Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey

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Abstract

Vegetable oil fuels have not been acceptable because they were more expensive than petroleum fuels. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for Diesel engines. Dilution of oils with solvents and microemulsions of vegetable oils lowers the viscosity, but some engine performance problems still exist. The purpose of the transesterification process is to lower the viscosity of the oil. Pyrolysis produces more biogasoline than biodiesel fuel. Soap pyrolysis products of vegetable oils can be used as alternative Diesel engine fuel. Methyl and ethyl esters of vegetable oils have several outstanding advantages among other new renewable and clean engine fuel alternatives. The main factors affecting transesterification are the molar ratio of glycerides to alcohol, catalyst, reaction temperature and pressure, reaction time and the contents of free fatty acids and water in oils. The commonly accepted molar ratios of alcohol to glycerides are 6:1–30:1.
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1. Introduction

Among liquid biofuels, biodiesel derived from vegetable oils is gaining acceptance and market share as Diesel fuel in Europe and the United States. Technical aspects of biodiesel are approached, such as the physical and chemical characteristics of methyl esters related to its performance in compression ignition engines (CIEs) [1]. Biodiesel has become more attractive

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recently because of its environmental benefits and the fact that it is made from renewable resources [2].

Although short term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking and thickening of the engine lubricant. These experiences led to the use of modified vegetable oil as a fuel. Although there are many ways and procedures to convert vegetable oil into a Diesel like fuel, the transesterification process was found to be the most viable oil modification process [3].

Transesterification is the process of using an alcohol (e.g. methanol, ethanol or butanol), in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to break the molecule of the raw renewable oil chemically into methyl or ethyl esters of the renewable oil, with glycerol as a by product. Biodiesel, defined as the mono-alkyl esters of fatty acids derived from vegetable oil or animal fat, in application as an extender for combustion in CIEs (Diesel), has demonstrated a number of promising characteristics, including reduction of exhaust emissions [4]. Transesterified, renewable oils have proven to be a viable alternative Diesel engine fuel with characteristics similar to those of Diesel fuel. The transesterification reaction proceeds with catalyst or without catalyst by using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms as follows:

$$\text{Triglycerides} + \text{Monohydric alcohol} \rightleftarrows \text{Glycerin} + \text{Mono-alkyl esters} \tag{1}$$
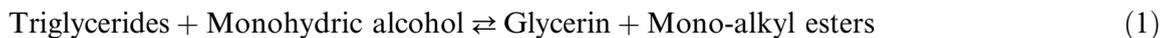
This study reviews the practicability of use of vegetable oils and their methyl and ethyl esters as biodiesel in CIEs.

1.1. Literature review

Vegetable oils have become more attractive recently because of their environmental benefits and the fact that it is made from renewable resources. More than 100 years ago, Rudolph Diesel tested vegetable oil as the fuel for his engine [5].

Vegetable oils have the potential to substitute for a fraction of the petroleum distillates and petroleum based petrochemicals in the near future. Vegetable oil fuels are not now petroleum competitive fuels because they are more expensive than petroleum fuels. However, with the recent increases in petroleum prices and the uncertainties concerning petroleum availability, there is renewed interest in using vegetable oils in Diesel engines. The Diesel boiling range material is of particular interest because it has been shown to reduce particulate emissions significantly relative to petroleum Diesel [6]. There are more than 350 oil bearing crops identified, among which only sunflower, safflower, soybean, cottonseed, rapeseed and peanut oils are considered as potential alternative fuels for Diesel engines [7,8].

The emergence of transesterification can be dated back as early as 1846 when Rochieder described glycerol preparation through ethanolysis of castor oil [9]. Since that time, alcoholysis has been studied in many parts of the world. Others researchers have also investigated the important reaction conditions and parameters on the alcoholysis of triglycerides, such as fish oils, tallow, soybean, rapeseed, cottonseed, sunflower, safflower, peanut and linseed oils [10–20]. Also, methyl esters have been prepared from palm oil by transesterification using methanol in the presence of a catalyst (KOH) in a batch reactor [21]. Soybean oil was transesterified into ethyl and methyl esters, and comparisons of the performances of the fuels with diesel [22,23] were made.

Methyl, ethyl, 2-propyl and butyl esters were prepared from canola and linseed oils through transesterification using KOH and/or sodium alkoxides as catalysts. In addition, methyl and ethyl esters were prepared from rapeseed and sunflower oils using the same catalysts [15]. 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. The success of rapeseed ethyl ester production would mean that biodiesel's two main raw materials would be agriculturally produced, renewable and environmentally friendly [12,16].

1.2. Fuel characterization

The biodiesel was characterized by determining its density, viscosity, higher heating value (HHV), cetane index, cloud and pour points, characteristics of distillation and flash and combustion points according to ISO norms [17]. The fuels are characterized by evaluation of the parameters required in ASAE EP X552. The tests are specific gravity, viscosity, cloud point, pour point, flash point, heat of combustion, total acid value, catalyst, fatty acid composition, boiling point, water and sediment, carbon residue (CR), ash, sulfur, cetane number (CN), copper corrosion, Karl Fischer water, particulate matter, iodine number and the elemental analysis.

The biodiesel esters were characterized for their physical and fuel properties, including density, viscosity, iodine value (IV), acid value, cloud point, pour point, gross heat of combustion and volatility. Methyl and ethyl esters prepared from a particular vegetable oil had similar viscosities, cloud points and pour points, whereas methyl, ethyl, 2-propyl and butyl esters derived from a particular vegetable oil had similar gross heating values. However, their densities, which were 2–7% higher than those of Diesel fuels, statistically decreased in the order of methyl similar to 2-propyl > ethyl > butyl esters [15]. The HHVs of the biodiesel fuels, on a mass basis, are 9–13% lower than D2 [24]. The viscosities of biodiesel fuels are twice that of D2. The cloud and pour points of D2 are significantly lower than those of the biodiesel fuels. The biodiesel fuels produced slightly lower power and torque and higher fuel consumption than D2.

Biodiesel is an efficient, clean, 100% natural energy alternative to petroleum fuels. Among the many advantages of biodiesel fuel are the following: safe for use in all conventional Diesel engines, offers the same performance and engine durability as petroleum Diesel fuel, non-flammable and non-toxic, reduces tailpipe emissions, visible smoke and noxious fumes and odors [25]. Biodiesel is better than Diesel fuel in terms of sulfur content (SC), flash point, aromatic content and biodegradability [26].

1.2.1. Methods for fuel analyses of vegetable oils

Physical analyses of vegetable oils are conducted according to the standard test methods: ASTM D445, ASTM D613 and ASTM D524 for kinematic viscosity (KV), CN and CR, respectively. However, since too low amounts of wheat grain, bay laurel leaf and corn marrow oils are available for determination of CN using the standard method, a calculated CN is established according to Goering et al. [7].

Chemical analyses of vegetable oils are conducted according to the standard test methods: ASTM D 2015-85, ASTM D5453-93, ASTM D482-91, AOCS CD1-25, 1993 and AOCS CD3

Table 1
Determination of physical and chemical properties using standard test methods

Property	Symbol	Standard method	Unit
Density	d	ASTM D4052-91	g/ml
Iodine value	IV	AOCS CD1-25 1993	cg I/g oil
Saponification value	SV	AOCS CD3 1993	mg KOH/g oil
Higher heating value	HHV	ASTM D2015-85	MJ/kg
Cloud point	CP	ASTM D2500-91	K
Pour point	PP	ASTM D97-93	K
Flash point	FP	ASTM D93-94	K
Cetane number	CN	ASTM D613	–
Kinematic viscosity	KV	ASTM D445	mm^2/s at 311 K
Sulfur content	SC	ASTM D5453-93	wt.%
Carbon residue	CR	ASTM D 524	wt.%
Ash content	AC	ASTM D482-91	wt.%

1993 for HHV, SC, ash content (AC), IV, and saponification value (SV) respectively. The other standard test methods for fuel properties are presented in Table 1.

2. Biodiesel fuels from vegetable oils

Vegetable oils are extracted or pressed to obtain crude oil. This usually contains free fatty acids (FFA), water, sterols, phospholipids, odorants and other impurities. The FFA and water contents have significant effects on the transesterification of glycerides with alcohols using alkaline and acid catalysts. Some glycerides contain higher levels of unsaturated fatty acids. They are liquids at

Table 2
Physical and chemical properties of vegetable oils

Vegetable oil	KV	CR	CN	HHV	AC	SC	IV	SV
Cottonseed	33.7	0.25	33.7	39.4	0.02	0.01	113.20	207.71
Poppyseed	42.4	0.25	36.7	39.6	0.02	0.01	116.83	196.82
Rapeseed	37.3	0.31	37.5	39.7	0.006	0.01	108.05	197.07
Safflowerseed	31.6	0.26	42.0	39.5	0.007	0.01	139.83	190.23
Sunflowerseed	34.4	0.28	36.7	39.6	0.01	0.01	132.32	191.70
Sesameseed	36.0	0.25	40.4	39.4	0.002	0.01	91.76	210.34
Linseed	28.0	0.24	27.6	39.3	0.01	0.01	156.74	188.71
Wheat grain	32.6	0.23	35.2	39.3	0.02	0.02	120.96	205.68
Corn marrow	35.1	0.22	37.5	39.6	0.01	0.01	119.41	194.14
Castor	29.7	0.21	42.3	37.4	0.01	0.01	88.72	202.71
Soybean	33.1	0.24	38.1	39.6	0.006	0.01	69.82	220.78
Bay laurel leaf	23.2	0.20	33.6	39.3	0.03	0.02	105.15	220.62
Peanut kernel	40.0	0.22	34.6	39.5	0.02	0.01	119.55	199.80
Hazelnut kernel	24.0	0.21	52.9	39.8	0.01	0.02	98.62	197.63
Walnut kernel	36.8	0.24	33.6	39.6	0.02	0.02	135.24	190.82
Almond kernel	34.2	0.22	34.5	39.8	0.01	0.01	102.35	197.56
Olive kernel	29.4	0.23	49.3	39.7	0.008	0.02	100.16	196.83

Source: Ref. [48].

Table 3
Fatty acid compositions of vegetable oil samples

Sample	16:0	16:1	18:0	18:1	18:2	18:3	Others
Cottonseed	28.7	0	0.9	13.0	57.4	0	0
Poppyseed	12.6	0.1	4.0	22.3	60.2	0.5	0
Rapeseed	3.5	0	0.9	64.1	22.3	8.2	0
Safflowerseed	7.3	0	1.9	13.6	77.2	0	0
Sunflowerseed	6.4	0.1	2.9	17.7	72.9	0	0
Sesameseed	13.1	0	3.9	52.8	30.2	0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Wheat grain[a]	20.6	1.0	1.1	16.6	56.0	2.9	1.8
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Corn marrow	11.8	0	2.0	24.8	61.3	0	0.3
Castor[b]	1.1	0	3.1	4.9	1.3	0	89.6
Tallow	23.3	0.1	19.3	42.4	2.9	0.9	2.9
Soybean	13.9	0.3	2.1	23.2	56.2	4.3	0
Bay laurel leaf[c]	25.9	0.3	3.1	10.8	11.3	17.6	31.0
Peanut kernel[d]	11.4	0	2.4	48.3	32.0	0.9	4.0
Hazelnut kernel	4.9	0.2	2.6	83.6	8.5	0.2	0
Walnut kernel	7.2	0.2	1.9	18.5	56.0	16.2	0
Almond kernel	6.5	0.5	1.4	70.7	20.0	0	0.9
Olive kernel	5.0	0.3	1.6	74.7	17.6	0	0.8
Coconut[e]	9.7	0.1	3.0	6.9	2.2	0	65.7

Source: Ref. [48].

[a] Wheat grain oil contains 11.4% of 8:0 and 0.4% of 14:0 fatty acids.
[b] Castor oil contains 89.6% ricinoloic acid.
[c] Bay laurel oil contains 26.5% of 12:0 and 4.5% of 14:0 fatty acids.
[d] Peanut kernel oil contains about 2.7% of 22:0 and 1.3% of 24:0 fatty acids.

ambient temperature. Table 2 shows the physical and chemical properties of vegetable oils. The fatty acids found in the vegetable oils are summarized in Table 3.

2.1. Direct use of oils

The use of vegetable oils as an alternative renewable fuel to compete with petroleum was proposed in the beginning of the 1980s [27]. The most advanced study with sunflower oil occurred in South Africa because of the oil embargo [2]. The first International Conference on Plant and Vegetable Oils as fuels was held in Fargo, North Dakota, in August 1982.

The advantages of vegetable oils as Diesel fuel are:

- Liquid nature-portability,
- Ready availability,
- Renewability,
- Higher heat content (about 88% of D2 fuel),
- Lower SC,
- Lower aromatic content,
- Biodegradability.

The disadvantages of vegetable oils as Diesel fuel are:

- Higher viscosity,
- Lower volatility,
- The reactivity of unsaturated hydrocarbon chains.

Although short term tests using neat vegetable oil showed promising results, problems appeared only after the engine had been operating on vegetable oil for longer periods of time. The problems met in long term engine tests, according to results obtained by earlier researchers [12,19,21], may be classified as follows: injector coking and trumpet formation on the injectors, more carbon deposits, oil ring sticking and thickening and gelling of the engine lubricant oil.

The major problem associated with the use of pure vegetable oils as fuels for Diesel engines is caused by the high fuel viscosity in compression ignition. The vegetable oils were all extremely viscous, with viscosities ranging 10–20 times greater than no. 2 Diesel fuel. Castor oil is in a class by itself with a viscosity more than 100 times that of no. 2 Diesel fuel [7]. Dilution, micro emulsification, pyrolysis and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity [28].

2.2. Dilution of vegetable oil

The viscosity of oil can be lowered by blending with pure ethanol. 25 parts of sunflower oil and 75 parts of Diesel were blended as Diesel fuel [29]. 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 [28].

The addition of 4% ethanol to D2 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 D2 fuel, it could assist the development of the combustion process through an unburned blend spray [30].

2.3. Using microemulsions for vegetable oil

To reduce the high viscosity of vegetable oils, microemulsions with immiscible liquids, such as methanol, ethanol and ionic or non-ionic amphiphiles have been studied [2,31]. Short engine performances of both ionic and non-ionic microemulsions of ethanol in soybean oil were nearly as good as that of D2 fuel [32].

All microemulsions with butanol, hexanol and octanol met the maximum viscosity requirement for D2 fuel. The 2-octanol was found to be an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil [2,31].

2.4. Biodiesel from vegetable oil via pyrolysis

Pyrolysis is the thermal degradation of vegetable oils by heat in the absence of oxygen, which results in the production of alkanes, alkenes, alkadienes, carboxylic acids, aromatics and small

amounts of gaseous products. Depending on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis and flash pyrolysis. The mechanism of pyrolysis of triglycerides was given by Schwab et al. [33].

The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum [34]. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Pyrolysis is conceptually simple to perform. A simple experimental setup for pyrolysis is depicted in Fig. 1. A thermogravimeter is used to obtain the effect of heating rate on the pyrolysis rate in experimental runs. It is interesting to determine how the heating rate affects the pyrolysis rate. The yields of pyrolysis of some vegetable oils are given in Table 4. The main components are alkanes and alkenes, which accounted for approximately 60% of the total feeder weight. Carboxylic acids accounted for another 9.6–16.1%. It is believed that as the reaction progresses, the residue becomes less reactive and forms stable chemical structures, and consequently, the activation energy increases as the decomposition level of the vegetable oil residue increases [35].

Catalytic cracking of vegetable oils to produce liquid biofuels has been studied by Pioch et al. [36]. The most interesting temperature range for the selectivities of cracking products as a function of pyrolysis temperature is between 825 and 1125 K [37]. The chemical compositions of the heavy hydrocarbons were similar to those present in petroleum refinery products.

The production of hydrogen by the catalytic steam reforming of sunflower oil [38] has been studied. The study was performed in a fixed bed reactor with a commercial nickel based catalyst for steam reforming naphtha. Sunflower oil was completely converted to hydrogen, methane and
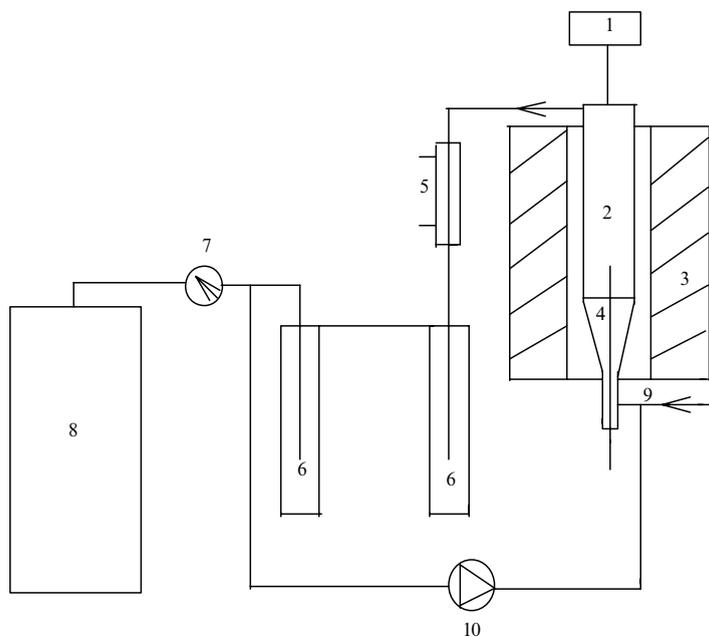

Fig. 1. Simplified experimental setting for vegetable oil pyrolysis. (1) Vegetable oil feeder, (2) Pyrolysis chamber, (3) Electric furnace, (4) Packing material, (5) Condenser, (6) Cold trap, (7) Gas volume measure, (8) Tight gas tank, (9) Sweeping gas stream, (10) Peristaltic pump.

Table 4
Yields of pyrolysis of vegetable oils (percent by weight)

	High oleic acid safflower		Soybean oil	
	N_2 sparge	Air	N_2 sparge	Air
Alkanes	37.5	40.9	31.1	29.9
Alkenes	22.2	22.0	28.3	24.9
Alkadienes	8.1	13.0	9.4	10.9
Carboxylic acids	11.5	16.1	12.2	9.6
Unresolved unsaturates	9.7	10.1	5.5	5.1
Aromatics	2.3	2.2	2.3	1.9
Unidentified	8.7	12.7	10.9	12.6

Source: Refs. [2,33,49].

carbon oxides, except for the runs performed at the lowest temperatures and an S/C ratio of 3. The hydrogen yield ranged from 72% to 87% of the stoichiometric potential, depending on the steam-to-carbon ratio and the catalyst temperature, which governed the equilibrium among the gas species.
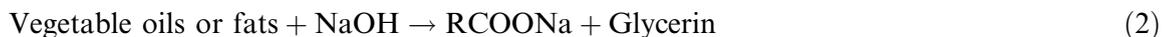
2.4.1. Pyrolysis of the vegetable oil soaps

In 1947, a large scale thermal cracking of tung oil calcium soap was reported [39]. Tung oil was saponified with lime and then thermally cracked to yield a crude oil, which was refined to produce Diesel fuel and small amounts of gasoline and kerosene. 68 kg of the tung oil soap produced 50 l of crude oil.

Pyrolyses of the vegetable oil soaps were performed in an apparatus designed for this purpose. The main element of this device was a tubular reactor of height 95.1 mm., ID 17.0 mm and OD 19.0 mm inserted vertically into an electrically heated tubular furnace. A similar pyrolysis apparatus was illustrated in the earlier study [40].

The saponification and pyrolysis of sodium soap of vegetable oil proceed as follows:

Saponification:

$$\text{Vegetable oils or fats} + \text{NaOH} \rightarrow \text{RCOONa} + \text{Glycerin} \tag{2}$$

Pyrolysis of Na soaps:

$$2\text{RCOONa} + (1/2)\text{O}_2 \rightarrow \text{R–R} + \text{Na}_2\text{CO}_3 + \text{CO}_2 \tag{3}$$

The soaps obtained from vegetable oils can be pyrolyzed into hydrocarbon rich products according to Eq. (3), with higher yields at the higher temperatures (Table 5 and Fig. 2). These findings are in general agreement with results given in the literature [41].

Fig. 2 shows a comparison of the distillation yields of sunflower oil and its methyl ester and liquid products from sunflower Na soap. Some 25–40 percent by weight of the fractions obtained from the fractional distillation of the vegetable oils are within the American Standard Testing Methods (ASTM) limits [24]. When the ASTM D86 procedure was used to distill the vegetable oils, they cleaved into a two phase distillate. Preliminary data indicate a complex mixture of

Table 5
Yields of decarboxylation products by pyrolysis from vegetable oil soaps (percent by weight)

Temperature (K)	Sunflower oil	Corn oil	Cottonseed oil	Soybean oil
400	2.8	2.3	3.1	2.9
450	8.4	8.6	8.5	8.8
500	29.0	28.5	31.3	32.6
520	45.4	46.2	48.0	49.2
550	62.4	65.5	67.2	68.0
570	84.6	84.0	83.9	85.1
590	92.7	93.0	93.5	93.4
610	97.5	97.1	97.5	97.8

Source: Ref. [48].
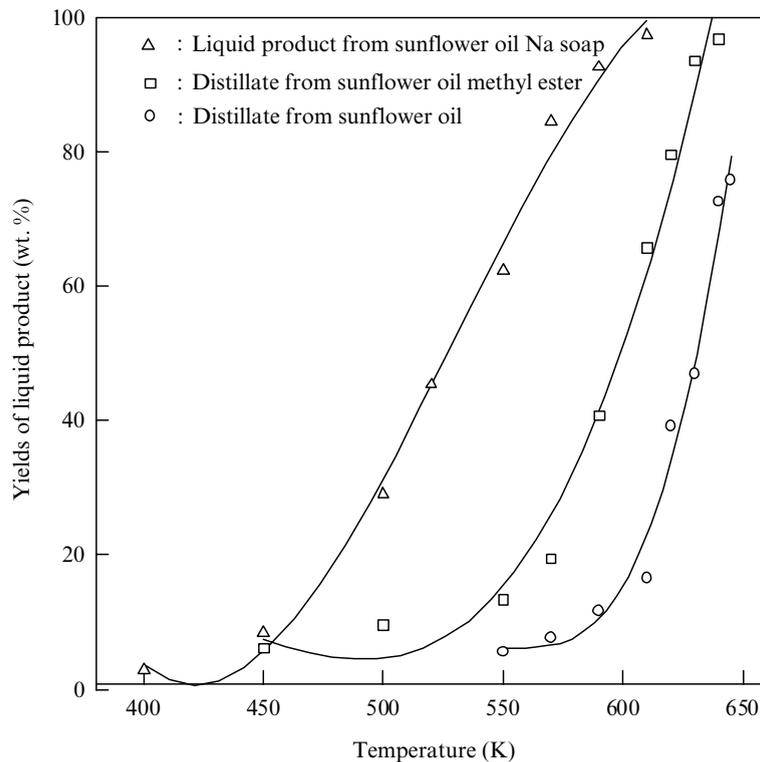
Fig. 2. Distillation curves for sunflower oil and methyl ester and Na soap of sunflower oil. Source: Ref. [48].

products including alkanes, alkenes and carboxylic compounds [7]. Typically, it was not possible to distill all of the vegetable oil and some brownish residue remained in the distillation flask. The value for the induction period of the distilled product was very low. The induction period values for the undistilled samples decreased very rapidly during storage, especially with exposure to light and air [16].

2.5. Biodiesel via transesterification from vegetable oil

Chemically, transesterification (also called alcoholysis) means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acids, removing the glycerin and creating an alcohol ester. The reaction is shown in Eq. (1). A catalyst is usually used to improve the reaction rate and yield. Theoretically, the transesterification reaction is an equilibrium reaction. In this reaction, however, a larger amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters, the proposed product.

Alcohols are primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms [42]. 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, however methanol is used because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). The the transesterification reaction can be catalyzed by alkalis, acids or enzymes.

Several alcoholysis catalysts, known to be effective for reactions between simple alcohols and soybean oil, were evaluated and found to be ineffective toward alcoholysis of ethylene glycol with soybean oil under traditional reaction conditions. An initial survey of alternative catalysts revealed that organometallic tin complexes were effective but unsatisfactory due to their toxicity and the difficulty in recovering the catalyst. Satisfactory performance for several alcoholysis reactions was achieved with calcium carbonate catalysts even though at higher temperatures, typically greater than 475 K [43].

The physical properties of the primary chemical products of transesterification are given in Tables 6 and 7.

2.5.1. Catalytic transesterification method

The catalyst is dissolved into the 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 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 glycerin. Crude glycerin, the heavier liquid, will collect at the bottom after several hours of settling. Phase separation can be

Table 6
Physical properties of chemicals related to transesterification

Name	Specific gravity (g/ml)	Melting point (K)	Boiling point (K)	Solubility (<10%)
Methyl myristate	0.875	291.0	–	–
Methyl palmitate	0.825	303.8	469.2	Benzene, EtOH, Et_2O
Methyl stearate	0.850	311.2	488.2	Et_2O, chloroform
Methyl oleate	0.875	253.4	463.2	EtOH, Et_2O
Methanol	0.792	176.2	337.9	H_2O, ether, EtOH
Ethanol	0.789	161.2	351.6	H_2O, ether
Glycerol	1.260	255.3	563.2	H_2O, ether

Source: Refs. [2,50].

Table 7
Melting points of fatty acids, methyl esters and mono-, di-, and triglycerides[a] (K)

Name	Fatty acid	Methyl ester	1-Monoglyceride	1,3-Diglyceride	Triglyceride
Myristic	327.6	336.1	342.8	289.5	266.7
Palmitic	292.0	303.8	312.3	253.4	238.2
Stearic	343.7	350.2	254.7	308.4	285.5
Oleic	340.0	349.5	352.6	294.7	270.6
Linoleic	330.2	336.7	346.3	278.7	260.1

Source: Refs. [2,51].
[a] Melting point of highest melting, most stable polymorphic form.

observed within 10 min and can be complete within 2 h of settling. Complete settling can take as long as 20 h.

After settling is complete, water is added at the rate of 5.5 percent by volume of the methyl ester of oil and then stirred for 5 min, and the glycerin is allowed to settle again. Washing the ester is a two step process, which is performed with extreme care.

A water wash solution at the rate of 28 percent by volume of oil and 1 g of tannic acid per liter of water is added to the ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This process is continued until the ester layer becomes clear. After settling, the aqueous solution is drained, and water alone is added at 28 percent by volume of oil for the final washing.

2.5.2. Supercritical methanol transesterification method

A typical supercitical methanol transesterification system is shown in Fig. 3. All the runs of SFE are performed in a cylindrical autoclave made of 316 stainless steel in which the pressure and temperature are monitored in real time, covering up to 100 MPa and 850 K, respectively. In a typical run, the autoclave is charged with a given amount of vegetable oil and liquid methanol with changed molar ratios [35]. After each run, the gas is vented, and the autoclave is poured into
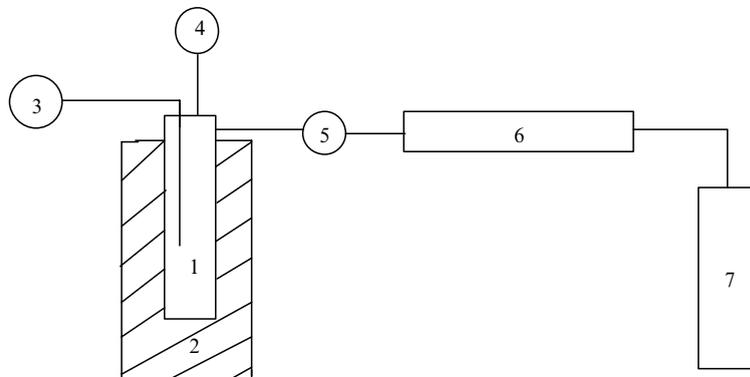
Fig. 3. Supercritical methanol transesterification system. (1) Autoclave, (2) Electrical furnace, (3) Temperature control monitor, (4) Pressure control monitor, (5) Product exit valve, (6) Condenser, (7) Product collecting vessel.

a collecting vessel. All the rest of the contents are removed from the autoclave by washing with methanol.

The variables affecting the methyl ester yield during the transesterification reaction, such as molar ratio of alcohol to vegetable oil and reaction temperature were investigated [35]. The viscosities of the methyl esters from the vegetable oils were slightly higher than that of no. 2 Diesel fuel (Table 8). The viscosity values of the methyl esters range from 2.8 to 3.5 mm^2/s at 311 K. The viscosity of no. 2 Diesel was measured at 311 K as 2.7 mm^2/s.

Fig. 4 shows a typical example of the relationship between the reaction time and the temperature. The critical temperature and the critical pressure of methanol are 512.4 K and 8.0 MPa, respectively. It was observed that increasing the reaction temperature, especially supercritical

Table 8
Viscosities of vegetable oils and methyl esters from the vegetable oils by transesterificaion (measured at 311 K as mm^2/s)

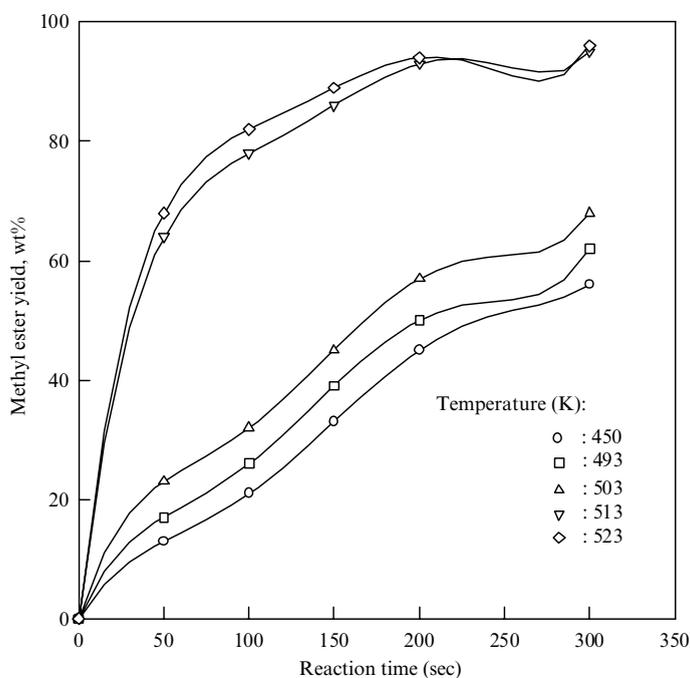| Test sample	Cottonseed	Hazelnut kernel	Poppyseed	Rapeseed	Safflowerseed	Sunflowerseed
Viscosity of no. 2 Diesel: 2.7 mm^2/s						
Vegetable oil	33.7	24.0	42.4	37.3	31.6	34.4
Methyl ester	3.1	2.8	3.5	3.3	2.9	3.2

Source: Ref. [35].

Fig. 4. Changes in yield percentage of methyl esters as treated with sub-critical 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. Source: Ref. [35].

Table 9
Yields of distillation of vegetable oil methyl esters (percent by weight)

Temperature (K)	Sunflower oil	Corn oil	Cottonseed oil	Soybean oil
450	6.1	6.8	7.9	8.2
500	9.5	9.9	10.6	11.0
550	13.3	14.7	15.6	16.5
570	19.4	20.8	22.0	23.6
590	40.7	43.6	44.0	45.2
610	65.7	68.4	71.3	72.1
620	79.6	80.5	82.3	84.2
630	93.6	95.8	96.5	96.8
640	96.8	97.2	97.6	97.9

Source: Ref. [48].

temperatures had a favorable influence on ester conversion. The yields of distillation of vegetable oil methyl esters are given in Table 9.

The variables affecting the ester yield during the transesterification reaction are molar ratio of alcohol to vegetable oil, reaction temperature, reaction time, water content and catalyst.

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 were greater than 1, more NaOH or KOH would be spent to neutralize the FFA. Water also caused soap formation and frothing. The resulting soaps caused an increase in viscosity, formation of gels and foams and made the separation of glycerol difficult [2,44].

The stoichiometric ratio for the transesterification reaction requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. Higher molar ratios result in greater ester production in a shorter time. The vagetable oils were transesterified at 1:6–1:40 vegetable oil-alcohol molar ratios in catalytic and supercritical alcohol conditions [12,35,45,46].

Catalysts are classified as alkali, acid or enzyme [13,19]. The transesterification reaction was performed using triglycerides and short chain alcohol by immobilized lipase in non-aqueous conditions. The long chain fatty acid ester, which is the product of this reaction, can be used as a Diesel fuel that does not produce sulfur oxide and minimizes the soot particulates [47].

Methyl esters were produced by transesterification of palm oil with methanol in the presence of a catalyst (KOH) in a batch reactor [20]. The transesterification reaction of rapeseed oil in supercritical methanol was investigated without using any catalyst. In addition, it was found that this new supercritical methanol process requires a shorter reaction time and a simpler purification procedure because of the unused catalyst [12].

The detailed analysis is described of the samples taken after suitable reaction times from the actual reaction mixture during the production of biodiesel fuel using methanolysis of rapeseed oil catalyzed by KOH [19].

Transesterification can occur at different temperatures, and the temperature influenced the reaction rate and yield of esters, depending on the oil used (Fig. 4). It was observed that increasing the reaction temperature, especially at supercritical temperatures, had a favorable influence on ester conversion [35].

2.6. Recovery of glycerin

The process of converting vegetable oil into biodiesel fuel is called transesterification and is luckily less complex than it sounds. Chemically, transesterification means taking a triglyceride molecule or a complex fatty acid, neutralizing the FFA, removing the glycerin and creating an alcohol ester. This is accomplished by mixing methanol with sodium hydroxide to make sodium methoxide. This dangerous liquid is then mixed into the vegetable oil. The entire mixture then settles. Glycerin is left on the bottom and methyl esters, or biodiesel, is left on top. The glycerin can be used to make soap (or any one of 1,600 other products), and the methyl esters are washed and filtered. The resulting biodiesel fuel, when used directly in a Diesel engine, will burn up to 75% cleaner than petroleum D2 fuel. The recovery of high quality glycerol as a biodiesel by product is a primary option to be considered to lower the cost of biodiesel.

3. Comparison of methyl and ethyl esters

In general, the physical and chemical properties and the performance of ethyl esters are comparable to those of the methyl esters. Methyl and ethyl esters have almost the same heat content. The viscosities of the ethyl esters are slightly higher, and the cloud and pour points are slightly lower, than those of the methyl esters. Engine tests demonstrated that methyl esters produced slightly higher power and torque than ethyl esters [17]. Some desirable attributes of the ethyl esters over methyl esters are: significantly lower smoke opacity, lower exhaust temperatures and lower pour point. The ethyl esters tended to have more injector coking than the methyl esters.

4. Engine performance tests

The methyl ester of vegetable oil was evaluated as a fuel in CIE by researchers [11,12]. They concluded that the performance of the esters of vegetable oil did not differ greatly from that of Diesel fuel. The brake power was nearly the same as with Diesel fuel, while the specific fuel consumption was higher than that of Diesel fuel. Based on crankcase oil analysis, engine wear rates were low but some oil dilution did occur. Carbon deposits inside the engine were normal, with the exception of intake valve deposits. The results showed the transesterification treatment decreased the injector coking to a level significantly lower than that observed with D2. Although most researchers agree that vegetable oil ester fuels are suitable for use in CIE, a few contrary results have also been obtained. The results of these studies point out that most vegetable oil esters are suitable as Diesel substitutes but that more long term studies are necessary for commercial utilization to become practical.

5. Biodiesel economy

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 recovery of high quality glycerol as a biodiesel by-product are primary options to be considered to lower the cost of biodiesel [2].

Most of the biodiesel that is currently made uses soybean oil, methanol and an alkaline catalyst. The high value of soybean oil as a food product makes 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 to biodiesel. The problem with processing these low cost oils and fats is that they often contain large amounts of FFA that cannot be converted to biodiesel using an alkaline catalyst [18].

A review of 12 economic feasibility studies shows that the projected costs for biodiesel from oilseed or animal fats have a range of US$0.30–0.69/l, including the meal and glycerin credits and the assumption of 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$0.54–0.62/l and US$0.34–0.42/l. With pre-tax Diesel priced at US$0.18/l in the US and US$0.20–0.24/l in some European countries, biodiesel is, thus, currently not economically feasible, and more research and technological development will be needed [46].

6. Conclusions

The vegetable oil fuels have not been acceptable because they are more expensive than petroleum fuels. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for Diesel engines.

Dilution of oils with solvents and microemulsions of vegetable oils lowers the viscosity, but some engine performance problems still exist. The purpose of the transesterification process is to lower the viscosity of the oil. The main factors affecting transesterification are molar ratio of glycerides to alcohol, catalyst, reaction temperature and pressure, reaction time and the contents of FFA and water in the oils. The commonly accepted molar ratios of alcohol to glycerides are 6:1–30:1.

Pyrolysis produces more biogasoline than biodiesel fuel. Soap pyrolysis products of vegetable oils can be used as alternative Diesel engine fuels.

Methyl and ethyl esters of vegetable oils have several outstanding advantages among the other new renewable and clean engine fuel alternatives.

Fuel characterization data show some similarities and differences between biodiesel fuels and Diesel:

- Specific weight is higher for biodiesel, heat of combustion is lower and viscosities are 1.3–2.1 times that of D2 fuel.
- Pour points for biodiesel fuels vary from 274 to 298 K higher for biodisel fuels depending on the feedstock.
- SC for biodiesel fuel is 20–50% that of D2 fuel.
- The esters all have higher levels of injector coking than D2 fuel.

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