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Biodiesel production: a review[1]

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Abstract

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. The cost of biodiesel, however, is the main hurdle to commercialization of the product. The used cooking oils are used as raw material, adaption of continuous transesterification process and recovery of high quality glycerol from biodiesel by-product (glycerol) are primary options to be considered to lower the cost of biodiesel. There are four primary ways to make biodiesel, direct use and blending, microemulsions, thermal cracking (pyrolysis) and transesterification. The most commonly used method is transesterification of vegetable oils and animal fats. The transesterification reaction is affected by molar ratio of glycerides to alcohol, catalysts, reaction temperature, reaction time and free fatty acids and water content of oils or fats. The mechanism and kinetics of the transesterification show how the reaction occurs and progresses. The processes of transesterification and its downstream operations are also addressed. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Biodiesel; Transesterification; Blending; Microemulsion; Thermal cracking

1. Introduction

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial (Krawczyk, 1996).

One hundred years ago, Rudolf Diesel tested vegetable oil as fuel for his engine (Shay, 1993). With the advent of cheap petroleum, appropriate crude oil fractions were refined to serve as fuel and diesel fuels and diesel engines evolved together. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, but usually only in emergency situations. Recently, because of increases in crude oil prices, limited resources of fossil oil and environmental concerns there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels. Continued and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by CO_2 (Shay, 1993). In a particular case, such as the emission of pollutants in the closed environments of underground mines, biodiesel fuel has the potential to reduce the level of pollutants and the level of potential or probable carcinogens (Krawczyk, 1996).

Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (Sonntag, 1979a). Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). The fatty acids found in vegetable oils are summarized in Table 1. Table 2 shows typical fatty acid compositions of common oil sources. Table 3 gives the compositions of crude tallow.

In beef tallow the saturated fatty acid component accounts for almost 50% of the total fatty acids. The higher stearic and palmitic acid contents give beef tallow the unique properties of high melting point and high viscosity.

Natural vegetable oils and animal fats are extracted or pressed to obtain crude oil or fat. These usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Even refined oils and fats contain small amounts of free fatty acids and water. The free fatty acid and water contents have significant effects on the transesterification of glycerides with alcohols

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Table 1
Chemical properties of vegetable oil (Goering et al., 1982a)

Vegetable oil	Fatty acid composition, % by weight									Acid [a] value	Phos [b] ppm	Peroxide [c] value
	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3			
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48	0.11	7.00	18.4
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00	0.07	8.00	64.8
Crambe	2.07	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85	0.36	12.00	26.5
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93	0.20	9.00	82.7
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.40	0.00	22.30	8.23	1.14	18.00	30.2
Soybean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31	0.20	32.00	44.5
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00	0.15	15.00	10.7

[a] Acid values are milligrams of KOH necessary to neutralize the FFA in 1 g of oil sample.

[b] Phosphatide (gum) content varies in direct proportion to phosphorus value.

[c] Peroxide values are milliquivalents of peroxide per 1000 g of oil sample, which oxidize potassium iodide under conditions of the test.

Table 2
Typical fatty acid composition-common oil source (Kincs, 1985)

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric	0.1	0.1	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	1.4	2.8	19.2
Palmitic	10.2	20.1	42.8	23.6	23.3	9.8
Stearic	3.7	2.6	4.5	14.2	19.4	3.0
Oleic	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic	53.7	55.2	10.1	10.7	2.9	2.2
Linolenic	8.6	0.6	0.2	0.4	0.9	0.0

using alkaline or acid catalysts. They also interfere with the separation of fatty acid esters and glycerol.

Considerable research has been done on vegetable oils as diesel fuel. That research included palm oil, soybean oil, sunflower oil, coconut oil, rapeseed oil and tung oil. Animal fats, although mentioned frequently, have not been studied to the same extent as vegetable oils. Some methods applicable to vegetable oils are not applicable to animal fats because of natural property differences. Oil from algae, bacteria and fungi also have been investigated. (Shay, 1993). Microalgae have been examined as a source of methyl ester diesel fuel (Nagel and Lemke, 1990). Terpenes and latexes also were studied as diesel fuels (Calvin, 1985).

Table 3
Properties and composition of crude beef tallow (Sonntag, 1979c)

Characteristics	
Iodine number	35–48
Saponification number	193–202
Titer, C	40–46
Wiley melting point, C	47–50
Fatty acid composition, wt.%	
Myristic	2–8
Palmitic	24–37
Stearic	14–29
Oleic	40–50
Linoleic	1–5
Glyceride composition, mole%	
Total GS_3	15–28
Total GS_2U	46–52
Total GSU_2	20–37
Total GU_3	0–2

Some natural glycerides contain higher levels of unsaturated fatty acids. They are liquids at room temperature. Their direct uses as biodiesel fuel is precluded by high viscosities. Fats, however, contain more saturated fatty acids. They are solid at room temperature and cannot be used as fuel in a diesel engine in their original form. Because of the problems, such as carbon deposits in the engine, engine durability and lubricating oil contamination, associated with the use of oils and fats as diesel fuels, they must be derivatized to be compatible with existing engines. Four primary production methodologies for producing biodiesel have been studied extensively. This paper reviews the technologies starting with the direct use or blending of oils, continuing with microemulsion and pyrolysis and finishing with an emphasis on the current process of choice, transesterification.

2. The production of biodiesel

2.1. Direct use and blending

Beginning in 1980, there was considerable discussion regarding use of vegetable oil as a fuel. Bartholomew (1981) addressed the concept of using food for fuel, indicating that petroleum should be the “alternative” fuel rather than vegetable oil and alcohol being the alternatives and some form of renewable energy must begin to take the place of the nonrenewable resources. The most advanced work with sunflower oil occurred in South Africa because of the oil embargo. Caterpillar Brazil, in 1980, used pre-combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alterations or adjustments to the engine. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful. Some short-term experiments used up to a 50/50 ratio.

The first International Conference on Plant and Vegetable Oils as fuels was held in Fargo, North Dakota in August 1982. The primary concerns discussed were the cost of the fuel, the effects of vegetable oil fuels on engine performance and durability and fuel preparation, specifications and additives. Oil production, oilseed processing and extraction also were considered in this meeting (ASAE, 1982).

A diesel fleet was powered with filtered, used frying oil (Anon, 1982). Used cooking oil and a blend of 95% used cooking oil and 5% diesel fuel were used. Blending or preheating was used as needed to compensate for cooler ambient temperatures. There were no coking and carbon build-up problems. The key was suggested to be filtering and the only problem reported was lubricating oil contamination (viscosity increase due to polymerization of polyunsaturated vegetable oils). The lubricating oil had to be changed every 4,000–4,500 miles.

The advantages of vegetable oils as diesel fuel are (1) liquid nature-portability, (2) heat content (80% of diesel fuel), (3) ready availability and (4) renewability. The disadvantages are (1) higher viscosity, (2) lower volatility and (3) the reactivity of unsaturated hydrocarbon chains (Pryde, 1983). Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines. The problems include (1) coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices, (2) carbon deposits, (3) oil ring sticking and (4) thickening and gelling of the lubricating oil as a result of contamination by the vegetable oils.

Mixtures of degummed soybean oil and No. 2 diesel fuel in the ratios of 1:2 and 1:1 were tested for engine performance and crankcase lubricant viscosity in a John Deere 6-cylinder, 6.6 L displacement, direct-injection, turbocharged engine for a total of 600 h (Adams et al., 1983). The lubricating oil thickening and potential gelling existed with the 1:1 blend, but it did not occur with the 1:2 blend. The results indicated that 1:2 blend should be suitable as a fuel for agricultural equipment during periods of diesel fuel shortages or allocations.

Two severe problems associated with the use of vegetable oils as fuels were oil deterioration and incomplete combustion (Peterson et al., 1983). Polyunsaturated fatty acids were very susceptible to polymerization and gum formation caused by oxidation during storage or by complex oxidative and thermal polymerization at the higher temperature and pressure of combustion. The gum did not combust completely, resulting in carbon deposits and lubricating oil thickening. Winter rapeseed oil as a diesel fuel was studied because of the high yield and oil content (45%) of winter rapeseed and the high (46.7%) erucic acid content of the oil (Peterson et al., 1983). The rate of gum formation of winter rapeseed oil was five times slower than that of high linoleic (75–85%) oil. The viscosities of 50/50 and 70/30 blends of winter rapeseed oil and diesel and whole winter rape oil were much higher (6–18 times) than No. 2 diesel. A blend of 70/30 winter rapeseed oil and No. 1 diesel was used successfully to power a small single-cylinder diesel engine for 850 h. No adverse wear and no effects on lubricating oil or power output were noted.

Canola oil is much more viscous than the other more commonly tested vegetable oils and, as with all fluids, the viscosity is temperature-dependent. At 10°C the viscosity of canola oil was 100 cSt; a 75/25 blend of canola oil and diesel fuel was 40 cSt; a 50/50 blend was 19 cSt; and the viscosity of diesel fuel was 4 cSt (Strayer et al., 1983). The flow rate of canola was lower than diesel at the same pressure and it dropped to almost zero at −4°C. Viscosity can be lowered by blending with pure ethanol. At 37°C, the viscosity of canola oil and 10% ethanol was 21.15 cSt, while that of straight canola oil was 37.82 cSt.

Crude, degummed and degummed-dewaxed sunflower oils, as well as crude, degummed and alkali refined cottonseed oils, were tested using a single-cylinder precombustion chamber engine (Engler et al., 1983). The results were negative. The processed oils which were slightly better than crude oils were not suitable for use as alternative fuels, even though they performed satisfactorily for a short time. The oils were not suitable because of carbon deposits and lubricating oil fouling.

25 parts of sunflower oil and 75 parts of diesel were blended as diesel fuel (Ziejewski et al., 1986). The viscosity was 4.88 cSt at 40°C, while the maximum specified ASTM value is 4.0 cSt at 40°C. It was considered not suitable for long term use in a direct-injection engine. The viscosity of a 25/75 high safflower oil and diesel blend was 4.92 cSt at 40°C. A mixture of 50/50 soybean oil and Stoddard solvent (48% paraffins and 52% naphthenes) from Union Oil Co. had a viscosity of 5.12 cSt at 38°C (Goering, 1984b). Both blends of safflower and soybean oil passed the 200 h EMA (Engine Manufacturers' Association) test.

Short term performance tests were conducted to evaluate crude soybean oil, crude-degummed soybean oil and soybean ethyl ester as complete substitutes for No. 2 diesel fuel in a 2.59 L, 3 cylinder 2600 series Ford diesel engine (Pryor et al., 1983). A longer term evaluation of the engine when using 100% crude soybean oil was prematurely terminated. Severe injector coking led to decreases in power output and thermal efficiency.

A long-term performance test was conducted using a fuel blend of 75% unrefined mechanically expelled soybean oil and 25% diesel fuel (Schlautman et al., 1986). The fuel blend was burned in a direct injection diesel engine for 159 h before the test was terminated because a constant load could not be held on the engine. A test failure occurred after 90 h into the screening test due to a 670% increase in the lubricating oil viscosity.

Schlick et al. (1988) evaluated the performance of a direct injection 2.59 L, 3 cylinder 2600 series Ford diesel engine operating on mechanically expelled-unrefined soybean oil and sunflower oil blended with number 2 diesel fuel on a 25:75 v/v basis. The power remained constant throughout 200 h of operation. Excessive carbon deposits on all combustion chamber parts precludes the use of these fuel blends, at least in this engine and under the specified EMA operating conditions.

Direct use of vegetable oils and/or the use of blends of the oils has generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems. The probable reasons for the problems and the potential solutions are shown in Table 4.

3. Microemulsions

To solve the problem of the high viscosity of vegetable oils, microemulsions with solvents such as methanol, ethanol and 1-butanol have been studied. A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1–150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles (Schwab et al., 1987). They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles (Pryde, 1984). Short term performances of both ionic and non-ionic microemulsions of aqueous ethanol in soybean oil were nearly as good as that of No. 2 diesel, in spite of the lower cetane number and energy content (Goering et al., 1982b). The durabilities were not determined.

Ziejewski et al. (1984) prepared an emulsion of 53% (vol) alkali-refined and winterized sunflower oil, 13.3% (vol) 190-proof ethanol and 33.4% (vol) 1-butanol. This nonionic emulsion had a viscosity of 6.31 cSt at 40°C, a cetane number of 25 and an ash content of less than 0.01%. Lower viscosities and better spray patterns (more even) were observed with an increase of 1-butanol. In a

Table 4
Known problems, probable cause and potential solutions for using straight vegetable oil in diesels (Harwood, 1984)

Problem	Probable cause	Potential solution
Short-term		
1. Cold weather starting	High viscosity, low cetane, and low flash point of vegetable oils	Preheat fuel prior to injection. Chemically alter fuel to an ester
2. Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) in vegetable oil. Other ash	Partially refine the oil to remove gums. Filter to 4-microns
3. Engine knocking	Very low cetane of some oils. Improper injection timing.	Adjust injection timing. Use higher compression engines. Preheat fuel prior to injection. Chemically alter fuel to an ester
Long-term		
4. Coking of injectors on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester
5. Carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester
6. Excessive engine wear	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation
7. Failure of engine lubricating oil due to polymerization	Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation.

200 h laboratory screening endurance test, no significant deteriorations in performance were observed, but irregular injector needle sticking, heavy carbon deposits, incomplete combustion and an increase of lubricating oil viscosity were reported.

Shipp nonionic (SNI) fuel containing 50% No. 2 diesel fuel, 25% degummed and alkali-refined soybean oil, 5% 190-proof ethanol and 20% 1-butanol was evaluated in the 200 h EMA screening test (Goering and Fry, 1984a). The fuel properties are summarized in Table 5. The fuel passed the 200 h EMA test, but carbon and lacquer deposits on the injector tips, in-take valves and tops of the cylinder liners were major problems. The SNI fuel performed better than a 25% blend of sunflower oil in diesel oil. The engine performances were the same for a microemulsion of 53% sunflower oil and the 25% blend of sunflower oil in diesel (Ziejewski et al., 1983). A microemulsion prepared by blending soybean oil, methanol, 2-octanol and cetane improver in the ratio of 52.7:13.3:33.3:1.0 also passed the 200 h EMA test (Goering, 1984b).

Schwab et al. (1987) used the ternary phase equilibrium diagram and the plot of viscosity versus solvent fraction to determine the emulsified fuel formulations. All microemulsions with butanol, hexanol and octanol met the maximum viscosity requirement for No. 2 diesel. The 2-octanol was an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil. Methanol was often used due to its economic advantage over ethanol.

3.1. Thermal cracking (pyrolysis)

Pyrolysis, strictly defined, is the conversion of one substance into another by means of heat or by heat with the aid of a catalyst (Sonntag, 1979b). It involves heating in the absence of air or oxygen (Sonntag, 1979b) and cleavage of chemical bonds to yield small molecules (Weisz et al., 1979). Pyrolytic chemistry is difficult to characterize because of the variety of reaction paths and the variety of reaction products that may be obtained from the reactions that occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum (Sonntag, 1979b).

The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Since World War I, many investigators have studied the pyrolysis of vegetable oils to obtain products suitable for fuel. In 1947, a large scale of thermal cracking of tung oil calcium soaps was reported (Chang and Wan, 1947). Tung oil was first 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 kgs of the soap from the saponification of tung oil produced 50 L of crude oil. Grossley et al. (1962) studied the temperature effect on the type of products obtained from heated glycerides. Catalysts have been used in many studies, largely metallic salts, to obtain paraffins and olefins similar to those present in petroleum sources.

Soybean oil was thermally decomposed and distilled in air and nitrogen sparged with a standard ASTM distillation apparatus (Niehaus et al., 1986; Schwab et al., 1988). Schwab et al. (1988) used safflower oil as a high oleic oil control. The total identified hydrocarbons obtained from the distillation of soybean and high oleic safflower oils were 73–77 and 80–88% respectively. The compositions of pyrolyzed oils are listed in Table 6 (Alencar et al., 1983; Schwab et al., 1988). 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%. Compositions were determined by GC-MS. The mechanisms for the thermal decomposition of a triacylglyceride are given in Fig. 1. The fuel properties are compared in Table 7.

Catalytic cracking of vegetable oils to produce biofuels has been studied (Pioch et al., 1993). Copra oil and palm oil stearin were cracked over a standard petroleum catalyst SiO_2/Al_2O_3 at 450°C to produce gases, liquids and solids with lower molecular weights. The condensed organic phase was fractionated to produce biogasoline and biodiesel fuels. The chemical compositions (heavy hydrocarbons) of the diesel fractions were similar to

Table 5
Properties of shipp nonionic fuel (Goering and Fry, 1984a)

Property	Value
Viscosity at 38°C, mm^2/s	4.03
Stability at 5°C, h	>24
Higher heating value, kJ/kg	41263
Stoichiometric air-fuel ratio	13.1
Flash point, C	28.3
Ramsbottom carbon residue, % of whole sample	0.14
Cetane No.	34.7

Table 6
Compositional data of pyrolysis of oils (Alencar et al., 1983; Schwab et al., 1988)

	Percent by weight			
	High oleic safflower		Soybean	
	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
Aromatics	2.3	2.2	2.3	1.9
Unresolved unsaturates	9.7	10.1	5.5	5.1
Carboxylic acids	11.5	16.1	12.2	9.6
Unidentified	8.7	12.7	10.9	12.6

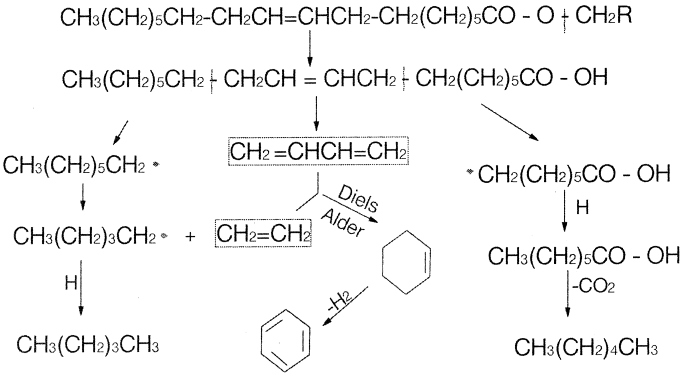


Fig. 1. The mechanism of thermal decomposition of triglycerides (Schwab et al., 1988).

Table 7
Fuel properties of thermally cracked soybean oil

	Soybean oil		Cracked soybean oil		Diesel fuel	
	a	b	a	b	a	b
Cetane number	38.0	37.9	43.0	43.0	51.0	40.0
Higher heating value, MJ/kg	39.3	39.6	40.6	40.3	45.6	45.5
Pour point C	−12.2	−12.2	4.4	7.2	−6.7 max	−6.7 max
Viscosity, cSt at 37.8°C	32.6	32.6	7.74	10.2	2.82	1.9–4.1

[a] Data from Niehaus et al. (1986).
[b] Data from Schwab et al. (1988).

fossil fuels. The process was simple and effective compared with other cracking processes according to the paper. There was no waste water or air pollution.

Rapeseed oil was pyrolyzed to produce a mixture of methyl esters in a tubular reactor between 500 and 850°C and in nitrogen (Billaud et al., 1995). A flow chart of the micropilot pyrolysis plant for methyl esters from rapeseed oil and a design of the pyrolysis reactor were outlined. The conversion of methyl colzate increased with an increase of the temperature of pyrolysis. To illustrate the distribution of cracking products as a function of pyrolysis temperature, the selectivities of the products (hydrocarbons, CO, CO_2 and H_2) obtained between 550–850°C with a constant residence time of 320 min and a constant dilution rate of 13 moles of nitrogen/mole of feedstock are provided in Table 8. The principal products were linear 1-olefins, *n*-paraffins and unsaturated methyl esters. High temperatures gave high yields of light hydrocarbons (66% molar ratio at 850°C).

The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived

Table 8
Selectivities of cracking products as a function of pyrolysis temperature (Billaud et al., 1995)

	Selectivity (molar % of carbon atoms cracked)						
	550°C	600°C	650°C	700°C	750°C	800°C	850°C
C_1–C_4 cut	10.0	18.6	28.2	38.7	35.1	45.1	66.1
C_5–C_9 cut	36.0	19.6	17.6	13.2	17.5	12.6	3.6
C_{10}–C_{14} cut	3.0	3.5	3.5	2.7	1.7	1.0	0.3
C_{15}–C_{18} cut	0.9	0.7	0.3	1.1	0.3	0.2	0.3
Aromatics	5.2	2.0	2.7	3.9	7.2	11.6	8.9
$C_{3:1}$–$C_{8:1}$ esters	8.5	16.6	10.3	7.2	5.9	4.1	0.9
$C_{9:1}$–$C_{16:1}$ esters	2.3	3.2	3.4	2.3	0.9	0.5	0.3
Saturated esters	2.0	1.2	1.6	2.4	3.7	3.1	2.6
CO	0.5	1.2	1.3	2.3	2.7	3.8	5.3
CO_2	0.3	0.6	0.6	1.1	1.5	1.6	2.1
Coke	6.1	3.8	4.2	4.7	2.2	3.1	4.5
Other products	25.2	29.0	25.3	20.4	21.3	13.3	5.1
	Selectivity (molar % of hydrogen atoms cracked)						
H_2	0.3	0.9	1.7	2.7	3.6	4.6	5.9

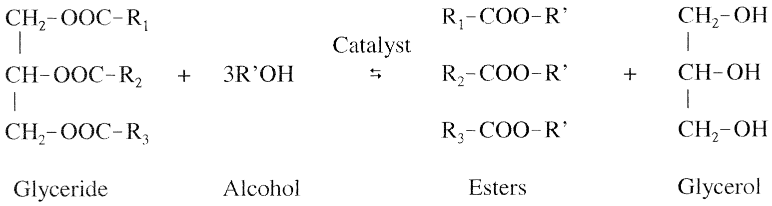


Fig. 2. Transesterification of triglycerides with alcohol.

gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produced some low value materials and, sometimes, more gasoline than diesel fuel.

3.2. Transesterification (Alcoholysis)

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. The reaction is shown in Fig. 2. 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 products side.

Alcohols are primary and secondary monohydric aliphatic alcohols having 1–8 carbon atoms (Sprules and Price, 1950). Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and NaOH is easily dissolved in it. To complete a transesterification stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield. The reaction can be catalyzed by alkalis, acids, or enzymes. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acids and hydrochloric acid are usually used as acid catalysts. Lipases also can be used as biocatalysts. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially.

For an alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous (Wright et al., 1944) because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of esters and renders the separation of ester and glycerol and the water washing difficult. Low free fatty acid content in triglycerides is required for alkali-catalyzed transesterification. If more water and free fatty acids are in the triglycerides, acid-catalyzed transesterification can be used (Keim, 1945). The triglycerides can be purified by saponification (known as alkali treating) and then transesterified using an alkali catalyst.

The physical properties of the primary chemical products of transesterification are summarized in Tables 9 and 10. The boiling points and melting points of the fatty acids, methyl esters, mono-, di- and triglycerides increase as the number of carbon atoms in the carbon chain increase, but decrease with increases in the number of double bonds. The melting points increase in the order of tri-, di- and monoglycerides due to the polarity of the molecules and hydrogen bonding.

After transesterification of triglycerides, the products are a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglycerides. Obtaining pure esters was not easy, since there were impurities in the esters, such as di- and monoglycerides (Ma, 1998). The monoglycerides caused turbidity (crystals) in the mixture of esters. This problem was very obvious, especially for transesterification of animal fats such as beef tallow. The impurities raised the cloud and pour points. On the other hand, there is a large proportion of saturated fatty acid esters in beef tallow esters (almost 50% w/w). This portion makes the cloud and pour points higher than that of vegetable oil esters. However, the saturated components

Table 9
Physical properties of chemicals related to transesterification (Zhang, 1994)

Name	Specific gravity, g/ml (°C)	Melting point (°C)	Boiling point (°C)	Solubility (>10%)
Methyl Myristate	0.875 (75)	18.8	–	–
Methyl Palmitate	0.825 (75)	30.6	196.0	Acids, benzene, EtOH, Et_2O
Methyl Stearate	0.850	38.0	215.0	Et_2O, chloroform
Methyl Oleate	0.875	−19.8	190.0	EtOH, Et_2O
Methanol	0.792	−97.0	64.7	H_2O, ether, EtOH
Ethanol	0.789	−112.0	78.4	$H_2O(\infty)$, ether (∞)
Glycerol	1.260	17.9	290.0	H_2O, EtOH

Table 10
Melting points of fatty acids, methyl esters and mono-, di-, and triglyceridea [a] (Formo, 1979)

Fatty acid		Melting point (°C)				
Name	Carbons	Acid	Methyl	1-Monoglyceride	1.3-Diglyceride	Triglyceride
Myristic	14	54.4	18.8	70.5	66.8	57.0
Palmitic	16	62.9	30.6	77.0	76.3	63.5
Stearic	18	69.6	39.1	81.5	79.4	73.1
Oleic	18:1	16.3	−19.8	35.2	21.5	5.5
Linoleic	18:2	−6.5	−35.0	12.3	−2.6	−13.1

[a] Melting point of highest melting, most stable polymorphic form.

have other value-added applications in foods, detergents and cosmetics.

The co-product, glycerol, needs to be recovered because of its value as an industrial chemical such as CP glycerol, USP glycerol and dynamite glycerol. Glycerol is separated by gravitational settling or centrifuging.

Transesterification is the process used to make biodiesel fuel as it is defined in Europe and in the USA. It also is used to make methyl esters for detergents and cosmetics. There are numerous transesterification citations in the scientific and patent literature (Bradshaw and Meuly, 1944; Freedman et al., 1984; Freedman et al., 1986; Schwab et al., 1987; Allen et al., 1945; Trent, 1945; Tanaka et al., 1981; Wimmer, 1992b; Ali, 1995; Ma et al., 1998a; Ma et al., 1998b; Ma et al., 1999).

3.2.1. The mechanism and kinetics

Transesterification consists of a number of consecutive, reversible reactions (Schwab et al., 1987; Freedman et al., 1986). The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol (Fig. 3). A mole of ester is liberated at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol.

The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps (Eckey, 1956). The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. When NaOH, KOH, K_2CO_3 or other similar catalysts were mixed with alcohol, the actual catalyst, alkoxide group is formed (Sridharan and Mathai, 1974). A small amount of water, generated in the reaction, may cause soap formation during transesterification. Fig. 4 summarizes the mechanism of alkali-catalyzed transesterification.

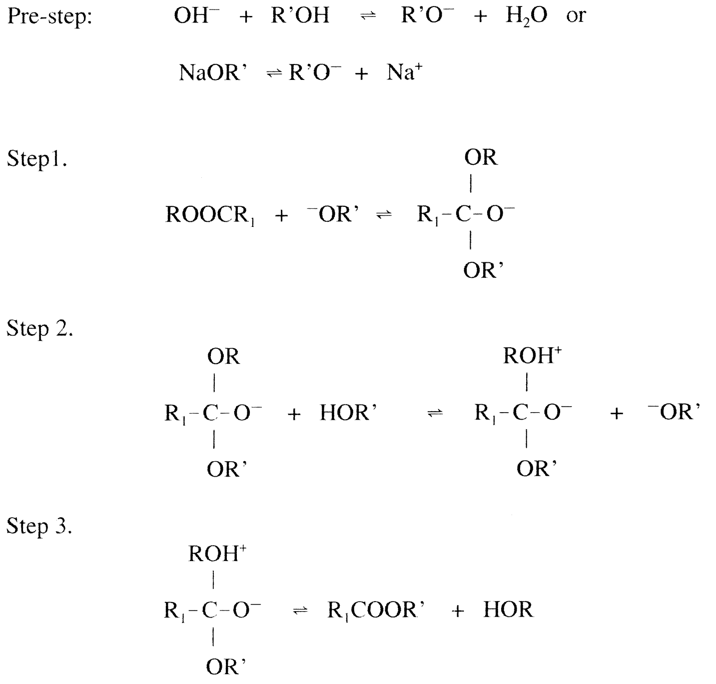
Freedman et al. (1986) studied the transesterification kinetics of soybean oil. The S-shaped curves of the effects of time and temperature on ester formation for a 30:1 ratio of butanol and soybean oil (SBO), 1% H_2SO_4 and 77–117°C at 10°C intervals indicated that the reaction began at a slowrate, proceeded at a faster rate and then slowed again as the reaction neared completion. With acid or alkali catalysis, the forward reaction followed pseudo-first-order kinetics for butanol:SBO = 30:1. However, with alkali catalysis the forward reaction followed consecutive, second-order kinetics for butanol:SBO = 6:1. The reaction of methanol with SBO at 6:1 molar ratio with 0.5% sodium methoxide at 20–60°C was a combination of second-order consecutive and fourth-order shunt reactions. The reaction rate constants for the alkali-catalyzed reaction were much higher than those for the acid-catalyzed reactions. Rate constants increased with an increase in the amount of catalyst used. The activation energies ranged from 8 to 20 kcal/mol. E_a for the shunt reaction triglyceride-glycerol was 20 kcal/mol.

$$\text{1. Triglyceride (TG)} + \text{R'OH} \underset{k_4}{\overset{k_1}{\rightleftharpoons}} \text{Diglyceride (DG)} + \text{R'COOR}_1$$

$$\text{2. Diglyceride (DG)} + \text{R'OH} \underset{k_5}{\overset{k_2}{\rightleftharpoons}} \text{Monoglyceride (MG)} + \text{R'COOR}_2$$

$$\text{3. Monoglyceride (MG)} + \text{R'OH} \underset{k_6}{\overset{k_3}{\rightleftharpoons}} \text{Glycerol (GL)} + \text{R'COOR}_3$$

Fig. 3. The transesterification reactions of vegetable oil with alcohol to esters and glycerol (Freedman et al., 1986).



Pre-step: $OH^- + R'OH \rightleftharpoons R'O^- + H_2O$ or

$NaOR' \rightleftharpoons R'O^- + Na^+$

Step1.

$$ROOCR_1 + {}^-OR' \rightleftharpoons R_1\text{-}\underset{OR'}{\overset{OR}{\underset{|}{\overset{|}{C}}}}\text{-}O^-$$

Step 2.

$$R_1\text{-}\underset{OR'}{\overset{OR}{\underset{|}{\overset{|}{C}}}}\text{-}O^- + HOR' \rightleftharpoons R_1\text{-}\underset{OR'}{\overset{ROH^+}{\underset{|}{\overset{|}{C}}}}\text{-}O^- + {}^-OR'$$

Step 3.

$$R_1\text{-}\underset{OR'}{\overset{ROH^+}{\underset{|}{\overset{|}{C}}}}\text{-}O^- \rightleftharpoons R_1COOR' + HOR$$

Where R-OH diglyceride, R_1 long chain alkyl group, and R'short alkyl group

Fig. 4. The mechanism of alkali-catalyzed transesterification of triglycerides with alcohol (Sridharan and Mathai, 1974; Eckey, 1956).

3.2.2. The effects of moisture and free fatty acids

Wright et al. (1944) noted that the starting materials used for alkali-catalyzed transesterification of glycerides must meet certain specifications. The glyceride should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value was greater than 1, more NaOH was required to neutralize the free fatty acids. Water also caused soap formation, which consumed the catalyst and reduced catalyst efficiency. The resulting soaps caused an increase in viscosity, formation of gels and made the separation of glycerol difficult. Bradshaw and Meuly (1944) and Feuge and Grose (1949) also stressed the importance of oils being dry and free (<0.5%) of free fatty acids. Freedman et al. (1984) stated that ester yields were significantly reduced if the reactants did not meet these requirements. Sodium hydroxide or sodium methoxide reacted with moisture and carbon dioxide in the air, which diminished their effectiveness. Transesterification does not require a nitrogen environment, despite the statements of Feuge and Grose (1949) and Gauglitz and Lehman (1963). The reactor was open to the atmosphere via a condenser. Oxygen dissolved in the oil escaped to the atmosphere when the reactant was heated. In addition, alcohol vapour facilitated this process.

The effects of free fatty acids and water on transesterification of beef tallow with methanol were investigated (Ma et al., 1998a). The results showed that the water content of beef tallow should be kept below 0.06% w/w and free fatty acid content of beef tallow should be kept below 0.5%, w/w in order to get the best conversion. Water content was a more critical variable in the transesterification process than were free fatty acids. The maximum content of free fatty acids confirmed the research results of Bradshaw and Meuly (1944) and Feuge and Grose (1949).

3.2.3. The effect of molar ratio

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three moles of fatty acid ester and one mole of glycerol. The molar ratio is associated with the type of catalyst used. An acid catalyzed reaction needed a 30:1 ratio of BuOH to soybean oil, while a alkali-catalyzed reaction required only a 6:1 ratio to achieve the same ester yield for a given reaction time (Freedman et al., 1986).

Bradshaw and Meuly (1944) stated that the practical range of molar ratio was from 3.3 to 5.25:1 methanol to vegetable oil. The ratio of 4.8:1 was used in some examples, with a yield of 97–98%, depending upon the quality of the oils. If a three step transesterification process was used, the ratio was reduced to 3.3:1. Methanol present in amounts of above 1.75 equivalents tended to prevent the gravity separation of the glycerol, thus adding more cost to the process.

Higher molar ratios result in greater ester conversion in a shorter time. In the ethanolysis of peanut oil, a 6:1

molar ratio liberated significantly more glycerine than did a 3:1 molar ratio (Feuge and Grose, 1949). Rapeseed oil was methanolyzed using 1% NaOH or KOH (Nye and Southwell, 1983).They found that the molar ratio of 6:1 of methanol to oil gave the best conversion. When a large amount of free fatty acids was present in the oil, a molar ratio as high as 15:1 was needed under acid catalysis (Sprules and Price, 1950). Freedman et al. (1984) studied the effect of molar ratio (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, sunflower, peanut and cotton seed oils behaved similarly and achieved highest conversions (93–98%) at a 6:1 molar ratio. Tanaka et al. (1981), in his novel two-step transesterification of oils and fats such as tallow, coconut oil and palm oil, used 6:1–30:1 molar ratios with alkali-catalysis to achieve a conversion of 99.5%.

A molar ratio of 6:1 was used for beef tallow transesterification with methanol (Ali, 1995; Zhang 1994). Zhang reported 80% by tallow weight of esters was recovered in the laboratory.

3.2.4. The effect of catalyst

Catalysts are classified as alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed (Freedman et al., 1984). However if a glyceride has a higher free fatty acid content and more water, acid-catalyzed transesterification is suitable (Sprules and Price, 1950; Freedman et al., 1984). The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Alkalis include sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide, sodium amide, sodium hydride, potassium amide and potassium hydride. (Sprules and Price, 1950). Sodium methoxide was more effective than sodium hydroxide (Freedman et al., 1984; Hartman, 1956) because of the assumption that a small amount of water was produced upon mixing NaOH and MeOH. The opposite result was observed by Ma et al. (1998a). NaOH and $NaOCH_3$ reached their maximum activities at 0.3 and 0.5% w/w of beef tallow, respectively. Sodium hydroxide was also chosen to catalyze the transesterifications because it is cheaper. Ester conversions at the 6:1 ratio for 1% NaOH and 0.5% $NaOCH_3$ were almost the same after 60 min (Freedman et al., 1984). Sodium hydroxide, however, is cheaper and is used widely in large-scale processing. The transesterification of soybean oil with methanol, ethanol and butanol, using 1% concentrated sulfuric acid, was unsatisfactory when the molar ratios were 6:1 and 20:1 (Freedman et al., 1984). A 30:1 ratio resulted in a high conversion to methyl ester. More recently, an immobilized lipase was employed to catalyze the methanolysis of corn oil in flowing supercritical carbon dioxide with an ester conversion of >98% (Jackson and King, 1996).

3.2.5. The effect of reaction time

The conversion rate increases with reaction time. Freedman et al. (1984) transesterified peanut, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93–98%). Ma et al. (1998a) studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to the mixing and dispersion of methanol into beef tallow. From one to five min, the reaction proceeded very fast. The apparent yield of beef tallow methyl esters surged from 1 to 38. The production of beef tallow slowed down and reached the maximum value at about 15 min. The di- and monoglycerides increased at the beginning and then decreased. At the end, the amount of monoglycerides was higher than that of diglycerides.

3.2.6. The effect of reaction temperature

Transesterification can occur at different temperatures, depending on the oil used. In methanolysis of castor oil to methyl ricinoleate, the reaction proceeded most satisfactorily at 20–35°C with a molar ratio of 6:1–12:1 and 0.005–0.35% (by weight of oil) of NaOH catalyst (Smith, 1949). For the transesterification of refined soybean oil with methanol (6:1) using 1% NaOH, three different temperatures were used (Freedman et al., 1984). After 0.1 h, ester yields were 94, 87 and 64% for 60, 45 and 32°C, respectively. After 1 h, ester formation was identical for the 60 and 45°C runs and only slightly lower for the 32°C run. Temperature clearly influenced the reaction rate and yield of esters.

3.2.7. The process of transesterification and downstream operations

Bradshaw and Meuly (1944) patented a process for making soap from natural oils or fats. This two step process included making fatty acid esters from oils, then producing soap from the esters. The crude oil was first refined to remove a certain amount of water, free fatty acids mucilaginous matter, protein, coloring matter and sugars. The water content was less than 1% after refining. Although the author did not mention the contents of other impurities after refining, the normal refining process met the requirements of the transesterification process. The oils were transesterified at the conditions of 25–100°C, 1.10–1.75 alcohol equivalents, 0.1–0.5% catalyst by weight of oil. The amount of alcohol needed was reduced substantially by working in steps. The temperature and consequently the speed of the reaction could be increased if a closed system or reflux was used. The reaction mixture was neutralized with a mild acid to stop the reaction. Upon standing, the glycerol and esters separated into two layers and the lower layer of glycerol was removed. The ester layer was fractionally distilled at atmospheric pressure or under reduced pressure (e.g. 399 Pa) and with 110 kPa of steam in the heating coils. C8 and then C10 methyl esters were obtained. The residue of C12, C14, C16 and saturated and unsaturated C18 fatty acid methyl esters were drawn off or were further separated by distillation, crystallization or other processes.

Trent (1945) patented a continuous transesterification process. Reactants were fed into a reactor through a steam heated coil in the upper part of the reactor. The transesterification reaction took place when the reactants were heated to the reaction temperature while passing through the heater. The reaction finished before the reactants and products mixture left the heater. The unreacted alcohol vapor was taken out and the products were neutralized before getting into the lower chamber of the reactor where the esters and glycerol were continuously separated (Fig. 5).

The process patented by Smith (1949) was almost the same as the process described by Bradshaw and Meuly (1944). The molar ratio increased to 6:1–12:1 and the reaction temperature range was 20–35°C. The reaction was monitored by the refractive index at 25°C, specific gravity at 15°C and the Gardner–Holdt viscosity. The mixture was distilled subsequently to remove the unreacted methanol. After the glycerol was removed, the esters were washed countercurrently and dried.

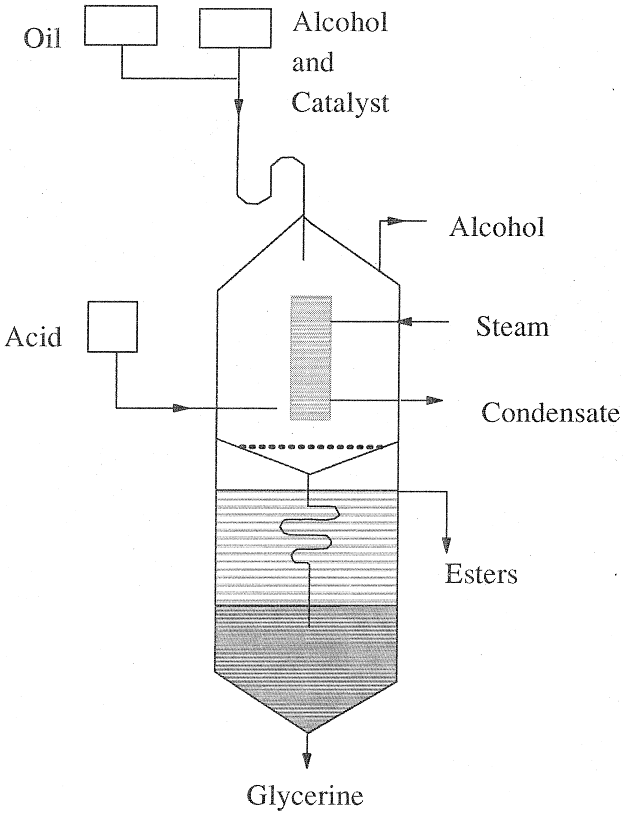


Fig. 5. A continuous transesterification reactor (Trent, 1945).

For high acid value oils, alkali- and then acid-catalyzed transesterifications were used (Sprules and Price, 1950). The free fatty acids were neutralized with alkali to form soap during the reaction. After the triglycerides were converted to esters, 5% by oil weight of sulfuric acid was added to neutralize the alkali catalyst, release the free fatty acids from the soap formed and acidify the system. The mixture was then transesterified for 3–4 h to make esters from the free fatty acids. The mixture was neutralized with an alkali salt such as calcium carbonate, filtered and freed of methanol by distillation. After the glycerine was separated, the esters were washed with warm water and distilled under vacuum of 133 Pa.

Allen et al. (1945) patented a continuous process whereby 224 part/min of refined coconut oil and 96 part/min of ethanol containing 0.75% of NaOH catalyst were homogenized and then pumped through a reaction coil for about 10 min at 100°C. The mixture passed through a preheater to bring the temperature to 110°C followed by loading into a packed column for separation of the ethanol vapour. The glycerol was separated out in a lower layer. The ester layer was washed and dried under vacuum.

Tanaka et al. (1981) provided a novel method for preparation of lower alkyl, i.e. methyl, esters of fatty acids by the alcoholysis reaction of fatty acid glycerides, e.g. naturally occurring oils or fats, with a lower alcohol in a two-step process. The first alcoholysis reaction was conducted at or near the boiling temperature of the lower alcohol for 0.5–2 h. The glycerol was separated by setting the mixture for 1–15 min at 40–70°C. The crude ester layer was then subjected to a second alcoholysis of 8–20% alcohol and 0.2–0.5% alkali catalyst for 5–60 min. An overall conversion of 98% or more of the starting fatty glycerides was achieved. The second reaction mixture thus admixed with a certain amount of water was left to settle at 40–70°C for 15 min or centrifuged. Impurities such as color compounds were in the aqueous phase and were removed with the water. In this process no methanol recovery was mentioned. Emulsion formation during water washing could be problematic, such as longer separation time and losses of esters and glycerol.

Zhang (1994) transesterified edible beef tallow with a free fatty acid content of 0.27%. The tallow was heated to remove moisture under vacuum, then kept at 60°C. Transesterification was conducted using 6:1 molar ratio of methanol/tallow, 1% (by the weight of tallow) NaOH dissolved in the methanol and 60°C for about 30 min. After separation of glycerol, the ester layer was transesterified again using 0.2% NaOH and 20% methanol at 60°C for about 1 h. The mixture was washed with distilled water until the wash water was clear. The purified ester was heated again to 70°C under vacuum to remove residual moisture. The laboratory scale process yielded 400 g of tallow ester from 500 g of beef tallow.

More recently, several patents were awarded on transesterification of natural oils and fats to make biodiesel fuel. Wimmer (1992a) blended 27.8 g of KOH, 240 L of methanol and 1618 kg of unrefined rape oil and stirred it for 20 min. Then, 6.9 g of KOH and 60 L of methanol were added. An additional 3 h was required for the completion of the reaction. Finally, 80 kg of water were added and the mixture was allowed to stand overnight at room temperature. The glycerol was separated from the esters. The rape seed oil methyl esters (<1.5% remaining glycerides and 0.008% ash) were used without further purification.

Wimmer (1992b) prepared methyl esters on a relatively small industrial scale by transesterifing glycerides with C1 – 5 alkanols or C2 – 5 alkoxyalkanols in the presence of basic catalysts. After the reaction was finished, 0.5–10% water or acid was added to neutralize the catalyst. Distillation of the ester phase after treatment with Fuller's earth or silica gel was optional.

However, in both processes (Wimmer, 1992a; Wimmer, 1992b), adding water before removing glycerol could form an emulsion, resulting in losses of esters and glycerol. Usually, transesterification reaction mixtures were allowed to cool to room temperature and the esters were separated with a separatory funnel. Unreacted methanol in the ester layer was removed by distillation or evaporation. The esters were further purified by dissolving in petroleum ether, adding glacial acetic acid or phosphoric acid to adjust the pH to 7, washing three times with water, drying the oil phase over anhydrous magnesium sulfate and filtering and removing solvent by evaporation (Freedman et al., 1984).

Stern et al. (1995) patented a method to make fatty acid esters from acid oil. The core of his method was to recover free fatty acids in the oil by transesterifing them with glycerol to form glycerides. After transesterification, a large portion of the glycerol was mixed with the ester wash water, then neutralized with acid. The salt was filtered and the alcohol evaporated. The separated free fatty acids reacted with the non-neutralized glycerol phase at about 200°C. The triglycerides (acidity of 3.2%) from the reaction were added to the next alcoholysis step. The ester obtained from the "starting oil plus glyceride" had a density of 880 kg/m^3, a flash point of 185°C, a flow point of −12°C, a filterable limit temperature (FLT) of −18°C, a neutralization number of 0.5% mg KOH/g and a methyl ester content >98%. It was suggested that it could be used as a substitute for gas oil.

Ma et al. (1998b, 1999) studied the transesterification process of beef tallow with methanol. Because the solubility of methanol in beef tallow was 19% w/w at 100°C (Ma et al., 1998b), mixing was essential to disperse the methanol in beef tallow in order to start the reaction. When the sodium hydroxide and methanol solution were added to the melted beef tallow in the reactor while stirring, the stirring time was insignificant (Ma et al., 1999). Reaction time was the controlling factor in determining the yield of beef tallow esters. They also pointed out that once the two phases were mixed and the reaction was started, stirring was no longer needed. The distribution of unreacted methanol between the beef tallow ester phase and the glycerol phase was studied to determine a efficient way of downstream operation (Ma et al., 1998b). After the reaction was finished, there was 60% w/w of unreacted methanol in the beef tallow ester phase and 40% w/w in the glycerol phase. The optimum operation sequence was to recover the unreacted methanol using vacuum distillation after transesterification, separation of ester and glycerol phases and then purification of beef tallow methyl esters.

3.2.8. Other types of transesterifications

Lee et al. (1995) transesterified oils and fats using branched-chain alcohols, such as isopropyl or 2-butyl (1:66) to reduce the crystallization temperature of biodiesel. The crystal temperatures of isopropyl and 2-butyl esters of soybean oil were 7–11 and 12–14°C lower than that of soybean oil methyl esters, respectively. The crystallization onset temperatures (T_{CO}) of isopropyl esters of lard and tallow were similar to that of methyl esters of soybean oil.

In-situ transesterification of oils was investigated (Harrington and Catherine, 1985; Kildiran et al., 1996). Harrington and Catherine (1985) compared the conventional and in-situ processes and found the acid catalyzed in-situ process for sunflower seed oil was better than that from the more conventional process. Ethyl, propyl and butyl esters of soybean fatty acids were obtained directly, in high yields, by in-situ alcoholysis of soybean oil (Kildiran et al., 1996). By increasing reaction temperature and time and by decreasing the particle size of the soybeans and the water content of ethanol, a purer product was obtained.

Jackson and King (1996) reported a direct methanolysis of triglycerides using an immobilized lipase in flowing supercritical carbon dioxide. Corn oil was pumped in a carbon dioxide stream at a rate of 4 μl/min and methanol at 5 μl/min to yield >98% fatty acid methyl esters. This process combined the extraction and transesterification of the oil. A continuous process may be possible (Ooi et al., 1996).

Muniyappa (1995) suggested the utilization of a higher shear mixing device for making esters from animal fat, but no data were given. Glycerolysis was investigated using a high shearing mixing device. The separated glycerol reacted with triglycerides to produce mono- and diglycerides, which are valuable chemical intermediates for detergents and emulsifiers. The author thought this process could lower the production cost of biodiesel fuel.

4. Conclusions

Of the several methods available for producing biodiesel, transesterification of natural oils and fats is currently the method of choice. The purpose of the process is to lower the viscosity of the oil or fat. Although blending of oils and other solvents and microemulsions of vegetable oils lowers the viscosity, engine performance problems, such as carbon deposit and lubricating oil contamination, still exist. Pyrolysis produces more biogasoline than biodiesel fuel. Transesterification is basically a sequential reaction. Triglycerides are first reduced to diglycerides. The diglycerides are subsequently reduced to monoglycerides. The monoglycerides are finally reduced to fatty acid esters. The order of the reaction changes with the reaction conditions. The main factors affecting transesterification are molar ratio of glycerides to alcohol, catalysts, reaction temperature and time and the contents of free fatty acids and water in oils and fats. The commonly accepted molar ratio of alcohol to glycerides is 6:1. Base catalysts are more effective than acid catalysts and enzymes. The recommended amount of base used to use is between 0.1 and 1% w/w of oils and fats. Higher reaction temperatures speed up the reaction and shorten the reaction time. The reaction is slow at the beginning for a short time and proceeds quickly and then slows down again. Base catalyzed transesterifications are basically finished within one hour. The oils or fats used in transesterification should be substantially anhydrous ($\leqslant 0.06\%$ w/w) and free of fatty acids ($>0.5\%$ w/w).

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. The remaining challenges are its cost and limited availability of fat and oil resources. There are two aspects of the cost of biodiesel, the costs of raw material (fats and oils) and the cost of processing. The cost of raw materials accounts for 60 to 75% of the total cost of biodiesel fuel (Krawczyk, 1996). The use of used cooking oil can lower the cost significantly. However, the quality of used cooking oils can be bad (Murayama, 1994). Studies are needed to find a cheaper way to utilize used cooking oils to make biodiesel fuel. There are several choices, first removing free fatty acids from used cooking oil before transesterification, using acid catalyzed transesterification, or using high pressure and temperature (Kreutzer, 1984). In terms of production cost, there also are two aspects, the transesterification process and by-product (glycerol) recovery. A continuous transesterification process is one choice to lower the production cost. The foundations of this process are a shorter reaction time and greater production capacity. The recovery of high quality glycerol is another way to lower production cost. Because little water is present in the system, the biodiesel glycerol is more concentrated. Unlike the traditional soap glycerol recovery process, the energy required to recover biodiesel glycerol is low due to the elimination of the evaporation process. In addition, the process also is simpler than soap glycerol recovery since there is a negligible amount of soap in biodiesel glycerol. This implies that the cost of recovering high quality glycerol from biodiesel glycerol is lower than that of soap glycerol and that the cost of biodiesel fuel can be lowered if a biodiesel plant has its own glycerol recovery facility.

With the increase in global human population, more land may be needed to produce food for human consumption (indirectly via animal feed). The problem already exists in Asia. Vegetable oil prices are relatively high there. The same trend will eventually happen in the rest of the world. This is the potential challenge to biodiesel. From this point of view, biodiesel can be used most effectively as a supplement to other energy forms, not as a primary source. Biodiesel is particularly useful in mining and marine situations where lower pollution levels are important. Biodiesel also can lower US dependence on imported petroleum based fuel.

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