in view of the climatic change that is presently an important element of energy use and development	[29,35,76,108,125,149,154,157,176]
Biodiesel has higher cetane number (about 60–65 depending on the vegetable oil) than petroleum diesel (53) which reduces the ignition delay	[2,27,29,35,41,53,58,65,122,126,149,176]
Production can be raised easily and is less time consuming	
No need for drilling, transportation, or refining like petroleum diesel. Therefore, each country has the ability to produce biodiesel as a locally produced fuel. Moreover, there is no need to pay tariffs or similar taxes to the countries from which oil and petroleum diesel is imported	[27,79,93,176]
Biodiesel has superior better lubricity properties. This improves lubrication in fuel pumps and injector units, which decreases engine wear, tear and increases engine efficiency	[29,58,79,122,126,149,162,179]
Biodiesel is safe for transportation, handling, distribution, utilization and storage due to its higher flash point (above 100–170 °C) than petroleum diesel (60–80 °C)	[2,27,29,53,122,123,149,154,179,181]
Biodiesel reduces the environmental effect of a waste product and can be made out of used cooking oils and lards	[79,93,128,154,176]
Biodiesel may not require engine modification up to B ₂₀ . However, higher blends may need some minor modification	[93]
Disadvantages of biodiesel	
Biodiesel has 12% lower energy content than diesel, this leads to an increase in fuel consumption of about 2–10%. Moreover, biodiesel has higher cloud point and pour point, higher nitrogen oxide emissions than diesel. It has lower volatilities that cause the formation of deposits in engines due to incomplete combustion characteristics	[2,29,47,53,58,79,93,118,131,134,180]
Biodiesel causes excessive carbon deposition and gum formation (polymerization) in engines and the oil gets contaminated and suffers from flow problem. It has relatively higher viscosity (11–18 times diesel) and lower volatility than diesel and thus needs higher injector pressure	[31,176]
Oxidation stability of biodiesels is lower than that of diesel. It can be oxidized into fatty acids in the presence of air and causes corrosion of fuel tank, pipe and injector	[108,176]
Due to the high oxygen content in biodiesel, advance in fuel injection and timing and earlier start of combustion, biodiesel produces relatively higher NO _x levels than diesel in the range of 10–14% during combustion	[27,53,93,99,108,111,113,119,135,149,182]
Biodiesel can cause corrosion in vehicle material (cooper and brass) such as fuel system blockage, seal failures, filter clogging and deposits at injection pumps	[79,93,108]
Use of biodiesel in internal combustion engine may lead to engine durability problems including injector cocking, filter plugging and piston ring sticking, etc.	[2,28]
As more than 95% of biodiesel is made from edible oil, there have been many claims that this may give rise to further economic problems. By converting edible oils into biodiesel, food resources are being used as automotive fuels. It is believed that large-scale production of biodiesel from edible oils may bring about a global imbalance in the food supply-and-demand market	[58]
Lower engine speed and power, high price, high engine wear, engine compatibility	[58]
Transesterification process is expensive (cost of fuel increases), these oils require expensive fatty acid separation or use of less effective (or expensive acid catalysts)	[108,112,118,124]
The transesterification has some environmental effects such as waste disposal and water requirement for washing, soap formation, etc.	[108,117]

standard EN 14214 has a Karl Fischer moisture specification of 0.050 wt% maximum tried [45,108,121].

7. Problems and potential solutions of using vegetable oils

The direct use of vegetable oils or blends has generally been considered to be impractical for both direct and indirect diesel engines. The high viscosity, low volatility, acid composition, free fatty acid and moisture content, gum formation due to oxidation and polymerization during storage and combustion, poor cold engine start-up, misfire, ignition delay, incomplete combustion, carbon deposition around the nozzle orifice, ring sticking, injector choking in engine and lubricating oil thickening are the major problems of using vegetable oils. In general, the problems associated with using straight vegetable oil in diesel engines are classified into short term and long term. Table 15 highlights the problems, probable causes and the potential solutions [8,43,53,58,80,81,88,89,99].

8. Advantages and disadvantages of biodiesel

Table 16 gives a summary of the advantages and disadvantages of biodiesel.

9. Economical viability of biodiesel

Biodiesel is an attractive renewable energy resource. However, there are some challenges that face this vital resource. These challenges include the high cost and limited availability of biodiesel feedstock beside the cheaper prices of crude petroleum. There are various factors contributing to the cost of biodiesel. These factors include feedstock prices, plant's capacity, feedstock quality, processing technology, net energy balance nature of purification and its storage, etc. However, the two main factors are the costs of feedstocks and the cost of processing into biodiesel. It has been found that the cost of feedstocks accounts for 75% of the total cost

of biodiesel fuel. Therefore, selecting the best feedstock is vital to ensure low biodiesel cost. It has been found that, considering non-edible oils as a feedstock for biodiesel can reduce this cost. In terms of production cost, there also are two aspects, the transesterification process cost and by-the product (glycerol) recovery. The continuous transesterification process is one choice to lower the production cost. The foundations of this process are a shorter reaction time and greater production capacity. The recovery of high quality glycerol is another way to lower biodiesel production cost. Therefore, biodiesel plant must have its own glycerol recovery facility [9,21,29,53,58,75,76,108].

According to IEA [183], biodiesel produced with current technology in OECD countries are still two to three times more expensive than gasoline and diesel. Moreover, a review of many economic feasibility studies around the world shows that biodiesel usually costs over US\$0.5 per liter compared to US \$0.35 per liter for normal diesel. Currently biodiesel cost is 1.5–3 times higher than the fossil diesel cost in developed countries. Biodiesel is thus currently not economically feasible, and more research and technological development are needed. Thus supporting policies such as tax credits are important to promote bio-diesel research and make their prices competitive with other conventional sources of energy [53,58,75,89,122,130,179,184].

10. Future of biodiesel

Acceptance of Kyoto protocol and clean development mechanism (CDM) will lead to more biodiesel production around the world. For instance, it is anticipated that this policy will lead to a total bio-fuel demand in EU of around 19.5 and 30.3 million tons in 2012 and 2020 respectively. Biodiesel production is expanding rapidly around the world, driven by energy security and other environmental concerns. Given geographic disparities between demand and supply potential, and supply cost, expanded trade in biodiesel appears to make sense. Global potential in biodiesel production is very unclear, but in the long run it could be a substantial percentage of transport fuel demand. Currently, biodiesel can be more effective if used as a complement to other energy sources.

With the increase in global human population, more land will be needed to produce food for human consumption. Thus, the insufficient lands could increase the production cost of biodiesel plants. This problem already exists in Asia where vegetable oil prices are relatively high. The same trend will eventually happen in the rest of the world. This is the potential challenge to biodiesel production. Therefore, non-edible oil, genetically engineered plants and microalgae feedstocks can be proper solutions for this problem and can ensure the sustainability of biodiesel production in the future [43,75,183,185].

11. Conclusion

Energy is an indispensable factor for human to preserve economic growth and maintain standard of living. Globally, the transportation sector is the second largest energy consuming sector after the industrial sector and accounts for 30% of the world's total delivered energy. This sector has experienced a steady growth in the past 30 years. It has been estimated that the global transportation energy use is expected to increase by an average of 1.8% per year from 2005 to 2035. Nearly all fossil fuel energy consumption in the transportation sector is from oil (97.6%). However, the expected depletion of fossil fuels and the environmental problems associated with burning them has encouraged many researchers to investigate the possibility of using alternative fuels. Among them, biodiesel seems a very promising resource. The wide range of available feedstock for biodiesel production represents one of the most

important advantages of producing biodiesel. From the literature, it has been found that feedstock alone represents more than 75% of the overall biodiesel production cost. Therefore, selecting the best feedstock is vital to ensure low production cost of biodiesel.

From this overview, it can be concluded that searching for biodiesel feedstocks should focus on those feedstocks that do not compete with food crops, do not lead to land-clearing and provide greenhouse-gas reductions. Non-edible oils such as *J. curcas* and *C. inophyllum*, and more recently microalgae and genetically engineered plants such as poplar and switchgrass have emerged to be very promising feedstocks for biodiesel production.

Oil extraction is the second step of biodiesel production. There are three main methods that have been identified for extraction of the oil, mechanical, solvent and enzymatic oil extraction. It has been found that the solvent extraction using n-hexane method results in the highest oil yield which makes it the most common type.

Biodiesel properties must adhere with the international biodiesel standard specifications such as the American Standards for Testing Materials (ASTM 6751-3) or the European Union (EN 14214) for biodiesel fuel. These properties can be improved by four methods: pyrolysis, dilution with hydrocarbons blending, Micro-emulsion, and transesterification. Transesterification is regarded as the best method among other approaches due to its low cost and simplicity. The properties of biodiesel are characterized by physicochemical properties. In this paper, some of these properties such as cetane number, density, viscosity, cloud and pour points, flash point, acid value, copper corrosion, glycerine and oxidation stability have been presented.

Biodiesel is currently not economically feasible, and more research and technological development are needed. As a recommendation, supporting policies are important to promote biodiesel research and make their prices competitive with other conventional sources of energy.

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