Progress and recent trends in biodiesel fuels

Ayhan Demirbas *

Sila Science, Trabzon, Turkey

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ABSTRACT

Fossil fuel resources are decreasing daily. Biodiesel fuels are attracting increasing attention worldwide as blending components or direct replacements for diesel fuel in vehicle engines. Biodiesel fuel typically comprises lower alkyl fatty acid (chain length C_{14}–C_{22}), esters of short-chain alcohols, primarily, methanol or ethanol. Various methods have been reported for the production of biodiesel from vegetable oil, such as direct use and blending, microemulsification, pyrolysis, and transesterification. Among these, transesterification is an attractive and widely accepted technique. The purpose of the transesterification process is to lower the viscosity of the oil. The most important variables affecting methyl ester yield during the transesterification reaction are the molar ratio of alcohol to vegetable oil and the reaction temperature. Methanol is the commonly used alcohol in this process, due in part to its low cost. Methyl esters of vegetable oils have several outstanding advantages over other new-renewable and clean engine fuel alternatives. Biodiesel fuel is a renewable substitute fuel for petroleum diesel or petrodiesel fuel made from vegetable or animal fats; it can be used in any mixture with petrodiesel fuel, as it has very similar characteristics, but it has lower exhaust emissions. Biodiesel fuel has better properties than petrodiesel fuel; it is renewable, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel seems to be a realistic fuel for future; it has become more attractive recently because of its environmental benefits. Biodiesel is an environmentally friendly fuel that can be used in any diesel engine without modification.

1. Introduction

The scarcity of conventional fossil fuels, growing emissions of combustion-generated pollutants, and their increasing costs will make biomass sources more attractive [1]. Petroleum-based fuels are limited reserves concentrated in certain regions of the world. These sources are on the verge of reaching their peak production. The fossil fuel resources are shortening day by day. The scarcity of known petroleum reserves will make renewable energy sources more attractive [2].

Biodiesel (Greek, bio, life + diesel from Rudolf Diesel) refers to a diesel-equivalent, processed fuel derived from biological sources. Biodiesel fuels are attracting increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines. Biodiesel, as an alternative fuel for internal combustion engines, is defined as a mixture of monoalkyl esters of long chain fatty acids (FAME) derived from a renewable lipid feedstock, such as vegetable oil or animal fat. Biodiesel typically comprises alkyl fatty acid (chain length C_{14}–C_{22}) esters of short-chain alcohols, primarily, methanol or ethanol. Biodiesel is the best candidate for diesel fuels in diesel engines. Biodiesel is now mainly being produced from soybean, rapeseed, and palm oils. The higher heating values (HHVs) of biodiesels are relatively high. The HHVs of biodiesels (39–41 MJ/kg) are slightly lower than those of gasoline (46 MJ/kg), petrodiesel (43 MJ/kg), or petroleum (42 MJ/kg), but higher than coal (32–37 MJ/kg) [3].

An alternative fuel to petrodiesel must be technically feasible, economically competitive, environmentally acceptable, and easily available. The current alternative diesel fuel can be termed biodiesel. Biodiesel can offer other benefits, including reduction of greenhouse gas emissions, regional development and social structure, especially to developing countries [4]. However, for quantifying the effect of biodiesel it is important to take into account several other factors such as raw material, driving cycle, and vehicle technology. Use of biodiesel will allow a balance to be sought between agriculture, economic development, and the environment [5]. Biodiesel methyl esters improve the lubrication properties of the diesel fuel blend. Biodiesel reduced long term engine wear in diesel engines. Biodiesel is a good lubricant (about 66% better than petrodiesel) [6].

Petroleum and diesel come in the category of non-renewable fuel and will last for a limited period of time. These non-renewable fuels also emit pollutants in the form of oxides of nitrogen, oxides of sulfur, oxides of carbon, lead, hydrocarbons, etc. Criteria pollutant emissions from biodiesel blends are now becoming a relevant subject due to the increase in consumption of this renewable fuel

* Address: Selcuk University, 42031 Konya, Turkey. Tel.: +90 462 230 7831; fax: +90 462 248 8508.
E-mail address: ayhandemirbas@hotmail.com.

worldwide. Biodiesel is the first and only alternative fuel to commercial diesel to have a complete evaluation of emission results. Biodiesel is derived from vegetable oils and hence is a renewable fuel. A renewable fuel such as biodiesel, along with lesser exhaust emissions is the need of the present scenario worldwide [6].

Biodiesel is pure, or 100%, biodiesel fuel. It is referred to as B100 or "neat" fuel. A biodiesel blend is pure biodiesel blended with petrodiesel. Biodiesel blends are referred to as BXX. The XX indicates the amount of biodiesel in the blend (i.e., a B80 blend is 80% biodiesel and 20% petrodiesel).

In general terms, biodiesel may be defined as a domestic, renewable fuel for diesel engines derived from natural oils like soybean oil that meets the specifications of ASTM D 6751. In technical terms (ASTM D 6751) biodiesel is a diesel engine fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated B100 and meeting the requirements of ASTM D 6751. Biodiesel, in application as an extender for combustion in CIEs (diesel), possesses a number of promising characteristics, including reduction of exhaust emissions [7]. Biodiesel is a mixture of methyl esters of long-chain fatty acids like lauric, palmitic, stearic, oleic, etc. The chemistry of conversion into biodiesel is essentially the same. Oil or fat reacts with methanol or ethanol in the presence of a sodium hydroxide or potassium hydroxide catalyst to form biodiesel, (m)ethyl esters, and glycerol.

Technical properties of biodiesel are given in Table 1. Biodiesel is a clear amber-yellow liquid with a viscosity similar to that of petrodiesel. Biodiesel is non-flammable and, in contrast to petrodiesel, is non-explosive, with a flash point of 423 K for biodiesel as compared to 337 K for petrodiesel. Unlike petrodiesel, biodiesel is biodegradable and non-toxic, and it significantly reduces toxic and other emissions when burned as a fuel.

Table 2 shows the fuel ASTM standards of biodiesel and petroleum diesel fuels. Important operating disadvantages of biodiesel in comparison with petrodiesel are cold start problems, lower energy content, higher copper strip corrosion, and fuel pumping difficulty from higher viscosity. Currently, biodiesel is more expensive to produce than petrodiesel, which appears to be the primary factor in preventing its more widespread use. Current worldwide production of vegetable oil and animal fat is not enough to replace liquid fossil fuel use [8].

Biodiesel is a technologically feasible alternative to fossil diesel, but nowadays biodiesel costs 1.5–3 times more than fossil diesel. As far as actual fuel costs are concerned, the cost of biodiesel currently is comparable to that of gasoline. Biodiesel will be a reasonably available engine fuel in the near future. Table 3 shows the availability of modern transportation fuels. The advantage of biodiesel in this aspect is that it is a derivative of natural products. As demand rises, the production of the required agricultural products can be increased to compensate [6].

2. Sources of biodiesel raw materials

Typical raw materials of biodiesel are rapeseed oil, canola oil, soybean oil, sunflower oil and palm oil. Beef and sheep tallow and poultry oil from animal sources and cooking oil are also sources of raw materials. There are various other biodiesel sources: almond, andiroba (*Carapa guianensis*), babassu (*Orbignia sp.*), barley, camelina (*Camelina sativa*), coconut, copra, cumaru (*Dipteryx odorata*), *Cynara cardunculus*, fish oil, groundnut, *Jatropha curcas*, karanja (*Pongamia glabra*), laurel, *Lesquerella fendleri, Madhuca indica*, microalgae (*Chlorella vulgaris*), oat, piqui (*Caryocar sp.*), poppy seed, rice, rubber seed, sesame, sorghum, tobacco seed, and wheat [9].

Vegetable oils are renewable fuels. They have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources. Vegetable oils are a renewable and potentially inexhaustible source of energy, with energy content close to that of diesel fuel. Global vegetable oil production increased from 56 million tons in 1990 to 88 million tons in 2000, following a below-normal increase. The source of this gain was distributed among the various oils. Global consumption rose 56–86 million tons, leaving world stocks comparatively tight [10].

A variety of biolipids can be used to produce biodiesel. These are (a) virgin vegetable oil feedstock; rapeseed and soybean oils are most commonly used, though other crops such as mustard, palm oil, sunflower, hemp, and even algae show promise; (b) waste vegetable oil; (c) animal fats including tallow, lard, and yellow grease; and (d) non-edible oils such as jatropha, neem oil, castor oil, and tall oil [6].

Various oils have been in use in different countries as raw materials for biodiesel production owing to its availability. Soybean oil is commonly used in United States and rapeseed oil is used in many European countries for biodiesel production, whereas, coconut oil and palm oils are used in Malaysia and Indonesia for biodiesel production [11–14]. In India and southeast Asia, the Jatropha tree (*Jatropha cursas*) [15], Karanja (*Pongamia pinnata*) [12,16,17] and Mahua (*M. indica*) [11] is used as a significant fuel source.

Commonly accepted biodiesel raw materials include the oils from soy, canola, corn, rapeseed, and palm. New plant oils that are under consideration include mustard seed, peanut, sunflower, and cotton seed. The most commonly considered animal fats include those derived from poultry, beef, and pork [18]. Rapeseed has been grown in Canada since 1936. Hundreds of years ago, Asians and Europeans used rapeseed oil in lamps. Cottonseed oil is used almost entirely as a food material. Sesame, olive, and peanut oils can be used to add flavor to a dish. Walnut oil is high-quality edible oil refined by purely physical means from quality walnuts.

Algae can grow practically anywhere where there is enough sunshine. Some algae can grow in saline water. All algae contain proteins, carbohydrates, lipids and nucleic acids in varying proportions. While the percentages vary with the type of algae, there are algae types that are comprised up to 40% of their overall mass by fatty acids [19]. The most significant distinguishing characteristic of algal oil is its yield and hence its biodiesel yield. According to some estimates, the yield (per acre) of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils [20]. Microalgae are the fastest-growing photosynthesizing organisms. They can complete an entire growing cycle every few days. Approximately 46 tons of oil/hectare/year can be produced from diatom algae. Different algae species produce different amounts

Table 1
Technical properties of biodiesel

Common name	Biodiesel (bio-diesel)
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C_{14}–C_{24} methyl esters or $C_{15-25}H_{28-48}O_2$
Kinematic viscosity range (mm²/s, at 313 K)	3.3–5.2
Density range (kg/m³, at 288 K)	860–894
Boiling point range (K)	>475
Flash point range (K)	420–450
Distillation range (K)	470–600
Vapor pressure (mm Hg, at 295 K)	<5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

Table 2
ASTM standards of biodiesel and petrodiesel fuels

Property	Test method	ASTM D975 (petrodiesel)	ASTM D6751 (biodiesel, B100)
Flash point	D 93	325 K min	403 K
Water and sediment	D 2709	0.05 max %vol	0.05 max %vol
Kinematic viscosity (at 313 K)	D 445	1.3–4.1 mm^2/s	1.9–6.0 mm^2/s
Sulfated ash	D 874	–	0.02 max %wt
Ash	D 482	0.01 max %wt	–
Sulfur	D 5453	0.05 max %wt	–
Sulfur	D 2622/129	–	0.05 max %wt
Copper strip corrosion	D 130	No. 3 max	No. 3 max
Cetane number	D 613	40 min	47 min
Aromaticity	D 1319	35 max %vol	–
Carbon residue	D 4530	–	0.05 max %mass
Carbon residue	D 524	0.35 max %mass	–
Distillation temp (90% volume recycle)	D 1160	555 K min–611 K max	–

Table 3
Availability of modern transportation fuels

Fuel type	Availability	
	Current	Future
Gasoline	Excellent	Moderate-poor
Biodiesel	Moderate	Excellent
Compressed natural gas (CNG)	Excellent	Moderate
Hydrogen fuel cell	Poor	Excellent

of oil. Some algae produce up to 50% oil by weight. The production of algae to harvest oil for biodiesel has not been undertaken on a commercial scale, but working feasibility studies have been conducted to arrive at the above number. Specially bred mustard varieties can produce reasonably high oil yields and have the added benefit that the meal left over after the oil has been pressed out can act as an effective and biodegradable pesticide [6].

3. Use of vegetable oils and animal fats in fuel engines

The interest in the use of renewable fuel started with the direct use of vegetable oils as a substitute for diesel. Vegetable oils have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources. More than 100 years ago, Rudolph Diesel tested vegetable oil as the fuel for his engine [21]. Vegetable oils have the potential to replace a fraction of the petroleum distillates and petroleum-based petrochemicals in the near future. However, their direct use in compression engines was restricted due to high viscosity which resulted in poor fuel atomization, incomplete combustion and carbon deposition on the injector and the valve seats causing serious engine fouling [22,23].

Chemically speaking, vegetable oils and animal fats are triglyceride molecules in which three fatty acid groups are esters attached to one glycerol molecule [24]. Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdoms that are made up of 1 mol of glycerol and three moles of fatty acids and are commonly referred to as triglycerides [25]. Triglyceride vegetable oils and fats include not only edible but also inedible vegetable oils and fats such as linseed oil, castor oil, and tung oil.

More than 350 oil-bearing crops have been identified, of which only soybean, palm, sunflower, safflower, cottonseed, rapeseed, and peanut oils are considered potential alternative fuels for diesel engines [26,27]. Table 4 shows the oil species that can be used in biodiesel production.

Biodiesel obtained from waste cooking vegetable oils has been considered a promising option. Waste cooking oil is available with relatively cheap price for biodiesel production in comparison with fresh vegetable oil costs. Table 5 shows comparison of properties of waste cooking oil, biodiesel from waste cooking oil and commercial diesel fuel. The properties of biodiesel and diesel fuels, in general, show many similarities, and therefore, biodiesel is rated as a realistic fuel as an alternative to diesel. The conversion of waste cooking oil into methyl esters through the transesterification process approximately reduces the molecular weight to one-third, reduces the viscosity by about one-seventh, reduces the flash point slightly and increases the volatility marginally, and reduces pour point considerably.

3.1. Vegetable oil and fat resources

World annual petroleum consumption and vegetable oil production is about 4.018 and 0.107 billion tons, respectively. Global vegetable oil production increased from 56 million tons in 1990 to 88 million tons in 2000, following a below-normal increase. Leading the gains in vegetable oil production was a recovery in world palm oil output, from 18.5 million tons in 1998 to 27.8 million in 2003. The major exporters of vegetable oils are Malaysia, Argentina, Indonesia, the Philippines, and Brazil. The major importers of vegetable oils are China, Pakistan, Italy, and the United King-

Table 4
Oil species for biodiesel production

Group	Source of oil
Major oils	Coconut (copra), corn (maize), cottonseed, canola (a variety of rapeseed), olive, peanut (groundnut), safflower, sesame, soybean, and sunflower
Nut oils	Almond, cashew, hazelnut, macadamia, pecan, pistachio and walnut
Other edible oils	Amaranth, apricot, argan, artichoke, avocado, babassu, bay laurel, beech nut, ben, Borneo tallow nut, carob pod (algaroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit (*Acrocomia sclerocarpa*), meadowfoam seed, mustard, okra seed (hibiscus seed), perilla seed, pequi, (*Caryocar brasiliensis* seed), pine nut, poppy seed, prune kernel, quinoa, ramtil (*Guizotia abyssinica* seed or Niger pea), rice bran, tallow, tea (camellia), thistle (*Silybum marianum* seed), and wheat germ
Inedible oils	Algae, babassu tree, copaiba, honge, jatropha or ratanjyote, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, and tall
Other oils	Castor, radish, and tung

Table 5
Comparison of properties of waste cooking oil, biodiesel from waste cooking oil and commercial diesel fuel

Fuel property	Waste cooking oil	Biodiesel from waste cooking oil	Commercial diesel fuel
Kinematic viscosity (mm^2/s, at 313 K)	36.4	5.3	1.9–4.1
Density (kg/L, at 288 K)	0.924	0.897	0.075–0.840
Flash point (K)	485	469	340–358
Pour point (K)	284	262	254–260
Cetane number	49	54	40–46
Ash content (%)	0.006	0.004	0.008–0.010
Sulfur content (%)	0.09	0.06	0.35–0.55
Carbon residue (%)	0.46	0.33	0.35–0.40
Water content (%)	0.42	0.04	0.02–0.05
Higher heating value (MJ/kg)	41.40	42.65	45.62–46.48
Free fatty acid (mg KOH/g oil)	1.32	0.10	–
Saponification value	188.2	–	–
Iodine value	141.5	–	–

Table 6
Oil and fat feedstock distribution top ten developed countries with self-sufficiency potential in 2006

Feedstock	%
Animal fats	52
Soybean oil	20
Rapeseed oil	11
Palm oil	6
Sunflower oil	5
Other vegetable oils	5

dom. A few countries such as the Netherlands, Germany, the United States, and Singapore are both major exporters as well as importers of vegetable oils [8]. Table 6 shows the oil and fat feedstock distribution of the top 10 developed countries with self-sufficiency potential in 2006 [6].

3.1.1. Inedible oil and fat resources

The inedible oils such as *J. curcas*, *M. indica*, *Ficus elastica*, *Azardirachta indica*, *Calophyllum* inophyllum jatropha, neem, *P. pinnata*, rubber seed, mahua, silk cotton tree, and tall oil microalgae are easily available in developing countries and are very economical comparable to edible oils.

The oils from neem (*A. indica*) and rubber (*Hevea brasiliensis*) have high free fatty acid (FFA) content. FFAs easily react with alkaline catalysts to form soap that prohibits the separation of biodiesel and glycerol. The soaps of FFAs also cause foaming in aqueous media. The resulting soaps also cause an increase in viscosity, formation of gels, and foams and make the separation of glycerol difficult [28,29].

The main commodity sources for biodiesel production from inedible oils are plant species such as jatropha or ratanjyote or seemaikattamankku (*J. curcas*), karanja or honge (*P. pinnata*), nagchampa (*C. inophyllum*), rubber seed tree (*Hevca brasiliensis*), neem (*Azadirachta indica*), mahua (*M. indica* and *Madhuca longifolia*), silk cotton tree (*Ceiba pentandra*), jojoba (*Simmondsia chinensis*), babassu tree, *Euphorbia tirucalli*, and microalgae. Tall oil fatty acids, obtained from kraft pulping, can be used as a source of raw material for biodiesel, or as a source of additives for petrodiesel [30]. They are easily available in many parts of the world and are very cheap compared to edible oils in India [31].

Two major species of the genus, *M. indica* and *M. longifolia*, are found in India. The oil of the rubber seed tree (*H. brasiliensis*) is a non-edible source of biodiesel production. It is found mainly in Indonesia, Malaysia, Liberia, India, Srilanka, Sarawak, and Thailand. Rubber seed kernels (50–60% of seed) contain 40–50% of brown oil [32]. Two major species of the genus, the oil palms *Elaeis guineensis* and *Elaeis oleifera*, are in Africa and Central/South America, respectively. Among vegetable oils, the price of palm oil is cheapest in

palm-producing countries such as Malaysia, Indonesia, Thailand, and Korea. Neem oil is a vegetable oil pressed from the fruits and seeds of Neem (*A. indica*), an evergreen tree that is endemic to the Indian subcontinent and has been introduced to many other areas native to India and Burma, growing in tropical and semitropical regions. Jojoba oil is produced in the seed of the jojoba (*S. chinensis*) plant, a shrub native to southern Arizona, southern California, and northwestern Mexico [33]. The oil of the silk cotton tree (*C. pentandra*) is a non-edible source of biodiesel production. The tree belongs to the family *Bornbacacea*. The silk cotton tree has great economic importance for both domestic and industrial uses in Nigeria. The seeds are also used as food/feed for humans and livestock in many parts of the world such as India, Tanzania, and Mozambique. *Ceiba pentendra* crude oil was extracted for 24 h using a Soxhlet extractor with *n*-hexane as a solvent [34]. Babassu tree is a species of palm tree that is a source of light yellow clear oil. There are both edible and non-edible species of babassu oils. A non-edible species of the oil is obtained from the babassu tree, which is widely grown in Brazil. The viscosity at 313.2 K and the Cetane number values of babassu oil are 3.6 cSt and 63, respectively [35].

Fatty acid profiles of *A. indica*, *C. inophyllum*, *J. curcas*, *P. pinnata* were found most suitable for use as biodiesel [36,37]. The seed oil of *Jatropha* was used as a diesel fuel substitute during World War II and as blends with diesel [38–40]. Thus *J. curcas* and *P. pinnata* (Karanja) are most suitable for the purpose of producing renewable fuel as biodiesel [41,42]. Jatropha and Karanja have high oil content (25–30%) [38,40].

From 1978 to 1996, the US Department of Energy's Office of Fuels Development funded a program to develop renewable transportation fuels from algae [20]. Most current research on oil extraction is focused on microalgae to produce biodiesel from algal oil. Algal oil processes into biodiesel as easily as oil derived from land-based crops. The lipid and fatty acid contents of microalgae vary in accordance with culture conditions. Algal oil contains saturated and monounsaturated fatty acids. The fatty acids were determined in the algal oil in the following proportions: 36% oleic (18:1), 15% palmitic (16:0), 11% stearic (18:0), 8.4% *iso*- 17:0, and 7.4% linoleic (18:2). The high proportion of saturated and monounsaturated fatty acids in this alga is considered optimal from a fuel quality standpoint in that fuel polymerization during combustion would be substantially less than what would occur with polyunsaturated fatty-acid-derived fuel [20].

Oil from algae, bacteria, and fungi have also been investigated [21]. Microalgae have been examined as a source of methyl ester diesel fuel [43], and terpenes and latexes also were studied as diesel fuels [44].

Algae can grow virtually anywhere with enough sunshine. Some algae can grow in saline water. The most significant distinguishing

characteristic of algal oil is in the yield and hence its biodiesel yield. According to some estimates, the yield (per acre) of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils [20]. Microalgae are the fastest growing photosynthesizing organisms. They can complete an entire growing cycle every few days. Approximately, 46 tons of oil/hectare/year can be produced from diatom algae. Different algae species produce different amounts of oil. Some algae produce up to 50% oil by weight. Microalgae have much faster growth rates than terrestrial crops. The per unit area yield of oil from algae is estimated to be between 5000 and 20,000 gallons per acre per year, which is 7–31 times greater than the next best crop, palm oil.

Palm oil is widely grown in south East Asia; 90% of the palm oil produced is used for food and the remaining 10% for non-food consumption, such as the production of oleo-chemicals [45]. An alternative use could be its conversion to liquid fuels and chemicals. Conversion of palm oil into biodiesel using methanol has been reported [46]. There are great differences between palm oil and palm kernel oil with respect to their physical and chemical characteristics. Palm oil contains mainly palmitic (16:0) and oleic (18:1) acids, the two common fatty acids, and about 50% saturated fat, while palm kernel oil contains mainly lauric acid (12:0) and more than 89% saturated fat [47].

3.2. Direct use of vegetable oils in Diesel engines

More than 100 years ago, Dr. Rudolph Diesel tested vegetable oil as fuel for his engine [21]. The main advantages of vegetable oils as diesel fuel are ready availability, renewability, lower sulfur and aromatic content, and biodegradability [26]. The main disadvantages of vegetable oils as diesel fuel are higher viscosity, lower volatility, and the reactivity of unsaturated hydrocarbon chains. The problems met in long-term engine tests, according to results obtained by earlier researchers, may be classified as follows: coking on injectors, more carbon deposits, oil ring sticking, and thickening and gelling of the engine lubricant oil [48–51]. All vegetable oils are extremely viscous, with viscosities ranging from 10 to 17 times greater than No. 2 diesel fuel (No. 2 diesel fuel is a diesel engine fuel with 10 to 20 carbon number hydrocarbons) [29,35].

Vegetable oils can be used as fuels for diesel engines, but their viscosities are much higher than that of common diesel fuel and require modifications of the engines [52]. Vegetable oils could only replace a very small fraction of transport fuel. Different methods have been considered to reduce the viscosity of vegetable oils such as dilution, microemulsification, pyrolysis, catalytic cracking and transesterification.

3.2.1. Dilution of vegetable oils

Dilution of vegetable oils with solvents lowers the viscosity, some engine performance problems, such as injector coking and more carbon deposits. The viscosity of oil can be lowered by blending with pure ethanol. Twenty-five parts of sunflower oil and 75 parts of diesel were blended as diesel fuel [53]. The viscosity was 4.88 cSt at 313 K, while the maximum specified ASTM value is 4.0 cSt at 313 K. This mixture was not suitable for long term use in a direct injection engine. Another study was conducted by using the dilution technique on the same frying oil [54]. The addition of 4% ethanol to No. 2 diesel fuel increases the brake thermal efficiency, brake torque and brake power, while decreasing the brake specific fuel consumption. Since the boiling point of ethanol is less than that of No. 2 diesel fuel, it could assist the development of the combustion process through an unburned blend spray [55].

3.2.2. Microemulsion of oils

Short-chain alcohols such as ethanol or methanol were used for microemulsions [56]. To reduce of the high viscosity of vegetable oils, microemulsions with immiscible liquids such as methanol and ethanol and ionic or non-ionic amphiphiles have been studied [56]. The 2-octanol was found an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil [29,57]. Ziejewski et al. (1984) prepared an emulsion of 53% (vol) alkali-refined and winterized sunflower oil, 13.3% (vol) ethanol and 33.4% (vol) 1-butanol. Lower viscosities and better spray patterns (more even) were observed with an increase of 1-butanol.

3.2.3. Pyrolysis and catalytic cracking

Pyrolysis is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst [58,59]. Pyrolysis and catalytic cracking of oils and fats result in production of alkanes, alkenes, alkadienes, cycloalkanes, alkylbenzenes, carboxylic acids, aromatics and small amounts of gaseous products [21,60–67]. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules [68]. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids.

Soybean oil was thermally decomposed and distilled in air and nitrogen sparged with a standard ASTM distillation apparatus [69,70]. The main components were alkanes and alkenes, which accounted for approximately 60% of the total weight. Carboxylic acids accounted for another 9.6–16.1%. Catalytic cracking of vegetable oils to produce biofuels has been studied [71]. Copra oil and palm oil stearin were cracked over a standard petroleum catalyst SiO_2/Al_2O_3 at 723 K to produce gases, liquids and solids with lower molecular weights. The condensed organic phase was fractionated to produce biogasoline and biodiesel fuels.

Pyrolysis of triglycerides has been investigated for more than 100 years, especially in areas of the world that lack deposits of petroleum. The liquid fuel produced from pyrolysis has similar chemical components to conventional petroleum diesel fuel [72].

Palm oil stearin and copra oil was subjected to conversion over different catalysts like silica–alumina and zeolite [71]. It was found that the conversion of palm and copra oil was 84 wt% and 74 wt%, respectively. The silica–alumina catalyst was highly selective for obtaining aliphatic hydrocarbons, mainly in the kerosene boiling point range [73]. Palm oil was converted into hydrocarbons using a shape selective zeolite catalyst [45]. Palm oil can be converted into gasoline, diesel and kerosene, light gases, coke and water with a yield of 70 wt%. The maximum yield of gasoline-range hydrocarbons was 40 wt% of the total product.

Palm oil has been cracked at atmospheric pressure at a reaction temperature of 723 K to produce biofuel in a fixed-bed microreactor. The reaction was carried out over microporous HZSM-5 zeolite, mesoporous MCM-41, and composite micromesoporous zeolite as catalysts. The products obtained were gas, organic liquid, water, and coke. The organic liquid product was composed of hydrocarbons corresponding to the gasoline, kerosene, and diesel boiling point ranges. The maximum conversion of palm oil, 99 wt%, and gasoline yield of 48 wt% was obtained with composite micromesoporous zeolite [74]. Table 7 presents the conversion of palm oil

Table 7
Catalytic cracking of palm oil over HZSM-5 with different Si/Al ratios

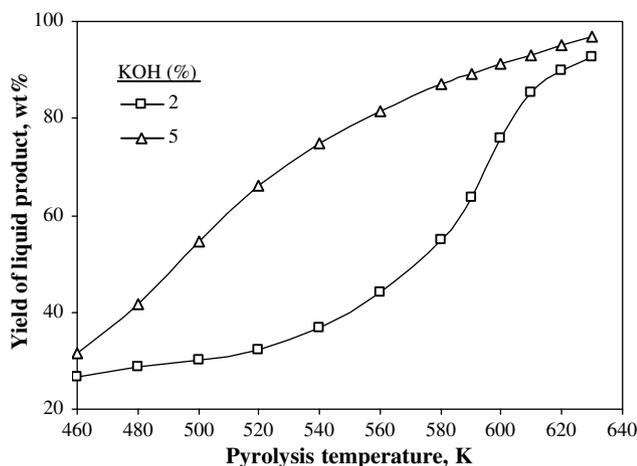| Catalyst ID	HZSM-5(50)	HZSM-5(240)	HZSM-5(400)
Conversion (wt%)	96.9	96.0	94.0
Gas yield (wt%)	17.5	14.0	8.2
Water yield (wt%)	6.8	4.6	6.1
OLP (wt%)			
Total organic liquid yield	70.9	76.0	78.0
Gasoline (wt%)	44.6	45.9	49.3
Kerosene (wt%)	19.6	24.6	26.1
Diesel (wt%)	6.7	5.5	2.6
Coke (wt%)	1.7	1.4	1.7

Source: Ref. [74].

Fig. 1. Yield of liquid products from pyrolysis of sunflower oil at different temperatures in presence of KOH. Pyrolysis time: 30 min.

over HZSM-5 with different Si/Al ratios of catalyst by catalytic cracking. The gasoline yield increased with an increase in the Si/Al ratio due to the decrease in the secondary cracking reactions and the drop in the yield of gaseous products [74].

Recycling and rerefining are the applicable processes for upgrading of vegetable oils by converting them into reusable products such as gasoline and diesel fuel. Possible acceptable processes are transesterification, cracking, and pyrolysis [75,76]. Fig. 1 shows the plots for yield of liquid products from pyrolysis of the sunflower oil at different temperatures in the presence of KOH. The nominal pyrolysis time was 30 min. The yields of liquid products increase with increasing temperature and amounts of KOH. The yield sharply increases between 580 and 610 K and then reaches a plateau value with a 2% KOH run. Qualitative observations show that the pyrolytic liquid products from the runs with KOH are highly viscous by comparing the waste-cooking sunflower oil. The repolymerization degree of the pyrolytic liquid products increases with increasing temperature [6].

3.2.3.1. Diesel-like fuel from tallow (beef) by pyrolysis. Tallow is a mixture of triglycerides, most of which are saturated; tristearin is usually the major component [29]. The tallow from animal sources is commonly used in soap production. In tallow the saturated fatty acid component accounts for almost 50% of the total fatty acids. The higher palmitic and stearic acid contents give tallow its unique properties of high melting point and high viscosity.

Table 8 shows the average composition of fatty acids in tallow [6]. The total fatty acids in the tallow samples were 51.1% by weight. The major fatty acids in the tallow were palmitic (28.7%), stearic (19.5), and oleic (44.4%). Higher palmitic and stearic acid contents give the tallow a high melting point [6].

Fig. 2 shows the effect of temperature on total liquid and diesel-like liquid yields from tallow by pyrolysis [6]. The reaction parameters of pyrolysis are temperature and resistance time. The
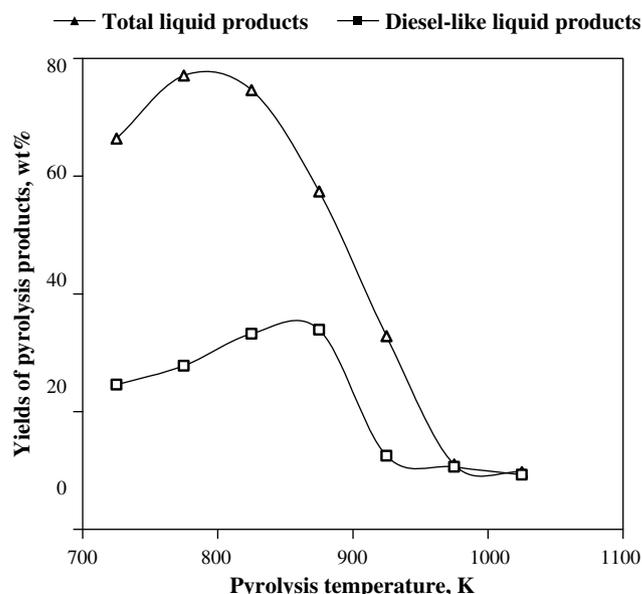
Table 8
Average composition of fatty acids in tallow (wt%)

Fatty acid	%
Myristic (14:0)	2.9
Palmitic (16:0)	28.7
Stearic (18:0)	19.5
Oleic (18:1)	44.4
Linoleic (18:2)	3.6
Linolenic (18:3)	0.9

Fig. 2. Effect of temperature on total liquid and diesel-like liquid yields from tallow by pyrolysis (reaction time: 45 min).

maximum total liquid product obtained from pyrolysis was 77.1% at 775 K. The yield of diesel-like liquid from pyrolysis of the tallow increases from 24.6% to 33.9% with increasing temperature from 725 to 875 K and then sharply decreases.

Fig. 3 shows the comparison of distillation curves of average distillation products obtained from pyrolysis and steam reforming of tallow to that of No. 2 diesel fuel. As can be seen from the figure, the first distillation products of 25% and 40% from pyrolysis and steam reforming, respectively, are similar to the distillation product from No. 2 diesel fuel.

3.2.4. Transesterification of oils and fats

Transesterification is a chemical reaction between triglyceride and alcohol in the presence of catalyst. It consists of a sequence of three consecutive reversible reactions where triglycerides are
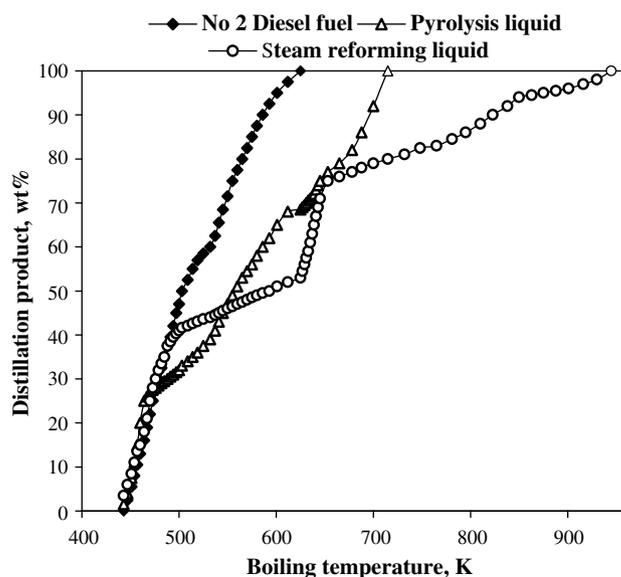

Fig. 3. Comparison of distillation curves of average distillation products obtained from pyrolysis and steam reforming of tallow to that of D 2 fuel.

$$
\begin{array}{llll}
CH_2\text{–OOC–}R_1 & & R_1\text{–COO–}R & CH_2\text{–OH} \\
| & & & | \\
CH\text{–OOC–}R_2 & +\ 3ROH \xrightleftharpoons{\ Catalyst\ } & R_2\text{–COO–}R\ + & CH\text{–OH} \\
| & & & | \\
CH_2\text{–OOC–}R_3 & & R_3\text{–COO–}R & CH_2\text{–OH} \\
\\
\text{Triglyceride} & \text{Alcohol} & \text{Esters} & \text{Glycerol}
\end{array}
$$

Fig. 4. Transesterification of triglycerides with alcohol.

$$
\begin{array}{llll}
CH_2\text{–OOC–}R_1 & & R_1\text{–COO–}R & CH_2\text{–OOCCH}_3 \\
| & & & | \\
CH\text{–OOC–}R_2 & +\ 3RCOOCH_3 \xrightleftharpoons{\ Lipase\ } & R_2\text{–COO–}R\ + & CH\text{–OOCCH}_3 \\
| & & & | \\
CH_2\text{–OOC–}R_3 & & R_3\text{–COO–}R & CH_2\text{–OOCCH}_3
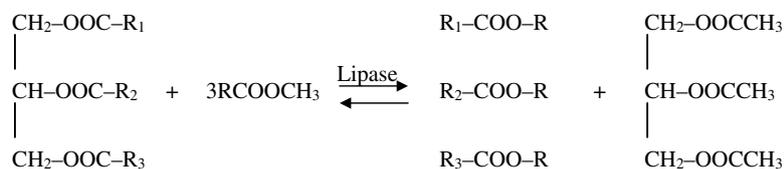\end{array}
$$

Fig. 5. Enzymatic biodiesel production by interesterification with methyl acetate.

converted to diglycerides and then diglycerides are converted to monoglycerides followed by the conversion of monoglycerides to glycerol. In each step an ester is produced and thus three ester molecules are produced from one molecule of triglycerides [16]. The transesterification reaction requires a catalyst such as sodium hydroxide to split the oil molecules and an alcohol (methanol or ethanol) to combine with the separated esters. Out of these three methods transesterification is the most viable process adopted known so far for the lowering of viscosity. It also gives glycerol as a byproduct which has a commercial value. Among all these alternatives, transesterification seems to be the best choice as the physical characteristics of fatty acid (m)ethyl esters (biodiesel) are very close to those of diesel fuel and the process is relatively simple. In the esterification of an acid, an alcohol acts as a nucleophilic reagent; in the hydrolysis of an ester, an alcohol is displaced by a nucleophilic reagent. This alcoholysis (cleavage by an alcohol) of an ester is called transesterification [77]. Fig. 4 shows the transesterification reaction of triglycerides with alcohol. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side.

Acid catalyst and alkali catalyst are used depending upon the nature of the oil used for biodiesel production. Another catalyst in study is lipase. Lipase has advantage over acid and alkali catalyst but its cost is a limiting factor for its use at large scale production of biodiesel. Choice of acid and alkali catalyst depends on the free fatty acids (FFA) content in the raw oil. FFA should not exceed a certain amount for transesterification to occur by an alkali catalyst. Fig. 5 shows enzymatic biodiesel production by interesterification with methyl acetate in the presence of lipase enzyme as catalyst.
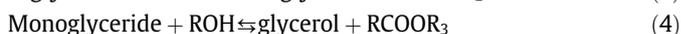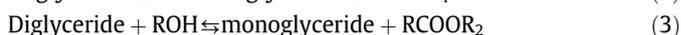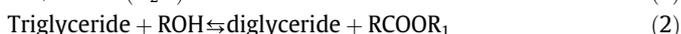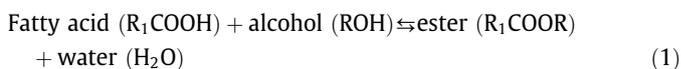
The emergence of transesterification can be dated back to as early as 1846 when Rochieder described glycerol preparation through the ethanolysis of castor oil [78]. Since that time alcoholysis has been studied in many parts of the world. Other researchers have also investigated the important reaction conditions and parameters in the alcoholysis of triglycerides such as fish oils, tallow, soybean, rapeseed, cottonseed, sunflower, safflower, peanut, and linseed oils [79–84].

4. Biodiesel from triglycerides via transesterification

The transesterification reaction proceeds with catalyst or without any catalyst by using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms. Among the alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently. Ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment [10]. However methanol is preferable because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). Table 9 shows comparison of various methanolic transesterification methods.

Triacylglycerols (vegetable oils and fats) are esters of long-chain carboxylic acids combined with glycerol. Carboxylic acids {R–C(=O)–O–H} can be converted into methyl esters {R–C(=O)–O–CH_3} by the action of a transesterification agent. The parameters affecting the methyl ester formation are reaction temperature, pressure, molar ratio, water content, and free fatty acid content. It was observed that increasing the reaction temperature had a favorable influence on the yield of ester conversion. The yield of alkyl ester increased when the oil-to-alcohol molar ratio was increased [6,29].

$$
\text{Fatty acid }(R_1COOH) + \text{alcohol }(ROH) \rightleftharpoons \text{ester }(R_1COOR)
$$
$$
+ \text{ water }(H_2O) \tag{1}
$$
$$
\text{Triglyceride} + ROH \rightleftharpoons \text{diglyceride} + RCOOR_1 \tag{2}
$$
$$
\text{Diglyceride} + ROH \rightleftharpoons \text{monoglyceride} + RCOOR_2 \tag{3}
$$
$$
\text{Monoglyceride} + ROH \rightleftharpoons \text{glycerol} + RCOOR_3 \tag{4}
$$

Transesterification consists of a number of consecutive, reversible reactions. The triglyceride is converted stepwise into diglyceride, monoglyceride, and, finally, glycerol (Eqs. (1)–(4)) in which 1 mol of alkyl esters is removed in each step. The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps [6]. The formation of alkyl esters from monoglycerides is believed to be the step that determines the reaction rate since monoglycerides are the most stable intermediate compound [29].

Table 9
Comparison of various methanolic transesterification methods

Method	Reaction temperature (K)	Reaction time (min)
Acid or alkali catalytic process	303–338	60–360
Boron trifluoride–methanol	360–390	20–50
Sodium methoxide–catalyzed	293–298	4–6
Non-catalytic supercritical methanol	523–573	6–12
Catalytic supercritical methanol	523–573	0.5–1.5

4.1. Catalytic transesterification methods

Vegetable oils can be transesterified by heating them with a large excess of anhydrous methanol and a catalyst. The transesterification reaction can be catalyzed by alkalis [85,86], acids [87,88], or enzymes [89–93]. Various studies have been carried out using different oils as raw material, different alcohols (methanol, ethanol, butanol), as well as different catalysts, including homogeneous ones such as sodium hydroxide, potassium hydroxide, and sulfuric acid, and heterogeneous ones such as lipases [94], CaO [95] and MgO [96].

4.1.1. Acid-catalyzed transesterification methods

Main acid-catalyzed transesterification methods are methanolic sulfuric acid [11,15,32,97,98], ferric sulfate [88], sulfonic acid [99], methanolic hydrogen chloride [49], and methanolic boron trifluoride [100].

Sulfuric acid, hydrochloric acid, and sulfonic acid are usually preferred as acid catalysts. The catalyst is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into the biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil.

The transesterification process is catalyzed by Brønsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow. The alcohol/vegetable oil molar ratio is one of the main factors that influence transesterification. An excess of the alcohol favors the formation of alkyl esters. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process. Fig. 6 shows the mechanism of acid-catalyzed esterification of fatty acids. The initial step is protonation of the acid to give an oxonium ion (1), which can undergo an exchange reaction with an alcohol to give the intermediate (2), and this in turn can lose a proton to become an ester (3). Each step in the process is reversible, but in the presence of a large excess of the alcohol, the equilibrium point of the reaction is displaced so that esterification proceeds virtually to completion.

Fig. 7 shows the mechanism of acid-catalyzed transesterification of vegetable oils [101]. In this instance, initial protonation of the ester is followed by addition of the exchanging alcohol to give the intermediate (4), which can be dissociated via the transition state (5) to give the ester (6).

4.1.2. Alkali catalytic transesterification methods

In the alkali catalytic methanol transesterification method, the catalyst (KOH or NaOH) is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into a biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil. The final mixture is stirred vigorously for 2 h at 340 K in ambient pressure. A successful transesterification reaction produces two liquid phases: ester and crude glycerol.
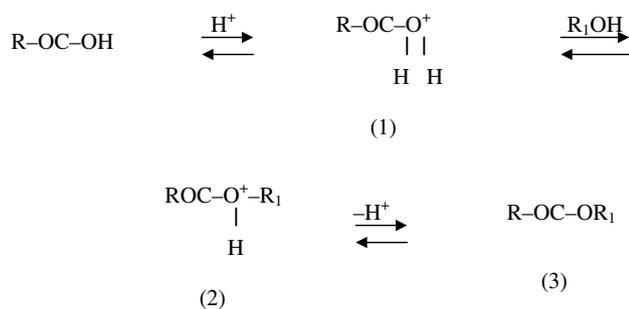
The alkali-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. The first step is the reaction of the base with the alcohol, producing an alkoxide and a protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate, from which the alkyl ester and the corresponding anion of the diglyceride are formed. Diglycerides and monoglycerides are converted by the same mechanism into a mixture of alkyl esters and glycerol. Alkaline metal alkoxides (as CH_3ONa for methanolysis) are the most active catalysts since they give very high yields (>98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water, which makes them inappropriate for typical industrial processes [102].

A number of detailed recipes for sodium-methoxide-catalyzed transesterification have been given [103]. The methodology can be used on quite a large scale if need be. The reaction between sodium methoxide in methanol and a vegetable oil is very rapid. It has been shown that triglycerides can be completely transesterified in 2–5 min at room temperature. The methoxide anion is prepared by dissolving the clean metals in anhydrous methanol. Sodium methoxide (0.5–2 M) in methanol effects transesterification of triglycerides much more rapidly than other transesterification agents. At equivalent molar concentrations with the same triglyceride samples, potassium methoxide effects complete esterification more quickly than does sodium methoxide. Because of the dangers inherent in handling metallic potassium, which has a very high heat of reaction with methanol, it is preferable to use sodium methoxide in methanol. The reaction is generally slower with alcohols of higher molecular weight. As with acidic catalysis, inert solvents must be added to dissolve simple lipids before methanolysis will proceed [103].

4.1.3. Enzyme-catalyzed transesterification

Biodiesel can be obtained from enzyme or biocatalytic transesterification methods [90–93]. Transesterification can be carried out chemically or enzymatically. In recent work three different lipases (*Chromobacterium viscosum*, *Candida rugosa*, and Porcine pancreas) were screened for a transesterification reaction of jatropha oil in a solvent-free system to produce biodiesel; only lipase from C. viscosum was found to give appreciable yield [40]. Immobilization of lipase (*C. viscosum*) on Celite-545 enhanced the biodiesel yield to 71% from the 62% yield obtained by using free tuned enzyme preparation with a process time of 8 h at 113 K. Immobilized C. viscosum lipase can be used for ethanolysis of oil. It was seen that immobilization of lipases and optimization of transesterification conditions resulted in adequate yield of biodiesel in the case of the enzyme-based process [40].

Although the enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in recent articles and patents. The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism that generates the enzyme, etc.) in order to establish suitable characteristics for an industrial application. However, the reaction yields as well as the reaction times are still unfavorable compared to the base-catalyzed reaction systems [102]. Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis.

4.2. Non-catalytic transesterification methods

There are two non-catalyzed transesterification processes. These are the BIOX process and the supercritical alcohol (methanol) process.
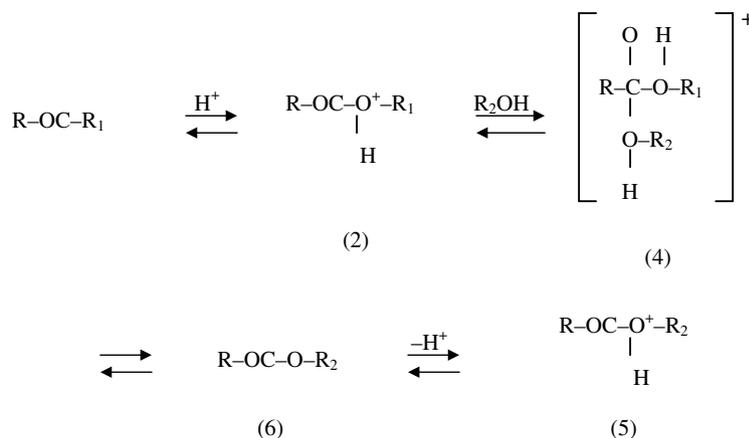
R–OC–OH $\xrightarrow[]{H^+}$ R–OC–O$^+$ with H H below $\xrightarrow[]{R_1OH}$

$$(1)$$

ROC–O$^+$–R$_1$ with H below $\xrightarrow[]{-H^+}$ R–OC–OR$_1$

$$(2) \qquad (3)$$

Fig. 6. Mechanism of acid-catalyzed esterification of fatty acids.

$$R–OC–R_1 \xrightleftharpoons[\leftarrow]{H^+} R–OC–O^+–R_1 \atop \quad | \atop \quad H \xrightleftharpoons[\leftarrow]{R_2OH} \begin{bmatrix} O \quad H \\ | \quad | \\ R–C–O–R_1 \\ | \\ O–R_2 \\ | \\ H \end{bmatrix}^+$$

$$(2) \hspace{6cm} (4)$$

$$\xrightleftharpoons[\leftarrow]{} R–OC–O–R_2 \xrightleftharpoons[\leftarrow]{-H^+} R–OC–O^+–R_2 \atop \qquad\qquad | \atop \qquad\qquad H$$

$$(6) \hspace{6cm} (5)$$

Fig. 7. Mechanism of acid-catalyzed transesterification of vegetable oils.

4.2.1. Biodiesel production with BIOX cosolvent process

The BIOX (cosolvent) process is a new Canadian process developed originally by Professor David Boocock of the University of Toronto that has attracted considerable attention. Dr. Boocock has transformed the production process through the selection of inert cosolvents that generate an oil-rich one-phase system. This reaction is over 99% complete in seconds at ambient temperatures, compared to previous processes that required several hours. BIOX is a technology development company that is a joint venture of the University of Toronto Innovations Foundation and Madison Ventures Ltd. BIOX's patented production process converts first the free fatty acids (by way of acid esterification) up to 10% FFA content and then the triglycerides (by way of transesterification), through the addition of a co-solvent, in a two-step, single phase, continuous process at atmospheric pressures and near-ambient temperatures. The co-solvent is then recycled and reused continuously in the process. The unique feature of the BIOX process is that it uses inert reclaimable cosolvents in a single-pass reaction taking only seconds at ambient temperature and pressure. The developers are aiming to produce biodiesel that is cost competitive with petrodiesel. The BIOX process handles not only grain-based feedstocks but also waste cooking greases and animal fats [104].

The BIOX process uses a cosolvent, tetrahydrofuran, to solubilize the methanol. Cosolvent options are designed to overcome slow reaction times caused by the extremely low solubility of the alcohol in the triglyceride phase. The result is a fast reaction, on the order of 5–10 min, and no catalyst residues in either the ester or the glycerol phase.

4.2.2. Supercritical alcohol transesterification

In the conventional transesterification of animal fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation, consumes the catalyst, and reduces catalyst effectiveness, all of which results in a low conversion [105]. The transesterification reaction may be carried out using either basic or acidic catalysts, but these processes require relatively time-consuming and complicated separation of the product and the catalyst, which results in high production costs and energy consumption. To overcome these problems, Kusdiana and Saka [106] and Demirbas [50,107] have proposed that biodiesel fuels may be prepared from vegetable oil via non-catalytic transesterification with supercritical methanol (SCM). A novel process of biodiesel fuel production has been developed by a non-catalytic supercritical methanol method. Supercritical methanol is believed to solve the problems associated with the two-phase nature of normal methanol/oil mixtures by forming a single phase as a result of the lower value of the dielectric constant of methanol in the supercritical state. As a result, the reaction was found to be complete in a very short time [108]. Compared with the catalytic processes under barometric pressure, the supercritical methanol process is non-catalytic, involves a much simpler purification of products, has a lower reaction time, is more environmentally friendly, and requires lower energy use. However, the reaction requires temperatures of 525–675 K and pressures of 35–60 MPa [50,106].

The stoichiometric ratio for transesterification reaction requires 3 mol of alcohol and 1 mol of triglyceride to yield 3 mol of fatty acid ester and 1 mol of glycerol. Higher molar ratios result in greater ester production in a shorter time. In one study, the vegetable oils were transesterified at 1:6 to 1:40 vegetable oil–alcohol molar ratios in catalytic and supercritical alcohol conditions [107].

Fig. 8 shows two-stages continuous biodiesel production process with subcritical water and supercritical methanol. In the first stage triglycerides rapidly hydrolyze to free fatty acids under 10 MPa pressure at 445 K temperature. When the pressure is reduced the mixture promptly separates into two phases and the water phase can be separated to recover glycerol [30]. Methanol becomes supercritical at a pressure of 10 MPa and temperature of 445 K, and the supercritical conditions favor rapid formation of methyl esters from the fatty acids.

Table 10 shows the comparisons between the catalytic methanol method and the supercritical methanol method for biodiesel from vegetable oils by transesterification. The supercritical methanol process is non-catalytic, involves simpler purification, has a lower reaction time, and is less energy intensive. Therefore, the supercritical methanol method would be more effective and efficient than the common commercial process [109].

4.2.3. Catalytic supercritical methanol transesterification

Catalytic supercritical methanol transesterification is carried out in an autoclave in the presence of 1–5% NaOH, CaO, and MgO as catalyst at 520 K. In the catalytic supercritical methanol transesterification method, the yield of conversion rises to 60–90% for the first minute [6]. Transesterification reaction of the crude oil of rapeseed with supercritical/subcritical methanol in the presence of a relatively low amount (1%) of NaOH was successfully carried out, where soap formation did not occur [110].

5. Effect of different parameters on production of biodiesel

The parameters affecting methyl ester formation are reaction temperature, pressure, molar ratio, water content, and free fatty
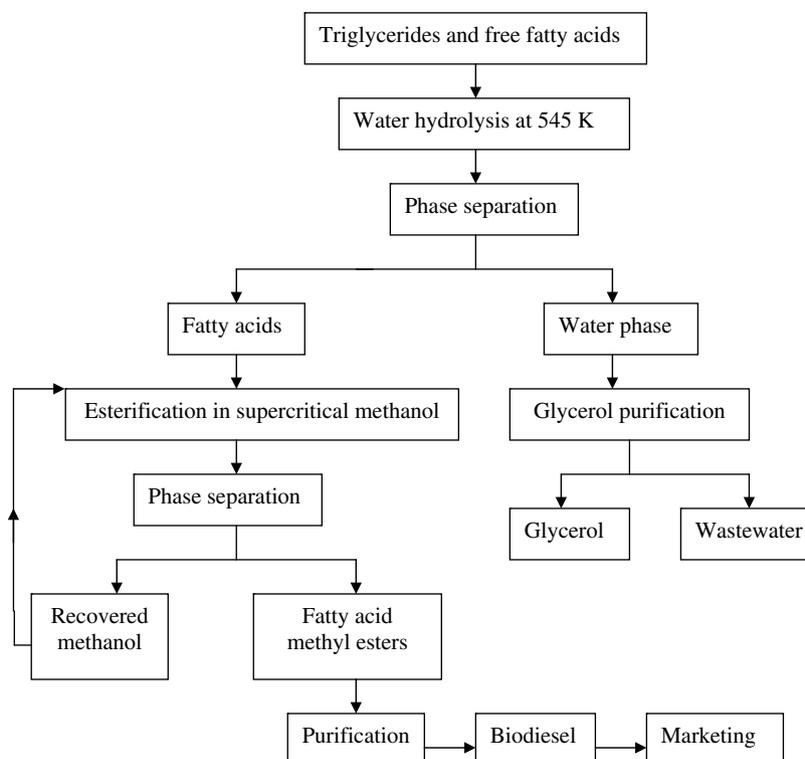
Fig. 8. Continuous biodiesel production process with subcritical water and supercritical methanol stages.

Table 10
Comparisons between catalytic methanol (MeOH) method and supercritical methanol (SCM) method for biodiesel from vegetable oils by transesterification

	Catalytic MeOH process	SCM method
Methylating agent	Methanol	Methanol
Catalyst	Alkali (NaOH or KOH)	None
Reaction temperature (K)	303–338	523–573
Reaction pressure (MPa)	0.1	10–25
Reaction time (min)	60–360	7–15
Methyl ester yield (wt%)	96	98
Removal for purification	Methanol, catalyst, glycerol, soaps	Methanol
Free fatty acids	Saponified products	Methyl esters, water
Smelling from exhaust	Soap smell	Sweet smelling

et al. [97] have taken 18:1 molar ratio during acid esterification and 6:1 molar ratio during alkaline esterification. Meher et al. [42] have taken 6:1 molar ratio during acid esterification and 12:1 molar ratio during alkaline esterification. Instead of taking molar ratio, Tiwary et al. [15] and Ghadge and Raheman [11] have used volume as a measure of ratio.

Higher molar ratios result in greater ester production in a shorter time. The vegetable oils are transesterified 1:6–1:40 vegetable oil–alcohol molar ratios in catalytic and supercritical alcohol conditions [107]. Fig. 9 shows the effect of the molar ratio of vegetable oil to methanol on the yield of methyl ester. As seen in Fig. 6, the cottonseed oil can be transesterified at 1:1, 1:3, 1:9, 1:20 and 1:40 vegetable oil–methanol molar ratios in subcritical and SCM conditions [107].
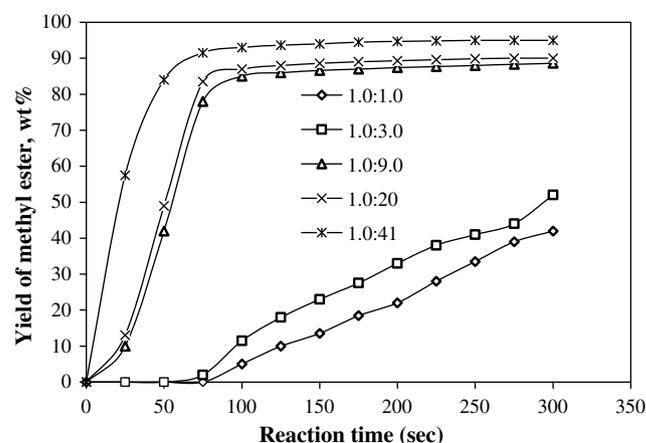
acid content. It is evident that at subcritical states of alcohol, the reaction rate is so low and gradually increased as either pressure or temperature rises. The most important variables affecting the methyl ester yield during transesterification reaction are molar ratio of alcohol to vegetable oil and reaction temperature.

5.1. Effect of molar ratio

The yield of alkyl ester increased when the molar ratio of oil to alcohol was increased [107]. In the supercritical alcohol transesterification method, the yield of conversion rises 50–95% for the first 10 min.

The stoichiometric ratio for transesterification reaction requires 3 mol of alcohol and 1 mol of triglyceride to yield 3 mol of fatty acid ester and 1 mol of glycerol. Ramadhas et al. [32] and Sahoo et al., [111] have reported 6:1 molar ratio during acid esterification and 9:1 vegetable oil-alcohol molar during alkaline esterification to be the optimum amount for biodiesel production from high FFA rubber seed oil and polanga seed oil, respectively. Veljkovic

Fig. 9. Effect of molar ratio of vegetable oil to methanol on yield of methyl ester. Temperature: 513 K, sample: methylester from cottonseed oil.

5.2. Effect of temperature

It was observed that increasing the reaction temperature, especially to supercritical conditions, had a favorable influence on the yield of ester conversion. In the alkali (NaOH or KOH) transesterification reaction, the temperature maintained by the researchers during different steps range between 318 and 338 K. The boiling point of methanol is 337.9 K. Temperature higher than this will burn the alcohol and will result in much lesser yield. A study [112] showed that temperature higher than 323 K had a negative impact on the product yield for neat oil, but had a positive effect for waste oil with higher viscosities.

Fig. 10 shows a typical example of the relationship between the reaction time and the temperature [107]. It was observed that increasing the reaction temperature, especially to supercritical temperatures, had a favorable influence on ester conversion [107].

5.3. Effect of water and free fatty acid (FFA) contents on the yield of biodiesel

In the transesterification process, the vegetable oil should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value is greater than 1, more NaOH or KOH is injected to neutralize the free fatty acids. Water can cause soap formation and frothing. The resulting soaps can induce an increase in viscosity, formation of gels and foams, and made the separation of glycerol difficult [11,63].

Water content is an important factor in the conventional catalytic transesterification of vegetable oil. In the conventional transesterification of fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation, consumes catalyst, and reduces catalyst effectiveness. Kusdiana and Saka [109] are of the opinion that water can pose a greater negative effect than presence of free fatty acids and hence the feedstock should be water free. Romano [113] and Canakci and Van Gerpen [114] insist that even a small amount of water (0.1%) in the transesterification reaction will decrease the ester conversion from vegetable oil. Presence of water and FFA in raw material cause soap formation and a decrease in yield of the alkyl ester, consume catalyst and reduce the effectiveness of catalyst [14]. At the same time the presence of water had a positive effect in the yield of methyl
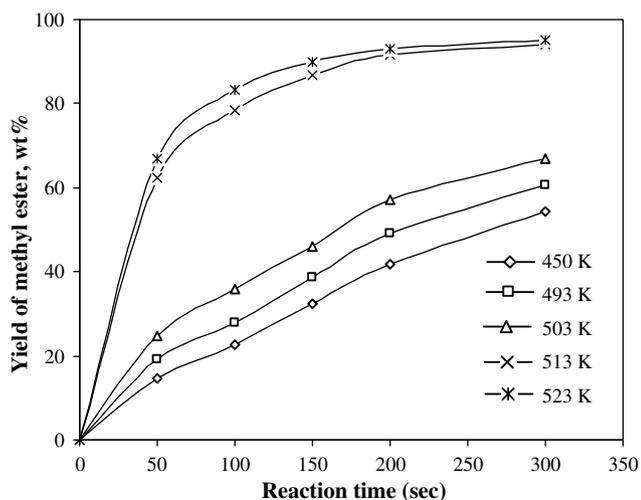
esters when methanol at room temperature was substituted by supercritical methanol [14]. The presence of water had negligible effect on the conversion while using lipase as a catalyst [115].

In conventional catalyzed methods, the presence of water has negative effects on the yields of methyl esters. However, in one study the presence of water affected positively the formation of methyl esters in our supercritical methanol method. Fig. 11 shows
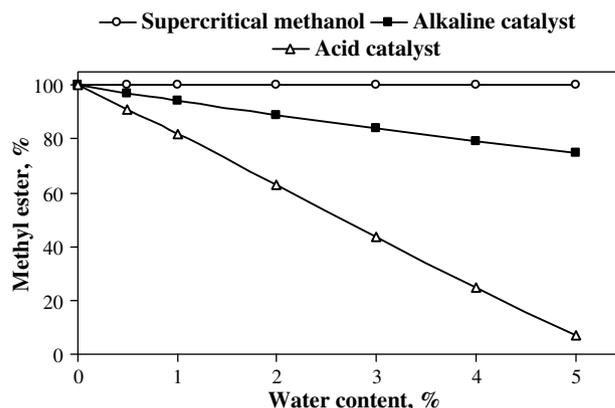
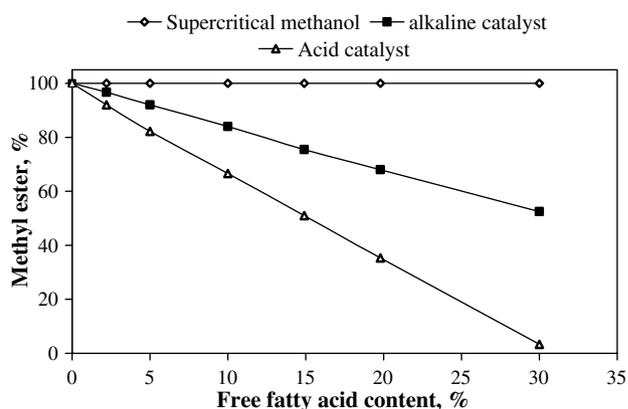**Fig. 11.** Yields of methyl esters as a function of water content in transesterification of triglycerides.

Fig. 12. Yields of methyl esters as a function of free fatty acid content in biodiesel production.

Fig. 10. Changes in yield percentage of methyl esters as treated with subcritical and supercritical methanol at different temperatures as a function of reaction time. Molar ratio of vegetable oil to methyl alcohol: 1:41. Sample: hazelnut kernel oil.
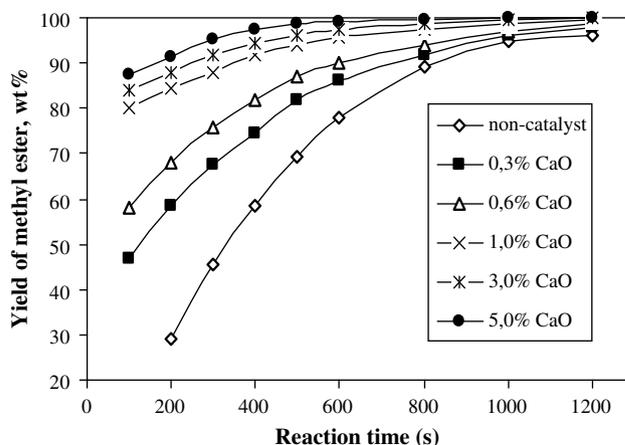
Fig. 13. Effect of CaO content on methyl ester yield. Temperature: 525 K; molar ratio of methanol to sunflower oil: 41:1.

the plots for yields of methyl esters as a function of water content in the transesterification of triglycerides. Fig. 12 shows the plots for yields of methyl esters as a function of free fatty acid content in biodiesel production [109].

5.4. Effect of catalyst content

Fig. 13 shows the relationship between the reaction time and the catalyst content. It can be affirmed that CaO can accelerate the methyl ester conversion from sunflower oil at 525 K and 24 MPa even if a small amount of catalyst (0.3% of the oil) was added. The transesterification speed obviously improved as the content of CaO increased from 0.3% to 3%. However, further enhancement of CaO content to 5% produced little increase in methyl ester yield [6].

6. Properties of biodiesel fuels

Biodiesels are characterized by their viscosity, density, cetane number, cloud and pour points, distillation range, flash point, ash content, sulfur content, carbon residue, acid value, copper corrosion, and higher heating value (HHV). The most important parameters affecting the ester yield during the transesterification reaction are the molar ratio of alcohol to vegetable oil and reaction temperature. The viscosity values of vegetable oil methyl esters decrease sharply after transesterification. Compared to D2 fuel, all of the vegetable oil methyl esters are slightly viscous. The flash point values of vegetable oil methyl esters are significantly lower than those of vegetable oils. There is high regression between the density and viscosity values of vegetable oil methyl esters. The relationships between viscosity and flash point for vegetable oil methyl esters are considerably regular.

These parameters are all specified through the biodiesel standard, ASTM D 6751. This standard identifies the parameters the pure biodiesel (B100) must meet before being used as a pure fuel or being blended with petroleum-based diesel fuel. Biodiesel, B100, specifications (ASTM D 6751 – 02 requirements) are given in Table 11.

The EN 14214 is an international standard that describes the minimum requirements for biodiesel produced from rapeseed fuel stock (also known as rapeseed methyl esters). Table 12 shows international standard (EN 14214) requirements for biodiesel.

6.1. Physical properties of biodiesel fuels

The physical properties of biodiesel are similar to those of diesel fuels. Viscosity is the most important property of biodiesels since it

affects the operation of fuel injection equipment, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The lower the viscosity of the biodiesel, the easier it is to pump and atomize and achieve finer droplets [116]. The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one third that of the triglyceride and reduces the viscosity by a factor of about eight. Viscosities show the same trends as temperatures, with the lard and tallow biodiesels higher than the soybean and rapeseed biodiesels. Biodiesels have a viscosity close to that of diesel fuels. As the oil temperature increases its viscosity decreases [6].

Vegetable oils can be used as fuel for combustion engines, but their viscosity is much higher than that of common diesel fuel and requires modifications to the engines. The major problem associated with the use of pure vegetable oils as fuels for diesel engines is high fuel viscosity in the compression ignition. Therefore, vegetable oils are converted into their methyl esters (biodiesel) by transesterification. The viscosity values of vegetable oils are between 27.2 and 53.6 mm²/s, whereas those of vegetable oil methyl esters are between 3.6 and 4.6 mm²/s. The viscosity values of vegetable oil methyl esters decrease sharply following the transesterification process. The viscosity of No. 2 diesel fuel is 2.7 mm²/s at 311 K [50]. Compared to No. 2 diesel fuel, all of the vegetable oil methyl esters are slightly viscous.

Ethyl esters of vegetable oils have several outstanding advantages among other new-renewable and clean-engine fuel alternatives. The variables affecting the ethyl ester yield during transesterification reaction, such as the molar ratio of alcohol to vegetable oil and reaction temperature, were investigated. Viscosities of the ethyl esters from vegetable oils were twice as high as that of No. 2 diesel fuel [117].

The flash point values of vegetable oil methyl esters are much lower than those of vegetable oils. An increase in density from 860 to 885 kg/m³ for vegetable oil methyl esters or biodiesels increases the viscosity from 3.59 to 4.63 mm²/s and the increases are highly regular. There is high regression between the density and viscosity values of vegetable oil methyl esters. The relationships between viscosity and flash point for vegetable oil methyl esters are irregular [6].

The cetane number (CN) is based on two compounds, hexadecane, with a CN of 100, and heptamethylnonane, with a CN of 15. The CN is a measure of the ignition quality of diesel fuels, and a high CN implies short ignition delay. The CN of biodiesel is generally higher than conventional diesel. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN. The CN of biodiesel from animal fats is higher than those of vegetable oils [8].

Two important parameters for low-temperature applications of a fuel are cloud point (CP) and pour point (PP). The CP is the temperature at which wax first becomes visible when the fuel is cooled. The PP is the temperature at which the amount of wax from a solution is sufficient to gel the fuel; thus it is the lowest temperature at which the fuel can flow. Biodiesel has a higher CP and PP compared to conventional diesel [118].

6.2. Higher combustion efficiency of biodiesel fuel

The oxygen content of biodiesel improves the combustion process and decreases its oxidation potential. The structural oxygen content of a fuel improves its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. Because of this the combustion efficiency of biodiesel is higher than that of petrodiesel, and the combustion efficiency of methanol/ethanol is higher than that of gasoline. A visual inspec-

Table 11
Biodiesel, B100, specifications (ASTM D 6751 – 02 requirements)

Property	Method	Limits	Units
Flash point	D 93	130 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity at 40 °C	D 445	1.9–6.0	mm²/s
Sulfated ash	D 874	0.020 max	wt%
Total sulfur	D 5453	0.05 max	wt%
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report	°C
Carbon residue	D 4530	0.050 max	wt%
Acid number	D 664	0.80 max	mg KOH/g
Free glycerine	D 6584	0.020	wt%
Total glycerine	D 6584	0.240	wt%
Phosphorus	D 4951	0.0010	wt%
Vacuum distillation end point	D 1160	360 °C max, at 90% distilled	°C

Table 12
International standard (EN 14214) requirements for biodiesel

Property	Units	Lower limit	Upper limit	Test-method
Ester content	% (m/m)	96.5	–	Pr EN 14103 d
Density at 15 °C	kg/m^3	860	900	EN ISO 3675/EN ISO 12185
Viscosity at 40 °C	mm^2/s	3.5	5.0	EN ISO 3104
Flash point	°C	>101	–	ISO CD 3679e
Sulfur content	mg/kg	–	10	–
Tar remnant (at 10% distillation remnant)	% (m/m)	–	0.3	EN ISO 10370
Cetane number	–	51.0	–	EN ISO 5165
Sulfated ash content	% (m/m)	–	0.02	ISO 3987
Water content	mg/kg	–	500	EN ISO 12937
Total contamination	mg/kg	–	24	EN 12662
Copper band corrosion (3 h at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Oxidation stability at 110 °C	hours	6	-	pr EN 14112 k
Acid value	mg KOH/g	–	0.5	pr EN 14104
Iodine value	–	–	120	pr EN 14111
Linoleic acid methyl ester	% (m/m)	–	12	pr EN 14103d
Polyunsaturated (⩾4 double bonds) methylester	% (m/m)	–	1	–
Methanol content	% (m/m)	–	0.2	pr EN 141101
Monoglyceride content	% (m/m)	–	0.8	pr EN 14105m
Diglyceride content	% (m/m)	–	0.2	pr EN 14105m
Triglyceride content	% (m/m)	–	0.2	pr EN 14105m
Free glycerine	% (m/m)	–	0.02	pr EN 14105m/pr EN 14106
Total glycerine	% (m/m)	–	0.25	pr EN 14105m
Alkali metals (Na + K)	mg/kg	–	5	pr EN 14108/pr EN 14109
Phosphorus content	mg/kg	–	10	pr EN14107p

tion of the injector types would indicate no difference between biodiesel fuels and petrodiesel in testing. The overall injector coking is considerably low. Biodiesel contains 11% oxygen by weight and no sulfur. The use of biodiesel can extend the life of diesel engines because it is more lubricating than petroleum diesel fuel. Biodiesel has better lubricant properties than petrodiesel [6].

The higher heating values (HHVs) of biodiesels are relatively high. The HHVs of biodiesels (39–41 MJ/kg) is slightly lower than that of gasoline (46 MJ/kg), petrodiesel (43 MJ/kg), or petroleum (42 MJ/kg), but higher than coal (32–37 MJ/kg).

6.3. Water content

The soap can prevent the separation of biodiesel from glycerol fraction [115]. In catalyzed methods, the presence of water has negative effects on the yields of methyl esters. On the other hand, water content of biodiesel reduces the heat of combustion. This means more smoke, harder starting, less power. Water will cause corrosion of vital fuel system components fuel pumps, injector pumps, fuel tubes, etc. Water, as it approaches 273 K begins to form ice crystals. These crystals provide sites of nucleation and accelerate the gelling of the residual fuel. Water is part of the respiration system of most microbes. Biodiesel is a great food for microbes and water is necessary for microbe respiration. The presence of water accelerates the growth of microbe colonies which can seriously plug up a fuel system.

6.4. Advantages of biodiesels

The biggest advantage of biodiesel is environmentally friendliness that it has over gasoline and petroleum diesel. The advantages of biodiesel as a diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content [29,119], higher cetane number, and higher biodegradability [86,120,121]. The main advantages of biodiesel given in the literature include its domestic origin, its potential for reducing a given economy's dependency on imported petroleum, biodegradability, high flash point, and inherent lubricity in the neat form [122,123].

6.4.1. Availability and renewability of biodiesel

Biodiesel can be made from domestically produced, renewable oilseed crops such as soybean, rapeseed, and sunflower. The risks of handling, transporting, and storing biodiesel are much lower than those associated with petrodiesel. Biodiesel is the only alternative fuel in which low-concentration biodiesel–diesel blends run on conventional unmodified engines. It can be stored anywhere that petroleum diesel fuel is stored. Biodiesel is safe to handle and transport because it is as biodegradable as sugar and has a high flash point compared to petroleum diesel fuel. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel. The most common blend is a mix of 20% biodiesel with 80% petroleum diesel, or B20 in recent scientific investigations; however, in Europe the current regulation foresees a maximum 5.75% biodiesel [6].

6.4.2. Lower emissions from biodiesel

In cities across the globe, the personal automobile is the single greatest polluter, as emissions from millions of vehicles on the road add up to a worldwide problem. The biodiesel impacts on exhaust emissions vary depending on the type of biodiesel and on the type of conventional diesel.

The commercial biodiesel fuel significantly reduced PM exhaust emissions (75–83%) compared to the petrodiesel base fuel. However, NO$_x$ exhaust emissions increased slightly with commercial biodiesel compared to the base fuel. The chain length of the compounds had little effect on NO$_x$ and PM exhaust emissions, while the influence was greater on HC and CO, the latter being reduced with decreasing chain length. Non-saturation in the fatty compounds causes an increase in NO$_x$ exhaust emissions [119].

Many studies on the performances and emissions of compression ignition engines, fuelled with pure biodiesel and blends with diesel fuel, have been conducted and are reported in the literature [124,125]. Fuel characterization data show some similarities and differences between biodiesel and petrodiesel fuels [21]. The sulfur content of petrodiesel is 20–50 times that of biodiesels. Biodiesel has demonstrated a number of promising characteristics, including reduction of exhaust emissions [7]. Dorado et al. [126] describe experiments on the exhaust emissions of biodiesel from olive oil methyl ester as alternative diesel fuel fueled in a Diesel direct injection Perkins engine.

Particular matter (PM-10) emissions and power of a Diesel engine fueled with crude and refined biodiesel from salmon oil has been investigated [127]. The results indicate a maximum power loss of about 3.5% and also near 50% of PM-10 reduction with respect to diesel when a 100% of refined biodiesel is used. Previous research has shown that biodiesel-fueled engines produce less carbon monoxide (CO), unburned hydrocarbon (HC), and particulate emissions compared to mineral diesel fuel but higher NO_x emissions [128].

Emissions of regulated air pollutants, including CO, HC, NO_x, PM and polycyclic aromatic hydrocarbons (PAHs) were measured and results show that B20 use can reduce both PAH emission and its corresponding carcinogenic potency [129].

For soybean-based biodiesel at this concentration, the estimated emission impacts for percent change in emissions of NO_x, PM, HC, and CO were +20%, −10.1%, −21.1%, and −11.0%, respectively [130]. The use of blends of biodiesel and diesel oil are preferred in engines in order to avoid some problems related to the decrease of power and torque and to the increase of NO_x emissions (a contributing factor in the localized formation of smog and ozone) that occurs with an increase in the content of pure biodiesel in a blend [129]. Emissions of all pollutants except NO_x appear to decrease when biodiesel is used. Average emission impacts of vegetable-oil-based biodiesel for CIEs are given in Fig. 14.

The use of biodiesel in a conventional diesel engine dramatically reduces the emissions of unburned hydrocarbons, carbon dioxide, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, ozone-forming hydrocarbons, and particulate matter. The net contribution of carbon dioxide from biomass combustion is small [131]. Reductions in net carbon dioxide emissions are estimated at 77–104 g/MJ of diesel displaced by biodiesel [132]. These reductions increase as the amount of biodiesel blended into the diesel fuel increases.

6.4.3. Biodegradability of biodiesel

Biodegradability of biodiesel has been proposed as a solution for the waste problem. Biodegradable fuels such as biodiesels have an expanding range of potential applications and they are environmentally friendly. Therefore, there is growing interest in degradable diesel fuels that degrade more rapidly than conventional disposable fuels. Biodiesel is non-toxic and degrades about four times faster than petrodiesel. Its oxygen content improves the biodegradation process, leading to a decreased level of quick biodegradation [6].
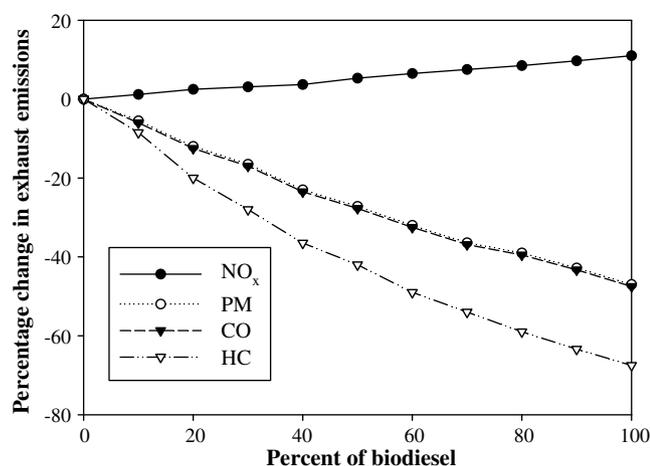
Table 13
Biodegradability data of petroleum and biofuels

Fuel sample	Degradation in 28 d (%)	Ref. No.
Gasoline (91 octane)	28	[121]
Heavy fuel (Bunker C oil)	11	[137,138]
Refined rapeseed oil	78	[134]
Refined soybean oil	76	[134]
Rapeseed oil methyl ester	88	[134]
Sunflower seed oil methyl ester	90	[134]

Biodiesel is reported to be highly biodegradable in freshwater as well as soil environments. 90–98% of biodiesel is mineralized in 21–28 days under aerobic as well as anaerobic conditions [133–135]. More than 98% degradation of pure biodiesel after 28 days is reported by Pasqualino et al. [133] in comparison to 50% and 56% by diesel fuel and gasoline, respectively.

The biodegradabilities of several biodiesels in the aquatic environment show that all biodiesel fuels are readily biodegradable. In one study, after 28 d all biodiesel fuels were 77–89% biodegraded; diesel fuel was only 18% biodegraded [136]. The enzymes responsible for the dehydrogenation/oxidation reactions that occur in the process of degradation recognize oxygen atoms and attack them immediately [134].

The biodegradability data of petroleum and biofuels available in the literature are presented in Table 13. In 28-d laboratory studies, heavy fuel oil had a low biodegradation of 11% due to its higher proportion of high-molecular-weight aromatics [137,138]. Gasoline is highly biodegradable (28%) after 28 d. Vegetables oils and their derived methyl esters (biodiesels) are rapidly degraded to reach a biodegradation rate of between 76% and 90% [120,134]. In their studies Zhang et al. [134] have shown that vegetable oils are slightly less degraded than their modified methyl ester.

6.4.4. Higher lubricity

Biodiesel methyl esters improve the lubrication properties of the diesel fuel blend. Fuel injectors and some types of fuel pumps rely on fuel for lubrication. Biodiesel reduced long term engine wear in test diesel engines to less than half of what was observed in engines running on current low sulfur diesel fuel. Lubricity properties of fuel are important for reducing friction wear in engine components normally lubricated by the fuel rather than crankcase oil [29,50]. Biodiesel provides significant lubricity improvement over petroleum diesel fuel. Lubricity results of biodiesel and petroleum diesel using industry test methods indicate that there is a marked improvement in lubricity when biodiesel is added to conventional diesel fuel. Even biodiesel levels below 1% can provide up to a 30% increase in lubricity. Lubricity results of biodiesel and petroleum diesel using industry test methods indicate that there is a marked improvement in lubricity when biodiesel is added to conventional diesel fuel. Even biodiesel levels below 1% can provide up to a 30% increase in lubricity [6].

6.4.5. Engine performance evaluation using biodisel

Biodiesels are mono-alkyl esters containing approximately 10% oxygen by weight. The oxygen improves the efficiency of combustion, but it takes up space in the blend and therefore slightly increases the apparent fuel consumption rate observed while operating an engine with biodiesel.

The high combustion temperature at high engine speed becomes the dominant factor, making both heated and unheated fuel to acquire the same temperature before fuel injection [139,140]. Various methods of using vegetable oil (Jatropha oil) and methanol such as blending, transesterification and dual fuel operation were studied experimentally [141]. Brake thermal efficiency was better in the dual fuel operation and with the methyl ester of Jatropha oil as compared to the blend. It increased form 27.4% with neat

Fig. 14. Average emission impacts of vegetable-oil-based biodiesel for CIEs.

Jatropha oil to a maximum of 29% with the methyl ester and 28.7% in the dual fuel operation [141].

It was showed that biodiesel decreased the injector coking to a level significantly lower than that observed with No. 2 diesel fuel [50,142]. Various engine performance parameters such as thermal efficiency, brake specific fuel consumption (BSFC), and brake specific energy consumption (BSEC). can be calculated from the acquired data. The torque, brake power and fuel consumption values associated with CIE fuels were determined under certain operating conditions. Kaplan et al. [143] compared sunflower oil biodiesel and diesel fuels at full and partial loads and at different engine speeds in a 2.5153 kW engine. The loss of torque and power ranged between 5% and 10%, and particularly at full load, the loss of power was closer to 5% at low speed and to 10% at high speed.

In an earlier study [144], the tests were performed with commercial diesel fuel and biodiesel. The maximum brake power values of biodiesel and diesel were 4.390 kW and 5.208 kW obtained at 2750 and 2500 rpm, respectively. According to these values, the commercial diesel fuel has the greatest brake power.

6.5. Disadvantages of biodiesel as diesel fuel

The major disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NO_x) emissions, lower engine speed and power, injector coking, engine compatibility, and high price [6].

The biodiesels on the average decrease power by 5% compared to that of diesel at rated load [14]. The maximum torque values are about 21.0 Nm at 1500 rpm for the diesel fuel, 19.7 Nm at 1500 rpm for the biodiesel. The torque values of commercial diesel fuel are greater than those of biodiesel. Peak torque applies less to biodiesel fuels than it does to No. 2 diesel fuel but occurs at lower engine speed and generally its torque curves are flatter [10].

The specific fuel consumption values of biodiesel are greater than those of commercial diesel fuel. The effective efficiency and effective pressure values of commercial diesel fuel are greater than those of biodiesel [144]. Important operating disadvantages of biodiesel in comparison with petrodiesel are cold start problems, the lower energy content, higher copper strip corrosion and fuel pumping difficulty from higher viscosity [5]. Fuel consumption at full load condition and low speeds generally is high. Fuel consumption first decreases and then increases with increasing speed. The reason is that, the produced power in low speeds is low and the main part of fuel is consumed to overcome the engine friction [145].

6.5.1. Thermal degradation of fatty acids during biodiesel production

The effects of oxidative degradation caused by contact with ambient air (autoxidation) during long-term storage present a legitimate concern in terms of maintaining the fuel quality of biodiesel.

Trans unsaturated fatty acids, or *trans* fats, are solid fats produced artificially by heating liquid vegetable oils in the presence of metal catalysts and hydrogen. This process, partial hydrogenation, causes carbon atoms to bond in a straight configuration and remain in a solid state at room temperature [146].

Physical properties that are sensitive to the effects of fatty oil oxidation include viscosity, refractive index, and dielectric constant. Fig. 6 shows the mechanism of peroxy radical formation on a methylene group. In oxidative instability, the methylene group ($-CH_2-$) carbons between the olefinic carbons are the sites of first attack [147].

Oxidation to CO_2 of biodiesel results in the formation of hydroperoxides. The formation of a hydroperoxide follows a well-known peroxidation chain mechanism. Oxidative lipid modifications occur through lipid peroxidation mechanisms in which free radicals and reactive oxygen species abstract a methylene hydrogen atom from polyunsaturated fatty acids, producing a carbon-centered lipid radical. Spontaneous rearrangement of the 1,4-pentadiene yields a conjugated diene, which reacts with molecular oxygen to form a lipid peroxyl radical. Abstraction of a proton from neighboring polyunsaturated fatty acids produces a lipid hydroperoxide (LOOH) and regeneration of a carbon-centered lipid radical, thereby propagating the radical reaction [148]. After hydrogen is removed from such carbons oxygen rapidly attacks and a LOOH is ultimately formed where the polyunsaturation has been isomerized to include a conjugated diene. This reaction is a chain mechanism that can proceed rapidly once an initial induction period has occurred. The greater the level of unsaturation in a fatty oil or ester, the more susceptible it will be to oxidation. Once the LOOHs have formed, they decompose and interreact to form numerous secondary oxidation products including higher-molecular-weight oligomers often called polymers.

7. The biodiesel economy

Certain transportation biofuels such as bioethanol, biodiesel, methyltetrahydrofuran and dimethyl ether can be sustainably obtained from biomass. In industrialized countries, the main biomass processes utilized in the future are expected to be the direct combustion of residues and wastes for electricity generation, bioethanol and biodiesel as liquid fuels, and combined heat and power production from energy crops. All biomass is produced by green plants converting sunlight into plant material through photosynthesis [149]. Fig. 15 shows the main steps of biomass technology.

A number of technical and economic advantages of biodiesel fuel are that (1) it prolongs engine life and reduces the need for maintenance (biodiesel has better lubricating qualities than fossil diesel), (2) it is safer to handle, being less toxic, more biodegradable, and having a higher flash point, and (3) it reduces some exhaust emissions [150].

Among the many advantages of biodiesel fuel are that it is safe for use in all conventional diesel engines, offers the same performance and engine durability as petroleum diesel fuel, is non-flammable and non-toxic, and reduces tailpipe emissions, visible smoke, and noxious fumes and odors [151]. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability [152]. Fig. 16 shows the biodiesel production of the European Union (1993–2005).

Among liquid biofuels, biodiesel derived from vegetable oils is gaining acceptance and market share as diesel fuel in Europe and the United States. By several important measures biodiesel blends perform better than petroleum diesel, but its relatively high production costs and the limited availability of some of the raw materials used in its production continue to limit its commercial application. Limiting factors of the biodiesel industry are feedstock prices, biodiesel production costs, crude oil prices, and taxation of energy products.

The economic advantages of biodiesel are that it reduces greenhouse gas emissions, helps to reduce a country's reliance on crude oil imports, and supports agriculture by providing new labor and market opportunities for domestic crops. In addition it enhances lubrication and is widely accepted by vehicle manufacturers [153,154].

The major economic factor to consider with respect to the input costs of biodiesel production is the feedstock, which is about 80% of the total operating cost. Other important costs are labor, methanol, and catalyst, which must be added to the feedstock. In some countries, filling stations sell biodiesel more cheaply than conventional diesel.

The cost of biodiesel fuels varies depending on the base stock, geographic area, variability in crop production from season to
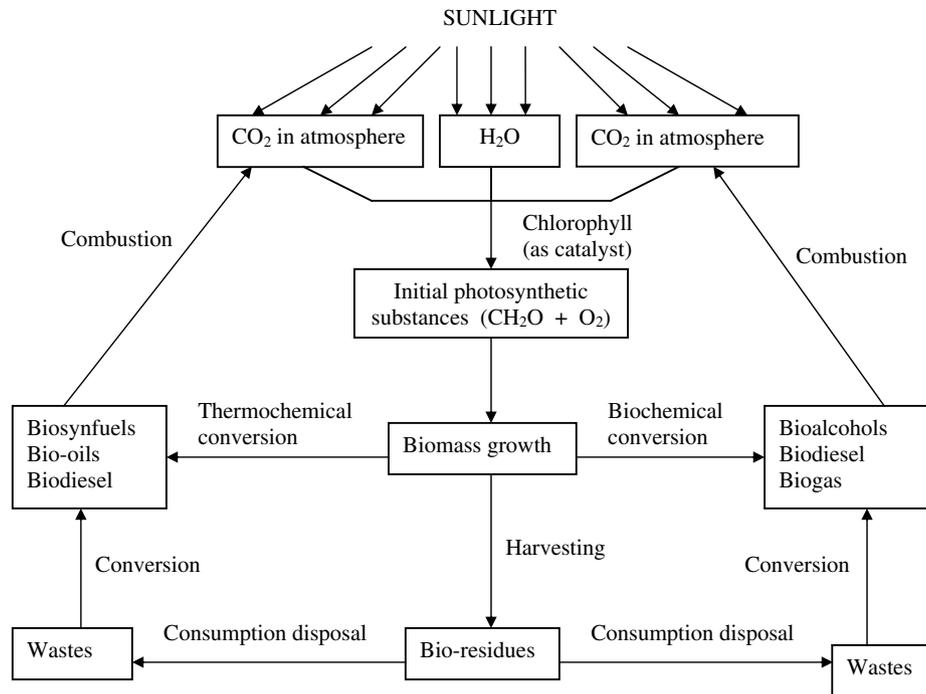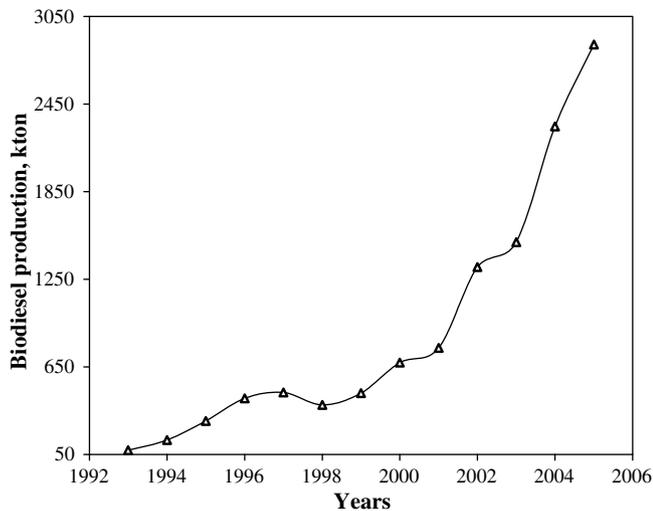
Fig. 15. Main steps of biomass technology.

Fig. 16. Biodiesel production of the European Union (1993–2005).

season, the price of crude petroleum, and other factors. Biodiesel costs more than twice petroleum diesel. The high price of biodiesel is in large part due to the high price of the feedstock. However, biodiesel can be made from other feedstocks, including beef tallow, pork lard, and yellow grease

The recent increase in the potential use of biodiesel is due not only to the number of plants but also to the size of the facilities used in its production. The tremendous growth in the biodiesel industry is expected to have a significant impact on the price of biodiesel feedstocks. This growth in the biodiesel industry will increase competition. An earlier evaluation of the potential feedstocks for biodiesel by Hanna et al. [155] also identified the expected price pressures on biodiesel feedstocks. Fiscal incentives for biodiesel such as reductions in feedstock and processing costs and tax exemptions will be the key tool for enhancing the use of biodiesel as an alternative fuel for transport in the near future.

7.1. Economic benefits of biodiesel

Biodiesel is a renewable fuel manufactured from vegetable oils, animal fats, and recycled cooking oils. Biodiesel offers many benefits [156]:

1. It is renewable.
2. It is energy efficient.
3. It displaces petroleum-derived diesel fuel.
4. It can be used in most diesel equipment with no or only minor modifications.
5. It can reduce global warming gas emissions.
6. It can reduce tailpipe emissions, including air toxins.
7. It is non-toxic, biodegradable, and suitable for sensitive environments.
8. It is made from either agricultural or recycled resources.

Blends of up to 20% biodiesel mixed with petrodiesel fuels can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment. Higher blends, even B100, can be used in many engines built with little or no modification. Transportation and storage, however, require special management. Material compatibility and warranty issues have not been resolved with higher blends.

Biodiesel has become more attractive recently because of its environmental benefits. The cost of biodiesel, however, is the main obstacle to commercialization of the product. With cooking oils used as raw material, the viability of a continuous transesterification process and the recovery of high-quality glycerol as a biodiesel byproduct are primary options to be considered to lower the cost of biodiesel [29,157].

Most of the biodiesel that is currently made uses soybean oil, methanol, and an alkaline catalyst. Methanol is preferred because it is less expensive than ethanol [158]. A base catalyst is preferred in transesterification because the reaction is quick and thorough. It also occurs at lower temperature and pressure than other processes, resulting in lower capital and operating costs for the biodie-

sel plant. The high value of soybean oil as a food product makes the production of a cost-effective fuel very challenging. However, there are large amounts of low-cost oils and fats, such as restaurant waste and animal fats that could be converted into biodiesel.

7.2. Biodiesel costs

Lower-cost feedstocks are needed since biodiesel from food-grade oils is not economically competitive with petroleum-based diesel fuel. Inedible plant oils have been found to be promising crude oils for the production of biodiesel. The cost of biofuel and demand of vegetable oils can be reduced by inedible oils and used oils, instead of edible vegetable oil. Around the world large amounts of inedible oil plants are available in nature.

The cost of biodiesel is higher than diesel fuel. Currently, there are seven producers of biodiesel in the United States. Pure biodiesel (100%) sells for about US$1.50 to US$2.00 per gallon before taxes. Fuel taxes add approximately US$0.50 per gallon [6].

Due to the underutilization of triglyceride processing equipment for rapeseed, soybean, sunflower oils, or animal fats are used as the only feedstock. Examining the feedstocks against each other does not provide for a valid comparison. Therefore, a comparison should be made based on how much of the processing equipment is actually utilized. If only 38% of the processing equipment is allocated to the costs of production when rapeseed or sunflower oils are used, the cost per gallon of biodiesel decreases. Also, the cost per gallon of biodiesel from animal fats decreases if none of the preprocessing capital costs are allocated to the total costs of production. The costs per gallon for the feedstocks are listed in Table 14.

The other reactant in producing biodiesel is methanol. Methanol is a readily available commodity in the chemical industry. It is produced from natural gas. Methanol is valued at around €250 to €280 per ton, but the price varies with the price of natural gas. A catalyst is necessary for the reaction, but the catalyst used varies from one biodiesel manufacturing plant to another. Sodium hydroxide, potassium hydroxide, and sulfuric acid are three commonly used catalysts.

Current production costs of rapeseed methyl ester (RME) amount to ca. €0.50 per liter (or 15 €/GJ). These costs depend on the prices of the biomass used and the size and type of the production plant. The short-term investment costs for a 400-MWth plant are about 150 €/kWth. In the long term, these costs may decrease by about 30% for a larger sized plant with a thermal input capacity of 1000 MWth, assuming economies of scale. Other important factors determining the production costs of RME are the yield and value of the byproducts of the biodiesel production process, such as oilseed cake (a protein-rich animal feed) and glycerine (used in the production of soap and as a pharmaceutical medium). Longer-term projections indicate a future decrease in RME production costs by more than 50%, down to ca. €0.20 per liter (or around 6 €/GJ). However, to provide the amount of energy equivalent to 1 l of petroleum-derived diesel, a larger amount of RME is needed due to its lower energy content [159,160].

A review of 12 economic feasibility studies shows that the projected costs for biodiesel from oilseed or animal fats have a range of US$0.30 to 0.69/l, including meal and glycerol credits and assuming reduced capital investment costs by having the crushing

and/or esterification facility added onto an existing grain or tallow facility. Rough projections of the cost of biodiesel from vegetable oil and waste grease are, respectively, US$0.54 to 0.62/l and US$0.34 to 0.42/l. With pretax diesel priced at US$0.18/l in the USA and US$0.20 to 0.24/l in some European countries, biodiesel is thus currently not economically feasible, and more research and technological development will be needed [50,161].

8. The biodiesel policy

If the biodiesel valorized efficiently at energy purpose, so would be benefit for the environment and the local population: Job creation, provision of modern energy carriers to rural communities, avoid urban migration and reduction of CO_2 and sulfur levels in the atmosphere. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector [162].

The attributes of energy policy may include international treaties, legislation on commercial energy activities (trading, transport, storage, *etc.*), incentives for investment, guidelines for energy production, conversion, and use (including efficiency and emission standards), taxation and other public policy techniques, energy-related research and development, energy economy, general international trade agreements and marketing, energy diversity, and risk factors for possible energy crisis. Current energy policies also address environmental issues including environmentally friendly technologies to increase energy supplies and encourage cleaner, more efficient energy use, air pollution, the greenhouse effect (mainly reducing carbon dioxide emissions), global warming, and climate change [5].

Given the history of petroleum politics, it is imperative that today's policy decisions ensure a free market for biodiesel. Producers of all sizes must be free to compete in this industry, without farm subsidies, regulations, and other interventions skewing the playing field. The production and utilization of biodiesel is facilitated firstly through the agricultural policy of subsidizing the cultivation of non-food crops. Secondly, biodiesel is exempt from the oil tax.

The production and utilization of biodiesel is facilitated firstly through the agricultural policy of subsidizing the cultivation of non-food crops. Secondly, biodiesel is exempt from the oil tax. The Common Agricultural Policy Reform of 1992 established crop-specific payments per hectare to compensate for the reduction or abolition of institutional prices. The reference set-aside share is currently 10%, but the applied set-aside rates have been adapted year by year, taking into account market forecasts. Furthermore, farmers are flexible in the management of their set-aside obligations [6].

Today it is all the more true that biodiesel threatens many economic and political interests, so biodiesel policy should be examined critically to prevent the industry from being controlled. The proportion of processed biodiesel in the diesel blend will be gradually increased. It must be developed national biodiesel programs with a long-term goal of 20% by volume quota by 2020 to reduce dependence on imported petroleum diesel and must be reduced pollution levels. In view of the escalating petroleum price and depleting sources of petroleum, the introduction of biodiesel is deemed critical. It will help to reduce the dependency on petroleum diesel fuel. The introduction of biodiesel as a diesel fuel substitute will help to reduce imports of petroleum diesel of petroleum-poor countries. The use of renewable biodiesel will help reduce the use of petroleum diesel and indirectly reduce the emissions of greenhouse gases such as carbon dioxide to the atmosphere. New demand for vegetable oils will be stimulated more efficient utilization of raw materials by using vegetable oil-based diesel substitutes. By creating the new demand for biodiesel, its price will be stabilized at a higher level.

Table 14
Costs per gallon for four feedstocks

Feedstock	Cost ($/gallon)
Animal fats	1.35
Rapeseed oil	1.46
Sunflower oil	2.35
Soybean oil	1.26

The source for biodiesel production is chosen according to the availability in each region or country. Any fatty acid source may be used to prepare biodiesel, but most scientific studies take soybean as a biodiesel source. Since the prices of edible vegetable oils, such as soybean oil, are higher than that of diesel fuel, waste vegetable oils and non-edible crude vegetable oils are preferred as potential low-priced biodiesel sources. Low-quality under used feedstocks have been used to produce biodiesel [9].

9. Conclusion

Alternative fuels for diesel engines have been becoming increasingly important due to diminishing petroleum reserves and the growing environmental concerns have made renewable fuels an exceptionally attractive alternative as a fuel for the future [163]. Biodiesel is derived from a varied range of edible and inedible vegetable oil, animal fats, used frying oil and waste cooking oil. The edible oil in use at present is soyabean, sunflower, rapeseed and palm. The inedible oil used as feedstock for biodiesel production includes *J. curcas*, *M. indica*, *F. elastica*, *A. indica*, *C.* inophyllum jatropha, neem, *P. pinnata*, rubber seed, mahua, silk cotton tree, waste cooking, microalgae, etc.

Transesterification is a chemical reaction between triglyceride and alcohol in the presence of catalyst or without catalyst. The purpose of the transesterification process is to lower the viscosity of the oil [164]. Methanol being cheaper is the commonly used alcohol during transesterification reaction. Homogeneous catalysts such as sulfuric acid, sodium hydroxide, potassium hydroxide and heterogeneous catalysts such as calcium oxide, magnesium oxide and others can be used in transesterification reaction. Non-catalyzed transesterification processes are the BIOX process and the supercritical alcohol (methanol) process.

The advantage in its usage is attributed to lesser exhaust emissions in terms of carbon monoxide, hydrocarbons, particulate matter, polycyclic aromatic hydrocarbon compounds and nitrited polycyclic aromatic hydrocarbon compounds. The main advantages of biodiesel given in the literature include its domestic origin, its potential for reducing a given economy's dependency on imported petroleum, biodegradability, high flash point, and inherent lubricity in the neat form. The biodiesel policy will help reducing of petroleum imports and saving of foreign exchange. The biodiesel high flash point makes it possible for its easy storage and transportation.

The main disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide emissions, lower engine speed and power, injector coking, engine compatibility, and high price.

Blends of up to 20% biodiesel mixed with petroleum diesel fuels can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment. Biodiesel can be used directly or as blends with diesel fuel in a diesel engine. Biodiesel is a biodegradable and renewable fuel. It contributes no net carbon dioxide or sulfur to the atmosphere and emits less gaseous pollutants than normal diesel. Carbon monoxide, aromatics, polycyclic aromatic hydrocarbons (PAHs) and partially burned or unburned hydrocarbon emissions are all reduced in vehicles operating on biodiesel.

Recently, biodiesel has been receiving increasing attention due to its less polluting nature and because it is a renewable energy resource as against the conventional diesel, which is a fossil fuel leading to a potential exhaustion. Biodiesel has become more attractive recently because of its environmental benefits. Biodiesel is an environmentally friendly fuel that can be used in any diesel engine without modification. Biodiesel fuels have generally been found to be nontoxic and are biodegradable, which may promote their use in applications where biodegradability is desired. Neat biodiesel and biodiesel blends reduce particulate matter (PM), hydrocarbons (HC) and carbon monoxide (CO) emissions and slightly increase nitrogen oxides (NO_x) emissions compared with petroleum-based diesel fuel used in an unmodified diesel engine [130].

The brake power of biodiesel was nearly the same as with petrodiesel, while the specific fuel consumption was higher than that of petrodiesel. Carbon deposits inside the engine were normal, with the exception of intake valve deposits. Biodiesel fuels can be performance improving additives in compression ignition engines. Performance testing showed that while the power decreased and the brake specific fuel consumption increased for all of the biodiesel samples, compared with No. 2 diesel fuel, the amount of the changes were in direct proportion to the lower energy content of the biodiesel.

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