

Review

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REVIEWS

Waste Cooking Oil—An Economical Source for Biodiesel: A Review

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Biodiesel (fatty acid methyl ester) is a nontoxic and biodegradable alternative fuel that is obtained from renewable sources. A major hurdle in the commercialization of biodiesel from virgin oil, in comparison to petroleum-based diesel fuel, is its cost of manufacturing, primarily the raw material cost. Used cooking oil is one of the economical sources for biodiesel production. However, the products formed during frying, such as free fatty acid and some polymerized triglycerides, can affect the transesterification reaction and the biodiesel properties. Apart from this phenomenon, the biodiesel obtained from waste cooking oil gives better engine performance and less emissions when tested on commercial diesel engines. The present paper attempts to review methods for the transesterification of waste cooking oil and the performance of biodiesel obtained from waste cooking oil in a commercial diesel engine. The paper also examines the basic chemistry involved during frying and the effects of the products formed in the frying process on biodiesel quality.

1. Introduction

The need for energy is increasing continuously, because of increases in industrialization and population. The basic sources of this energy are petroleum, natural gas, coal, hydro, and nuclear.¹ Petroleum diesel continues to be a major fuel worldwide. Canada consumes ~23 million tonnes (~26 billion liters) of diesel annually and 46% of this is utilized in the transportation sector. The United States consumes 178 million tonnes of diesel fuel annually, and the global consumption is 934 million tonnes of diesel fuel per year.² The major disadvantage of using petroleum-based fuels is that, day by day, the fossil fuel reserves are decreasing. Another disadvantage is atmospheric pollution created by the use of petroleum diesel. Petroleum diesel combustion is a major source of greenhouse gas (GHG). Apart from these emissions, petroleum diesel is also major source of other air contaminants including NO_x, SO_x, CO, particulate matter, and volatile organic compounds (VOCs).³ The decreasing fossil fuel reserves, and the atmospheric pollution created by petroleum-based fuels, have necessitated the need for an alternative source of energy.

Biomass is one of the better sources of energy. Fuels from renewable biomass have the potential to reduce the amount of CO₂, particulate matter, and GHG emissions. This is because the carbon contained in biomass-derived fuel is biogenic and renewable.² Therefore, petroleum-based fuels can be complemented by fuels obtained from renewable sources. Many researchers have tried to develop vegetable-oil-based derivatives that approximate the properties and performance of petroleum-based diesel fuel. Biodiesel (monoalkyl esters) is one of such alternative fuel, which is obtained by the transesterification of triglyceride oil with monohydric alcohols. It has been well-reported that biodiesel obtained from canola and soybean oil acts very well as a diesel fuel substitute.^{4,5} However, a major barrier in the commercialization of biodiesel production from

vegetable oil is its high manufacturing cost, which is due to the higher cost of virgin vegetable oil. The cost of vegetable oil has a crucial role in the economics of the biodiesel. According to Nelson et al.,⁶ the significant factors that affect the cost of biodiesel are feedstock cost, plant size, and value of the glycerine byproduct.⁶ Noordam and Wither have observed that one of the most crucial variables that affects the cost of biodiesel is the cost of the raw materials.⁷

Waste cooking oil, which is much less expensive than pure vegetable oil, is a promising alternative to vegetable oil for biodiesel production. Restaurant waste oils and rendered animal fats are less expensive than food-grade canola and soybean oil.⁸ Currently, all these waste oils are sold commercially as animal feed. However, since 2002, the European Union (EU) has enforced a ban on feeding these mixtures to animals, because, during frying, many harmful compounds are formed and, if the waste cooking oil is used as an additive to feeding mixtures for domestic animals, then it could result in the return of harmful compounds back into the food chain through the animal meat.⁹ Hence, the waste cooking oil must be disposed of safely or be used in a way that is not harmful to human beings.

The quantity of waste cooking oil generated per year by any country is huge. The disposal of waste cooking oil is problematic, because disposal methods may contaminate environmental water. Many developed countries have set policies that penalize the disposal of waste oil through the water drainage.¹⁰ The production of biodiesel from waste cooking oil is one of the better ways to utilize it efficiently and economically. The data on the requirements of diesel fuel and availability of waste cooking oil in any country indicate that the biodiesel obtained from waste cooking oil may not replace diesel fuel completely. However, a substantial amount of diesel fuel can be prepared from waste cooking oil, which would partly decrease the dependency on petroleum-based fuel.

The amount of waste cooking oil generated in each country varies, depending on the use of vegetable oil. An estimate of the potential amount of waste cooking oil collected in the EU

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is ~700 000–1 000 000 tonnes/yr.¹¹ A report published by Wiltsee showed that, on an average, 9 pounds of yellow grease per person were produced annually in the United States.¹² According to Zhang et al.,¹³ ~120 000 tonnes/yr of yellow grease is produced in Canada. Note that the waste cooking oil/waste fryer grease (WFG) is categorized by its free fatty acid (FFA) content. For example, if the FFA content of waste cooking oil is <15%, then it is called “yellow grease”; otherwise, it is called “brown grease”.¹⁴ Because of the production of such large quantities of waste cooking oil, a substantial amount of biodiesel can be produced from this material. A preliminary case study conducted on the requirement of biodiesel in Canada to meet the B5 requirement reported that 610 million liters of the biodiesel are required per year.² Hence, a substantial portion of the biodiesel (of the 5% requirement in Canada) can be replaced by the biodiesel obtained from waste cooking oil. The properties of the biodiesel from waste cooking oil would be largely dependent on the physicochemical properties of these feedstocks.

The following sections review the physical and chemical properties of the frying oil, the methods of preparation of biodiesel from waste cooking oil, the effects of different compounds formed during the frying process on biodiesel quality, the testing of biodiesel obtained from waste cooking oil, and the economics and pilot-plant design for the production of biodiesel from waste cooking oil.

2. Physical and Chemical Changes in Vegetable Oil during Frying

The production of healthy foods, with improved sensory characteristics, is very important for human consumption and health. Heat has a crucial role during food preparation. Food is subjected to different degrees of heat during cooking, boiling and frying, etc. Depending on the degree of heating, various physical and chemical changes occur in food constituents.

Frying is one of the most popular methods of food preparation in modern times, with the reason being the excellent taste of the fried food. The oil (lipids) is an integral part of frying. In frying, oil is heated in air and in the presence of light at temperatures of 160–200 °C for relatively long periods of time. For economical reasons, the same oil/fat is used many times or continuously. Generally, in public restaurants, frying is conducted in the same oil for several days; however, in household frying, fat is exchanged after several weeks.⁹ Obviously, the conditions used for frying cause major physical and chemical changes in the oil, which differs from oil to oil, depending on their composition. Some common physical changes observed in vegetable oil after frying are (i) an increase in the viscosity, (ii) an increase in the specific heat, (iii) a change in the surface tension, (iv) a change in color, and (v) an increase in the tendency of fat to foam.⁹ The studies conducted by Nawar¹⁵ and Mittelbach and Enzelsberger¹⁶ on frying oil suggest that, during frying, basically three types of reactions occur: thermolytic, oxidative, and hydrolytic.

2.1. Thermolytic Reactions. A thermolytic reaction occurs in the absence of oxygen at very high temperatures. If the triglycerides that contain saturated fatty acids are heated at very high temperature (180 °C) in the absence of oxygen, then they produce series of normal alkanes, alkenes, lower fatty acids, symmetric ketones, oxopropyl esters, CO, and CO₂. Unsaturated fatty acids form basically dimeric compounds, including dehydromers, saturated dimers, and polycyclic compounds. Unsaturated fatty acids also react with other unsaturated fatty acids via the Diels–Alder reaction, forming dimers and trimers. In

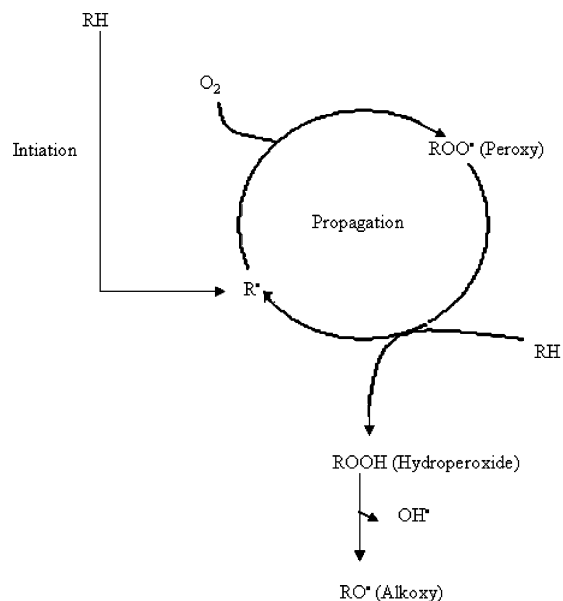


Figure 1. Scheme for the free-radical autoxidation mechanism.¹⁵

the case of glycerides, this reaction happens between acyl groups within the same molecule.¹⁵

2.2. Oxidative Reactions. Unsaturated fatty acids may react with molecular oxygen via a free-radical mechanism, as shown in Figure 1. Hydroperoxides formed as a primary product during the reaction may further form many other compounds, such as isomeric hydroperoxides that contain conjugated diene groups. Hydroperoxides also produce many chemicals with a significant variation in molecular weight, flavor threshold, and biological significance. The alkoxy radical is formed via scission of the O–O bond of hydroperoxides. This alkoxy radical may gain or lose H atom(s) to form the hydroxy or keto derivatives, respectively. Various chemicals such as aldehydes, hydrocarbons, semialdehydes, and acids are formed by decomposition of alkoxy radicals. In the presence of excess oxygen, alkoxy and peroxy radicals can be transformed into dimeric and oligomeric compounds.¹⁵

2.3. Hydrolytic Reactions. The steam produced during the preparation of food causes the hydrolysis of triglycerides, resulting in the formation of FFA, glycerol, and monoglycerides and diglycerides.¹⁶ The change in oil composition by the hydrolytic reaction can be quantified by measuring the monoglyceride and diglyceride content and not the FFA content of oil, because some of the FFA are lost during frying.¹⁷

As a combined result of all these chemical reactions, many undesirable compounds are formed during frying whose toxicological effects upon their consumption are not known fully. Ultimately, the polar content of the oil increases upon repetitive heating.¹⁷ The quality of the edible oil after frying is generally assessed based on its polar content. The polar content of fresh unused oil is usually between 0.4 and 6.4 mg/100 g.¹⁸ Most European countries have set maximum polar content level of 25% in edible oil i.e., the fats and oils must be discarded when its polar fraction is more than 25%.¹⁸ A study conducted on sunflower oil, olive oil, and a mixture of the two oils showed that after 20 fryings, the polar content of sunflower oil is increased by 640% and that of olive oil by 480%. After 40 fryings, all the used oils contain a polar fraction of >25%.¹⁸ Another study that was performed on sunflower oil showed that the frequent addition of fresh oil throughout frying minimized thermoxidative and hydrolytic changes in the frying oil, even after 20 repeated fryings.¹⁸

The amount and type of undesirable products formed during frying affect either the biodiesel properties or the transesterification reaction. Therefore, it is important to know the amount of undesirable products, especially the type of polar compound that is formed during the reaction. These fractions are generally examined via high-performance size exclusion chromatography (HPSEC) for the distribution of individual compounds.¹⁷ To remove the undesirable compounds in waste cooking oil, pretreatment of the same is necessary before the transesterification reaction. As discussed previously, waste cooking oil is an economical source of biodiesel but transport and pretreatment of waste cooking oil are the only additional costs involved in the production of biodiesel from waste cooking oil. The following section describes various transesterification methods that have been recommended for the efficient and economical production of alternative renewable liquid fuels from waste cooking oil.

3. Transesterification Methods for Waste Cooking Oil

The transesterification of waste cooking oil can be performed using alkaline, acidic, and enzymatic catalysts. Depending on the undesirable compounds (especially FFA and water), each catalyst has its own advantages and disadvantages.

3.1. Alkali-Catalyzed Transesterification. Common alkaline catalysts (such as NaOH, KOH, and NaOCH₃) are well-known for the transesterification reaction of edible oil.¹⁹ The rate of the alkaline-catalyzed transesterification reaction is fast, compared to that using acids, and it is reported that the rate could be as high as 4000 times, compared to that using an acidic catalyst.¹⁹ The application of an alkaline catalyst in the transesterification of waste cooking oil is somewhat limited, because the FFA in waste cooking oil reacts with the alkaline catalyst (KOH, NaOH) and forms soap. The soap formed during the reaction prevents the glycerol separation, which drastically reduces the ester yield. The water in waste cooking oil also affects the methyl ester yield by favoring a saponification reaction.²⁰ Despite these two serious problems, many researchers have studied the transesterification of waste cooking oil using an alkaline catalyst.

Used sunflower oil (which has an acid value of ~4) was transesterified with methanol, using alkaline catalysts such as KOH and NaOH and different molar ratios of methanol to oil (4.5:1, 6:1, 9:1).²¹ The effects of various parameters such as the variation in oil quality, the molar ratio of methanol to oil, the type and amount of alkaline catalyst, the time and temperature of reaction on the yield, and the properties of esters were studied. The optimum conditions developed for the production of good-quality biodiesel from used sunflower oil were as follows: molar ratio of methanol to oil, 6:1, with 1% of KOH; reaction temperature, 25 °C; and reaction time, 30 min. It was observed that, under the optimal conditions of methanolysis, the quality of the used frying oil did not have an essential effect on the quality of methyl esters produced. An increase in the quantity of a catalyst and molar ratio of methanol to oil did not change the yield or quality of the esters. Of the two catalysts NaOH and KOH, 1% KOH has given the best yields and viscosities of the esters.²¹ Similarly, a comparison of the catalytic activities of KOH and NaOH for the transesterification of waste cooking oil with an FFA content of 2.76 has been reported by Dorado et al.²² According to this study, the KOH-catalyzed transesterification proceeds quicker than the NaOH-catalyzed reaction. The optimization of other reaction parameters (such as temperature, molar ratio of oil to alcohol, reaction time, and stirring) is also reported.

NaOH has been used by many researchers for the transesterification of waste cooking oil, despite its slower reaction rates. The transesterification of waste cooking oil that has an acid value in the range of 0.42–2.07, using NaOH as a catalyst, has been reported by Felizardo et al.²³ The effects of the molar ratio of alcohol to oil (3.6–5.4), the acid value (0.4–2.07), and the sodium hydroxide/frying oil mass ratio (0.2–1.0) on the percentage of ester yield were studied. Oils with an acid value of 0.42 mg KOH/g gave a maximum yield of ester at methanol-to-oil molar ratio of 4.8 and a catalyst/oil ratio of 0.6.²³ Using the same type of catalyst (NaOH), the transesterification of waste cooking oil with an acid value of 1.24 was performed with methanol.²⁴ The optimization of the reaction conditions and the effect of washing of ester with hot water on the glycerine content of biodiesel was also reported. Three alternative reaction conditions, which included the molar ratio of oil to alcohol (1:6–1:5), catalyst amount (1%–2%), and time (30–120 min) at a reaction temperature of 55 °C to produce 100% ester, were suggested.²⁴ In the above-reported cases, KOH and NaOH catalysts performed well, the probable reason being the very low FFA content in waste cooking oil. Hence, the problem of saponification was not serious. If the FFA content is >1% and if an alkaline catalyst must be used, then a greater amount of catalyst should be added to neutralize the FFA.

The transesterification of processed waste cooking oil (with citric acid added to the waste cooking oil, to remove solids) and unprocessed waste cooking oil was performed with methanol using KOH (1.75 wt %) and 1:6 molar ratio of oil to alcohol at room temperature.²⁵ Excess catalyst was used to neutralize the FFA present in the waste cooking oil. The ester yield was 51 wt % with processed waste oil and 58 wt % with unprocessed waste cooking oil. The properties of the processed and unprocessed waste cooking oil methyl esters did not compare well with the canola and greenseed canola methyl esters. For example, these esters had poor cold-temperature properties and a poor lubricity number. Using the same concept, hydrogenated soybean ethyl ester (HYSEE) was produced from used french fry oil and ethanol (1:6 molar ratio) using 1.43% of KOH as a main treatment catalyst.²⁶ For each 1% of FFA, an excess of 0.197 g of KOH was added. To avoid an emulsion in the washing phase, 1-octanol and tannic acid were added, along with water. The conversion to biodiesel was ≥92%.²⁶ Similarly, Dorado et al.¹⁰ have reported the transesterification of waste cooking oils from different sources such as palm oil and hydrogenated fat from Brazil (5.12% FFA), olive oil from Spain (2.24% FFA), and a mixture of several vegetable oils from Germany (1.28% FFA), using KOH as a catalyst. The transesterification was performed in two steps, using a stoichiometric amount of methanol and the necessary amount of KOH, supplemented with the additional amounts of KOH to neutralize the FFA. It was observed that a two-step transesterification process without any costly purification steps is a good method for biofuel production from waste cooking oils of different origins with FFA ≤3%. The conversion efficiency was in the range of 88%–95% after a two-step transesterification process using a basic catalyst.¹⁰

Apart from KOH and NaOH, sodium methoxide has been proven to be a very good alkaline catalyst for the transesterification of oils. The transesterification of three fatty materials such as soybean oil (acid index of 0.53%), waste cooking oil (acid index of 0.47%), and tallow (acid index of 6.8%) using sodium methoxide as a catalyst was reported by Alcantara et al.²⁷ The optimized reaction conditions for the transesterification reaction were as follows: molar ratio of methanol to oil, 7.5;

Table 1. Effects of Various Treatments on the Physical and Chemical Properties of Waste Cooking Oil^a

property	Batch 1			Batch 2		
	raw	T1	T2	raw	T1	T2
moisture content (%)	1.1	0.5	0.4	1.4	0.6	0.4
density (kg/m ³)	0.937	0.925	0.921	0.39	0.929	0.922
kinematic viscosity (mm ² /s)	190.2	130.1	85.3	201.3	110.2	70.1
acid value	5.3	4.4	3.9	6.3	4.9	4.3
iodine value	104.3	103.7	105.2	115.3	117.2	116.2
PV (meq/kg)	5.6	5.3	4.6	6.3	5.7	4.4
saponification number	204.3	194.2	184.2	195.1	194.3	193.9
unsaponifiable matter (% w/w)	3.9	2.7	1.9	4.9	3.0	2.1
energy value (kJ/g)	37.2	38.8	38.6	37.9	38.3	39.1

^a Data taken from ref 11. The term "T1" represents the first stage of pretreatment and heating at 65 °C, followed by sedimentation. The term "T2" represents the second stage of pretreatment and heating at 65 °C, followed by sedimentation.

reaction temperature, 60 °C; catalyst, 1% sodium methoxide; and stirring speed, 600 rpm. Under the optimized conditions, all the substrates showed a >95% conversion to methyl ester. Even though it is well-reported that the performance of the alkaline catalyst is not good in the presence of high FFA (>1%), these authors have reported that the acidity index of the fat was not a critical factor when using sodium methoxide as a catalyst. The reusability of a glycerine phase free of methanol, as a catalyst for the transesterification of fresh waste cooking oil, was also examined. It was reported that the used catalyst showed a slightly longer induction period, but after 1 h, the conversion obtained with used and fresh catalysts was almost the same.²⁷ Catalytic activities of NaOH, KOH, sodium methoxide, and potassium methoxide were compared for the transesterification of used frying oil with methanol that had an FFA content of 1.15%.²⁸ The effects of operation variables such as the molar ratio of alcohol to oil (3:1–9:1), the catalyst concentration (0.1%–1.5%), the temperature (25–65 °C), and the catalyst type on the ester yield were studied. The biodiesel with the best properties was obtained using a methanol/oil molar ratio of 6:1, potassium hydroxide as the catalyst (1%), and temperature of 65 °C. Two-stage transesterification with a separation of glycerol after the first stage was determined to be better than a one-stage process.²⁸

The use of a liquid amine-based catalyst for the transesterification of neat vegetable and frying oil has been reported recently.²⁹ Four amine-based catalysts (such as diethylamine (DEA), dimethylethanol amine (DMAE), tetramethyl diaminoethane (TEMED), and tetramethylammonium hydroxide (TMAH) (as 25% solution in methanol)) were screened for the transesterification reaction. The highest conversion of 98% was achieved with TMAH as a catalyst at 65 °C in 90 min. In this case, a large amount (13%) of liquid amine catalysts is required for the transesterification reaction. Amines used in the reaction not only act as a solvent for reactants but also for the products. Hence, the chemical equilibrium is shifted to the right side thus favoring more product. Also, when a solvent is used for both the oil and biodiesel, which has less solvent power for the glycerol, then it facilitates the glycerol formation in a separate phase.²⁹

As stated previously, the products of oil decomposition cause a deterioration in oil quality, which can lead to reduced ester yield during biodiesel production and the formation of unwanted products. The negative effects of undesirable compounds can be avoided by pretreatment of the waste cooking oil. Different types of pretreatments (such as steam injection, column chromatography, neutralization, and film vacuum evaporation) have been used for the purification of waste cooking oil prior to transesterification.

Steam injection and sedimentation treatment were performed on waste cooking oil, and the effects of such refining on the

properties of the oil and the corresponding esters were studied by Supple et al.¹¹ Effects of these treatments on physical and chemical properties of waste cooking oil are given in Table 1. Some of the important changes observed in the oil after first and second treatment were (i) a reduction in moisture content, (ii) a reduction in FFA, and (iii) a substantial reduction in viscosity and increase in energy value with treatment. The treated raw oil, obtained after treatment 1 (referenced hereafter as T1) and after treatment 2 (referenced hereafter as T2) was transesterified with methanol (6:1 molar ratio of methanol to oil) using KOH (1%) as a catalyst at 60°C. Substantial increase in ester yield was observed after each treatment for both the batches. The decrease in moisture content from 1.4% to 0.4% and FFA from 6.3% to 4.3% corresponded with the increased yield of ester (from 67.5% to 83.5%).¹¹

Column chromatography is another efficient technique that is used for the purification of waste cooking oil. The effects of the purification of waste fryer grease (waste cooking oil) on the yield of methyl esters by column chromatography was studied.³⁰ Restaurant grease that contained 10.6% free fatty acids and 0.2% water was purified by passing it through the column, which contained 50% magnesium silicate plus 50% aluminum oxide (basic).³⁰ In this process, the FFA and water contents decreased from 10.6 to 0.23 wt % and from 0.2% to 0.02 wt %, respectively. The conversion of crude grease before column chromatography was 25% after 24 h of reaction, which increased to 96% when purified grease was used.

The transesterification of pretreated waste cooking oil was performed in two different stages, using KOH as a catalyst at 65 °C for 90 min.⁹ Various pretreatment methods were used for waste cooking oil to reduce its FFA, water, and polymer content. FFA was removed by neutralization with alkalis (such as KOH or NaOH) and removed as soaps. Also, waste cooking oil with a higher polymer content was treated with activated charcoal, which was removed by adsorption. Of all these methods, film vacuum evaporation was more suitable for deacidification and drying. Drying was performed under moderate conditions of 159 °C and 20 mbar pressure. Deacidification required more severe conditions of 200–280 °C and 0.1–8 mbar. The final yield of the methyl esters obtained for treated waste cooking oil was 96%.⁹

Potassium hydroxide (KOH), and sodium hydroxide (NaOH), can act as effective catalysts for the transesterification of the waste cooking oil if the FFA content is <1%. The final product yield seems to be dependent on the FFA content of the waste cooking oil. Additional alkaline catalyst is required to neutralize the FFAs of the waste cooking oil, which would affect the cost of the biodiesel. The amount of liquid amine catalyst required (13%) for the transesterification is very high. Also, the removal of this catalyst from the ester phase is not cost-effective. The removal of impurities such as FFA, water, and polymers prior

Table 2. Effect of Various Parameters on Acid-Catalyzed Transesterification^a

Parameter	Molar Ratio (Methanol:Oil)	Catalyst (H ₂ SO ₄) (%)	FFA (%)	Temperature (°C)	Time (hrs)	Water (%)	Conversion (%)
Effect of Temperature	6:1	3	0	25	48	0	~ 10
				45			~ 55
				60			~ 85
Effect of Time of Reaction	6:1	3	0	60	48	0	~ 88
					96		~ 95
Effect of Molar ratio	3.3:1	3	0	60	48	0	~ 77
	3.9:1						~ 80
	6:1						~ 87
	20:1						~ 95
	30:1						~ 98
Effect of Catalyst Concentration	6:1	1	0	60	48	0	~ 72
		3					~ 88
		5					~ 95
Effect of FFA	6:1	3	5	60	96	0	~ 90
			10				~ 88
			15				~ 80
			20				~ 73
			33				~ 60
Effect of water	6:1	3	0	60	96	0.1	~ 92
						0.5	~ 90
						1	~ 82
						3	~ 32
						5	~ 5

^a Data taken from ref 20.

Table 3. Reaction Conditions for Transesterification of Used Oils and Yields of Liquid Fuels^a

alcohol	molar ratio (alcohol:oil)	temperature (°C)	time (h)	catalyst	Ester Yield (wt %)	
					2 days at 25 °C	7 days at 5 °C
methanol	3.6:1	65	40	0.1% H ₂ SO ₄	79.3	64.0
methanol		50	24	0.4% KOH	91.9	85.3
ethanol	3.6:1	73	40	0.1% H ₂ SO ₄	66.9	54.8
ethanol		50	24	0.4% KOH	28.9	
1-propanol	3.5:1	90	40	0.1% H ₂ SO ₄	92.2	76.2
1-propanol		50	24	0.4% KOH	42.7	
2-propanol	3.5:1	80	40	0.1% H ₂ SO ₄	78.7	54.4
2-propanol		50	24	0.4% KOH	51.2	
1-butanol	3.6:1	105	40	0.1% H ₂ SO ₄	78.1	61.9
1-butanol		50	24	0.4% KOH	59.5	
2-ethoxyethanol	4.2:1	125	40	0.1% H ₂ SO ₄	53.5	39.2
2-ethoxyethanol		50	24	0.4% KOH	37.0	

^a Data taken from ref 33.

to the alkali-catalyzed transesterification can improve the yield and the quality of the esters from waste cooking oil; however, it would increase the cost of pretreatment. Ultimately, this will lead to an increase in the cost of biodiesel.

3.2. Acid-Catalyzed Transesterification. One limitation in the alkali-catalyzed process is its sensitivity to the purity of reactants, especially to both water and FFA.³¹ The FFA and water make the use of an alkaline catalyst difficult, because of soap formation and then difficulty in product separation. Freedman et al.³² have reported that an acid catalyst is insensitive to FFA and is better than the alkaline catalyst for vegetable oil with > 1% FFA. The only disadvantage of an acidic catalyst is a slower reaction rate.

The transesterification of edible oil using strong acids (Brønsted acids) such as sulfuric and hydrochloric acid are available in literature reports. The acid-catalyzed transesterification of pure soybean oil was studied by Canakci and Gerpen.²⁰ The effects of the molar ratio of oil to methanol (1:3.3 to 1:30), reaction temperature (25 to 60 °C), H₂SO₄ concentration (1%–5%), reaction time (48 and 96 h), water content (0.1%–5%), and FFA amount (0%–33%) on the conversion of oil were studied. Results obtained are summarized in Table 2. The data

showed that even 5% FFA or 0.5 wt % water decreased the conversion of oil to esters to <90%. The water formed by the reaction of FFA and methanol also inhibited the reaction. Higher alcohols increased the oil conversion when the reaction was conducted just below the boiling temperature of the alcohol.²⁰

The transesterification of used oils collected from the cafeterias at the University of Guelph, Canada, using an acidic catalyst (H₂SO₄) and an alkaline catalyst (KOH), was compared by Nye et al.³³ Two types of used oils (partially hydrogenated soybean oil and margarine) were transesterified with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-ethoxyethanol. The ester yields (see Table 3) were calculated when the product was allowed to settle for 48 h at 25 °C, followed by the removal of solids by gravity and filtration. The filtrate was then allowed to stand at 5 °C for 7 days and refiltered. Composition of the esters showed that fuel obtained at 5 °C is richer in ester than those collected at 25 °C, because of better crystallization at lower temperature. Acid-catalyzed esters had higher yields, compared to the base-catalyzed reaction, except for methyl esters. However, more reaction time was required for the acid-catalyzed reaction. All the acid-catalyzed esters had low viscosities (< 13 cP), except for methyl ester. The performance of the best ester

Table 4. Comparison of Two Catalysts for the Preparation of Methyl Esters from Waste Oils^a

methanol/oil ratio	catalyst	reaction time (h)	conditions	ester yield (wt % of fresh oil)
0.2–0.28	0.01%–2% KOH	1–2	no heat	83–92
0.38	0.12% barium acetate and 0.34% calcium acetate	2–3	high temperature and high pressure	87–94

^a Data taken from ref 36.

was examined in a high-speed diesel engine as fuel. No problems were observed with regard to starting, smoothness in running, and smokiness of the exhaust.³³

Catalytic activities of HCl and H₂SO₄ for the transesterification of waste palm oil was compared.³⁴ Compared to HCl, H₂SO₄ was a better catalyst. The use of excess alcohol can reduce the longer reaction time that is required for the acid-catalyzed reaction. Thus, Brønsted acid-catalyzed transesterification requires high catalyst concentration and a higher molar ratio to reduce the reaction time. Lewis acids can also act as a catalyst for the transesterification of vegetable oil. Basu et al.³⁵ have developed a process to produce esters from feedstocks that have a high FFA content, diglycerides and monoglycerides, using calcium and barium acetate as a catalyst. This catalyst does not form soap with FFA. The optimized ratio of calcium to barium acetate was 3:1; however, ratios higher than 3:1 promote the formation of salts. The temperature (200–250 °C) and pressure (400–600 psi) required for this reaction is quite high. Another disadvantage of this process is that barium compounds used in this reaction are highly toxic in nature. The solubility of barium compounds in methanol is quite high; therefore, data on the leaching of barium compounds in the ester phase would be very useful.³⁵ Rose and Norris³⁶ have compared two catalysts such as KOH and a combination of barium and calcium acetate for the preparation of methyl esters from waste cooking oil. Various reaction parameters and ester yields are shown in Table 4.³⁶ At high temperature and pressure, the latter has been observed to exhibit a high yield of 87%–94%.

Recently, a method has been developed for the simultaneous esterification and transesterification of waste oils using homogeneous Lewis acids based on carboxylic salts of the metals (Cd, Mn, Pb, Zn).³⁷ Catalytic activities of these catalysts are related to the Lewis acid strength of the metals (which must have an optimal intermediate value) and to the molecular structure of the anion. Acetates and stearates of calcium, barium, magnesium, cadmium, manganese, lead, zinc, cobalt, and nickel were tested for their catalytic activity for the transesterification of waste oil at a molar ratio of oil to alcohol of 1:12 and a temperature of 200 °C for 200 min. The influence of water and FFA on the catalyst activity has been studied. Stearates showed better performance than acetates, because of better solubility in the oil. This catalyst showed better performance than the Brønsted acids at lower catalyst concentration and a lower molar ratio of oil to alcohol.³⁷

Hence, homogeneous acid catalysts are good for the transesterification of waste oil with a high FFA content. However, other than the slow reaction rate, and the requirement of high catalyst concentration and high temperature, separation of the catalyst and leaching of the catalyst can be serious issues with homogeneous acid catalysts.

Currently, the focus of the biodiesel research is on the use of a solid acid catalyst for the transesterification of the low-grade oils that have a high FFA content. The advantages of using a solid acid catalyst are (i) they are insensitive to FFA content, (ii) esterification and transesterification can be performed simultaneously, and (iii) removal of the catalyst is easy. Recently, a report has been published that emphasizes the use

of a solid acid catalyst for the transesterification of oil with a high FFA content. The ideal solid acid catalyst for the transesterification of waste cooking oil should have characteristics such as an interconnected system of large pores, a moderate to high concentration of strong acid sites, and a hydrophobic surface.³⁸

3.3. Acid- and Alkali-Catalyzed Two-Step Transesterification. Acidic and alkaline catalysts have their own merits and demerits in the transesterification of waste cooking oil. Hence, looking at the characteristics of both the catalysts, many researchers have used both acidic and alkaline catalysts for the synthesis of biodiesel from waste cooking oil. An acidic catalyst can be used initially to convert FFA to the esters and to decrease the FFA level to $\leq 1\%$. In the second stage, the transesterification of oil can be performed using an alkaline catalyst.

A process was developed by Canakci et al.,¹⁴ where the high-FFA feedstock was initially treated using an acidic catalyst (H₂SO₄) to reduce the FFA level to $< 1\%$. The pretreated feedstock (with $< 1\%$ FFA) was then transesterified with methanol, using an alkaline catalyst (KOH). The effects of the type of alcohol (methanol and ethanol), the amount of acid catalyst (0, 5, 15, and 25 wt %), and reaction time (1, 15, 30, and 60 min) on the reduction of the FFA level were studied with a synthetic mixture of 20% and 40% palmitic acid in soybean oil, as well with yellow grease (12% FFA) and brown grease (33% FFA) as a feedstock.¹⁴ Some of the important conclusions drawn from this study are given as follows:

- (1) Two-step acid-catalyzed esterification followed by an alkaline-catalyzed reaction, improved the methyl ester yield from waste cooking oil;
- (2) The reaction rate increased as the amount of acid catalyst increased;
- (3) When ethanol was used during the reaction, the rate of decrease in the FFA level of the synthetic mixture was faster than that observed with methanol; and
- (4) The two-step acid-catalyst pretreatment process was successful in decreasing the acid value of yellow and brown grease to < 2 mg KOH/g. However, a higher molar ratio of methanol to FFA (40:1) and more reaction time (1 h) are required when yellow and brown grease are used for transesterification compared to synthetic mixture of virgin oil and FFA. This may be due to the presence of some unsaponifiable matter in yellow and brown grease.

Using the same two-stage transesterification, esters of waste cooking oil with methanol, ethanol, and different mixtures of methanol and ethanol have been prepared by Titipong et al.³⁹ Mixtures of alcohols were used, to take the advantage of the better solvent properties of ethanol and the desired equilibrium conversion using methanol. An ester yield of $> 90\%$ was obtained when the two-stage method was used. In the case of mixed alcohols, a small amount of ethyl esters was also formed along with methyl esters. Physical properties of mixed esters were similar to the diesel fuel.³⁹

Lepper and Friesenhagen⁴⁰ have patented a two-stage acidic and basic catalytic process for the production of fatty acid esters of short-chain aliphatic alcohols from fats and/or oils with an FFA content of $> 1\%$. The oil phase was subjected to esterifi-

cation with monohydroxy alcohols in the presence of acidic catalyst (sulfuric acid, *p*-toluene sulfonic acid, alkyl benzene sulfonic acid) at temperatures of <120 °C, preferably in the range of 50–100 °C and under pressures no higher than 5 bar and in the presence of a liquid entraining agent (glycerol or ethylene glycol) that is substantially immiscible with the oil phase. The liquid entraining agent is useful to remove the water formed during the acid-catalyzed reaction. The treated oil with the reduced acid number was then transesterified using an alkaline catalyst (KOH or sodium methylate). The residue of the glycerol phase was successfully reused in nine successive reactions without any further addition of glycerol and catalyst. This procedure was found economical and efficient for the transesterification of waste cooking oils with a high FFA content.⁴⁰ Thus, utilization of acid and alkaline catalysts in first and second stages, respectively, overcome the problem of a slow reaction rate with acid catalyst and formation of soap with an alkaline catalyst and ultimately increases the ester yield.

However, the two-stage method also faces the problem of catalyst removal in both stages. The problem of catalyst removal in the first stage can be avoided by neutralizing the acidic catalyst, using extra alkaline catalyst in the second stage. However, the use of extra catalyst will add to the cost of the biodiesel.

3.4. Enzyme-Catalyzed Transesterification. Chemical (acid or alkali)-catalyzed transesterification of waste cooking oil has problems, such as pretreatment of feedstock, recovery of glycerol, removal of the catalyst, and the energy-intensive nature of the process (high stirring speed, and temperature required for good conversions).⁴¹ Enzyme (such as lipase)-catalyzed reactions have advantages over traditional chemical-catalyzed reactions: the generation of no byproducts, easy product recovery, mild reaction conditions, and catalyst recycling. Also, enzymatic reactions are insensitive to FFA and water content in waste cooking oil.^{41,42} The enzymatic alcoholysis of pure triglycerides with or without solvent has been well-documented in the literature.^{43–45} Generally, in the presence of organic solvents, high yields of alkyl esters could be obtained.⁴⁴ However, the alcoholysis of long-chain and branched alcohols proceeds efficiently in an organic-solvent-free system. However, the organic-solvent-free methanolysis does not give high conversion, because of inactivation of the enzyme by methanol.⁴⁶

Synthesis of biodiesel using enzymes such as *Candida antarctica* (SP-435), *Mucor meihei* (Lipozyme), *Geotrichum candidum*, *Pseudomonas cepacia* (PS-30), and *Burkholderias cepacia* (IM-BS-30) is well reported in the literature. Nelson et al.⁴⁷ screened four lipases—*M. meihei* (Lipozyme IM 60), *C. antarctica* (SP 435), *G. candidum*, and *P. cepacia* (PS 30)—as catalysts for the transesterification of olive oil, soybean oil, and tallow with short-chain alcohols. The reaction conditions developed for tallow were proved to be effective for the transesterification of waste cooking oil. The optimized reaction conditions developed for the transesterification of tallow were as follows: temperature, 45 °C; stirring speed, 200 rpm; enzyme concentration, 12%–25%, based on triglycerides; molar ratio of alcohol to oil, 3:1, and reaction time, 4–8 h (for primary alcohols) and 16 h (for secondary alcohols). *M. meihei* was most effective for the transesterification of tallow using primary alcohols (95% conversion) and lipase from *C. antarctica* and *P. cepacia* (PS-30) were most efficient using secondary alcohols (90% conversion). In the case of methanol, the reaction was very sensitive to the amount of water added to the reaction mixture, because water reduced the yield of ester that was formed. A similar case was observed with 95% ethanol when

M. meihei was used as a catalyst. In the case of secondary alcohols, the small amount of water (3–100 μ L) improved the conversions when *C. antarctica* and *P. cepacia* were used as catalysts. The probable reason might be that, in the presence of water and secondary alcohols, the enzyme was not inhibited and gave more conversion. Hexane was used as a solvent for primary alcohols; however, for branched-chain alcohols, better conversions were obtained without solvents.⁴⁷

Because organic-solvent-free methanolysis does not give high conversions, Watanbe et al.⁴⁶ have conducted the transesterification of waste cooking oil via the stepwise addition of methanol, which prevented inactivation of the lipase (*C. antarctica*). Another major advantage of stepwise methanolysis is that the contaminants (FFA and water) in waste vegetable oil have little or no effect on the efficiency of a stepwise methanolysis and the reusability of an immobilized biocatalyst.⁴⁶ The transesterification of waste vegetable oil was performed in a three-step flow methanolysis with three fixed-bed bioreactors, a three-step batch methanolysis, and a one-step flow methanolysis. Methanol was divided equally for all the three steps in fixed-bed reactors. Ninety percent of the waste oil was converted to the corresponding methyl esters by feeding the substrate mixture into the first, second, and third reactors at flow rates of 6, 6, and 4 mL/h, respectively. In the one-step methanolysis of waste oil, a mixture of waste oil and 90% methyl ester that contained eluate (1:3 w/w) and an equimolar amount of methanol, relative to total fatty acids in the waste oil, was fed into a reactor that was packed with 3 g of immobilized *C. antarctica* lipase at a flow rate of 4 mL/h, and the methyl ester content in the eluate reached a value of 90%. The products of oxidation and hydrolytic reactions in the vegetable oil did not inhibit the methanolysis of acylglycerols.⁴⁶

Although Nelson et al.⁴⁷ have reported that *P. cepacia* is not a good catalyst for the transesterification of waste cooking oil with primary alcohols, many researchers have tried different ways to get maximum conversion using this lipase. Transesterification of the waste cooking oil has been performed with 95% ethanol using *P. cepacia*.⁴¹ The optimized conditions (temperature of 38.4 °C, time of 2.47 h, a lipase PS-30 content of 13.12 wt %, and a molar ratio of ethanol to waste cooking oil of 6.6:1) obtained by factorial design and response surface methodology gave a maximum yield of 85 wt %. The addition of PS-30 after 1 h of the reaction did not significantly improve the conversion of ethyl ester above the value predicted by the model (85 wt %). However, the addition of supported lipase SP435 (5 wt %) from *C. antarctica* after 1 h of reaction with PS-30 increased the ester yield to 96 wt %. The addition of PS-30 lipase in the first step and the addition of SP 435 in the second step increased the ester yield from 85 wt % to 96 wt %.⁴¹

The effect of immobilization on the catalytic activity of *P. cepacia* lipase was examined by Hsu et al.⁴⁸ *P. cepacia* lipase (PS-30) was immobilized within a phyllosilicate sol–gel matrix (IM PS-30) and then used for the transesterification of waste fryer grease with primary and secondary alcohols. The reaction was conducted under solvent-free conditions but in the presence of molecular sieves (0.4%), to eliminate water using both free and immobilized PS-30 lipase. The solvent-free condition did not give good conversions with methanol. This process gave poor conversion (47%–89%) when free lipase was used. However, immobilized lipase gave better conversions (84%–94%) for both primary and secondary alcohols. The results are shown in Table 5. In the case of 95% ethanol, high ester yields of 81 and 94 wt % were obtained with free and immobilized

Table 5. Yield of Esters Obtained from Restaurant Grease Using Different Alcohols and Enzymes^{40–48}

alcohol	Alkyl Ester Yield (%)					
	Gran-T. I.	Gran-C.a.	SP435	IM PS-30	free ^b IM PS-30	IM PS-30 ^b
methanol	4	27	60	88	47	94
ethanol	87	76	70	88	81	88
ethanol (95%)	64	41	30	86	81	94
propanol	87	79	52	87	87	87
2-propanol	61	59	87	46	75	90
butanol	90	56	88	97	89	94
isobutanol	97	89	94	72	87	84

^a Data taken from refs 40–48. Reaction conditions were as follows (unless noted otherwise): molar ratio of grease to alcohol, 1:4; enzyme loading, 10 wt %; reaction time, 24 h; reaction temperature, 40 °C; and no solvent. ^b Reaction conditions were as follows: molar ratio of grease to alcohol, 1:4; 100 mg immobilized lipase or 10 mg free lipase powder; reaction temperature, 50 °C; reaction time, 18 h; and 0.4% molecular sieves.

lipases, respectively. Nelson et al.⁴⁷ have observed that the ethyl ester yield was low (68%) in the case of *M. meihei* lipase with 95 wt % alcohol, compared to that with absolute alcohol (98%), when reaction was conducted with tallow in the presence of hexane.⁴⁷ However, according to Wu et al.,⁴¹ 85% conversion of recycled restaurant grease was obtained using 95% ethanol and PS-30 lipase in 2.47 h, using 13.7 wt % of PS-30 lipase at 38.4 °C. Using the same lipase (PS-30) immobilized within an phyllosilicate, a sol–gel matrix (IM PS-30) effectively converted grease and tallow to ethyl esters in a yield of >95%. The final conversion of grease or tallow to alkyl esters was aided by the addition of molecular sieves (0.4 wt % of substrates) to the reaction mixture. Immobilized lipase can be used six times without a significant loss of activity, whereas free lipase lost 50% of its initial activity after second cycle and all activity after the third cycle.⁴⁸

The performance of different lipases for the solvent-free transesterification of restaurant grease with a single-step addition of normal alcohols and branched-chain alcohols was compared with that using IM PS-30 lipase by Hsu et al.⁴⁹ Lipases used in this study included *Thermomyces ianuginose* and *C. antarctica* supported on granulated silica (denoted hereafter as Gran-T.I., and Gran C.a., respectively), *C. antarctica* supported on macroporous acrylic resin (SP435), and *P. cepacia* immobilized within phyllosilicate sol–gel matrix (IM PS-30). The ester yields with different alcohols and lipases are shown in Table 5.

In this study, Gran-T.I., Gran-C.a., and SP435 produced low ester yields when methanol and 95% ethanol were used, as these lipases were deactivated with a single-step addition of alcohols. Similar observation was made by Nelson et al.⁴⁷ However, IM PS-30 did not deactivate (98% ester yield in 48 h) with the single-step addition of alcohols, because the lipase was constrained in the matrix. SP435 was a good catalyst for branched alcohols. Similar observation was also made by Nelson et al.⁴⁷ and Hsu et al.⁴⁹ Gran-T.I. was good for all alcohols except for methanol and 2-propanol. IM PS-30 was an excellent enzyme for normal alcohols but was not good for branched alcohols. Reaction media with a water concentration of <0.5 wt %, in the case of lipase, resulted in highest conversions. The addition of molecular sieves improved the methyl ester yield by 20%, using IM PS-30. However, reactions that were catalyzed by granulated lipases were not affected by molecular sieves.⁴⁹

Hsu et al.⁴² have studied the continuous transesterification of waste cooking oil with ethanol using immobilized lipase from *Burkholderias cepacia* (IM-BS-30) as a catalyst in a recirculating packed-column reactor. The effects of feed flow rate (5–50 mL/min), temperature (40–60 °C), reaction time (8–48 h), and reusability of the enzyme on the product yield was studied. The optimized conditions for 96 wt % ester yield were as follows: feed flow rate, 30 mL/min; temperature, 50 °C; molar ratio of substrates (ethanol to grease), 4:1; and reaction time, 48 h.⁴²

Thus, immobilization has a substantial effect on the catalytic activity of lipase, especially when feedstock with high FFA and water contents is used for the transesterification. Immobilized enzymes such as *P. cepacia* and *B. cepacia* are efficient enzymes for the transesterification of waste cooking oil that is contaminated with FFA and water.

3.5. Catalyst-Free Technology for Transesterification. Novel methanolysis processes are being developed for the synthesis of biodiesel from vegetable oils using noncatalytic methods. The disadvantages that result from the use of a catalyst and its removal from the products are eliminated if a noncatalytic transesterification reaction of vegetable oils with alcohol is realized. The use of supercritical methanol for the production of biodiesel is one such emerging technology.

In the case of a supercritical fluid process, the reactor pressure and temperature are manipulated to influence the thermophysical properties of solvent (methanol), such as dielectric constant, viscosity, specific gravity, and polarity. Liquid methanol is a polar solvent and has hydrogen bonding between the hydroxide oxygen and the hydroxide hydrogen to form methanol clusters. In supercritical methanol, with increasing temperature, the degree of hydrogen bonding decreases, which helps to reduce the polarity of methanol in a supercritical state. The decrease in the polarity of methanol increases the solubility of oil in it. Because of the hydrophobic nature of nonpolar triglycerides, they are well-solvated in supercritical methanol to form a single-phase oil/methanol mixture. The higher solubility of oil in methanol increases the rate of formation of methyl esters dramatically in the supercritical state. The ionic product, which is an important parameter for chemical reactions, can also be improved by increasing the pressure. Therefore, in the supercritical methanol treatment of vegetable oil, methanol not only acts as a solvent but also as an acid catalyst.^{50,51}

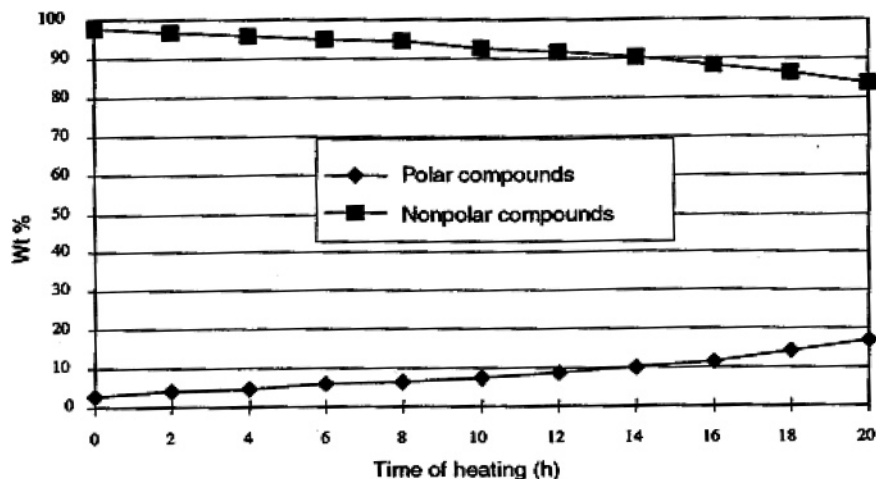
The biodiesel production from pure vegetable oil such as rapeseed using supercritical methanol has been performed by Saka and Kusdiana.⁵² It was demonstrated that preheating to a temperature of 350 °C and treatment for 240 s in supercritical methanol were sufficient to convert rapeseed oil to methyl esters. Although the properties of the methyl esters prepared by this method were similar to those prepared by the common method with a basic catalyst, the yield of methyl ester obtained by the supercritical method was higher.⁵²

Kinetic analysis of the transesterification reaction of rapeseed oil in subcritical and supercritical methanol revealed that the rate of formation of methyl esters from rapeseed oil increased dramatically in the supercritical state. At subcritical temperatures (<239 °C), the reaction rates are low, but at the supercritical state (at 350 °C), the rate constant increased by a factor of ~85. The optimized reaction conditions developed for the synthesis of methyl esters from rapeseed oil were a temperature of 350 °C and a molar ratio of oil to methanol of 1:42.⁵³ Although the use of supercritical alcohol for the transesterification of pure

Table 6. Comparison of the Yields of Methyl Esters in Supercritical Methanol and via Alkaline-Catalyzed and Acid-Catalyzed Methods^a

vegetable oil	FFA content ^b (wt %)	water content (wt %)	Yield of Methyl Esters (wt %)		
			alkaline-catalyzed	acid-catalyzed	supercritical methanol
rapeseed oil	2.0	0.02	97.0	98.4	98.5
palm oil	5.3	2.1	94.4	97.8	98.9
used frying oil ^c	5.6	0.2	94.1	97.8	96.9
waste palm oil	>20.0	>61.0	no reaction	no reaction	95.8

^a Data taken from ref 51. ^b Given as the weight percentage of free fatty acids, relative to vegetable oil. ^c Obtained from a household in Kyoto City.

**Figure 2.** Formation of polar compounds during the heating of rapeseed oil.¹⁶

vegetable oil is well reported in the literature, the application of this technique for the transesterification of waste cooking oil is not well-documented.

As described previously, waste cooking oil is usually contaminated with many impurities, with FFA and water being the major impurities. To extend the use of the supercritical methanol method for the transesterification of waste cooking oil, the effect of water and FFAs on the yield of methyl esters was studied.^{50,51} The reactivity of the transesterification of triglycerides and the alkyl esterification of fatty acid was investigated using different supercritical alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-octanol).⁵⁰ Esterification and transesterification reactions were conducted out under identical conditions, such as a temperature of 300 °C and an oil/fatty acid to alcohol molar ratio of 1:42. The result demonstrated that the alkyl esterification had higher reaction rates, compared to the transesterification. The rate of esterification of saturated and unsaturated fatty acids with various alcohols was also studied. Saturated fatty acids such as palmitic and stearic acids had slightly lower reactivity than that of the unsaturated fatty acids (such as oleic, linoleic, and linolenic acids). Among all the supercritical alcohols, the rate of transesterification was faster when supercritical methanol was used.⁵⁰ To investigate the effect of water on the yield of methyl esters in the transesterification of triglycerides and the methyl esterification of fatty acids, the reaction was conducted at a temperature of 350 °C, a pressure of 43 MPa, and an oil/fatty acids to alcohol molar ratio of 1:42.⁵¹ The presence of water did not have a significant effect on the yield, because complete conversions of oil were always achieved, regardless of the water content. However, the fatty acid esterification reaction was affected by the presence of water. The supercritical methanol method is determined to be more water-tolerant than the conventional method using an alkaline catalyst. The yield of methyl esters obtained from various raw materials that contained different amounts of water and FFA via the supercritical methanol method is shown in Table 6. Waste palm oil with water and FFA contents over 61 wt % and

20 wt %, respectively, produced 95.8 wt % of ester using the supercritical methanol method. However, the feed did not produce any ester while using acid and alkaline methods. These results proved that crude vegetable oil as well as their wastes could be readily used for biodiesel production by the supercritical methanol method.

Despite having all the above advantages, the supercritical methanol method has some serious disadvantages. These include the requirement of high temperature (350 °C) and high pressure (45 MPa). In addition, this method requires a large amount of methanol (1:42 molar ratio of oil to alcohol). Therefore, to apply this method on an industrial scale, further investigations of the production process, such as continuous operation and scaling up, as well as economic evaluations, are needed.

4. Effects of Various Products Formed in the Frying Process on Biodiesel Quality

During frying, vegetable oil undergoes various physical and chemical changes, and many undesirable compounds are formed. The effect of all these compounds on human health is not fully known. The effects of various undesirable compounds formed during frying on biodiesel quality have been investigated by Mittelbach and Enzelsberger.¹⁶ The refined rapeseed oil was heated at 180 °C for 20 h, and over that heating period, because of the various physical and chemical changes, the polar content of oil increases, as shown in Figure 2. After 20 h, the heated rapeseed oil was transesterified with methanol using KOH as a catalyst at room temperature. HPSEC analysis of the esters showed that, along with methyl esters, dimeric fatty acid methyl ester was also observed. The polymers formed during the heating of oils are cleaved, and, during the transesterification reaction, they form monomeric and dimeric fatty acid methyl esters. The oligomeric compounds formed during frying increase the molecular mass and reduce the volatility of the oil. Therefore, fatty acid esters obtained from frying oil influences the fuel characteristics (such as increasing the viscosity and reducing

the burning characteristics), leading to a greater amount of Conradson carbon residue (CCR). Higher CCR amounts correspond to an increase in glycerides as well as FFAs, soaps, remaining catalyst, and other impurities.⁵⁴ In the biodiesel ASTM standards, this value is limited to 0.05%. It was shown that, in the case of methyl esters obtained from heated rapeseed, as the amount of dimeric and polymeric fatty acid methyl esters was increased from 0.7 wt % to 5.7 wt %, the CCR value was also increased from 0.02 to 0.17. However, dimeric and polymeric methyl esters had no negative influence on engine performance in long-term performance tests when 100% ester from frying oil was used as fuel in two city buses.¹⁶

5. Testing of Biodiesel Obtained from Waste Cooking Oil

The study of biodiesel from waste cooking oil is not complete unless it is tested in a commercial diesel engine. Many studies have been conducted where the performance of biodiesel obtained from waste cooking oil was compared with that of petroleum-based diesel fuel, mainly in terms of emissions, engine performance, and fuel consumption.

Mittelbach et al.⁵⁵ tested methyl esters that were prepared using waste cooking oil for their emissions in a vehicle with an inertia weight of 1360 kg that was powered by a 2.3-L turbocharged four-cylinder, four-stroke, direct-injection diesel engine with exhaust gas recirculation (EGR), under transient operating conditions on a chassis dynamometer. The vehicle was tested using methyl esters of used frying oil as fuel, under the U.S. Federal Test Procedure (US-FTP) and in the Highway Fuel Economy Test (HWFET). Test results were compared with US-2D reference fuel. The ester fuel showed slightly lower hydrocarbon (HC) and CO emissions but increased NO_x, compared to US-2D fuel, under US-FTP 72 and almost doubled the NO_x values under the HWFET test. Particulate emissions were reduced significantly under both conditions when ester fuel was used. The reason was that the higher oxygen content of ester fuel provided more oxygen for combustion and soot oxidation. The fuel consumption of ester fuel was higher, compared to US-2D fuel, the reason being the lower net calorific value of the ester. The polycyclic aromatic hydrocarbon (PAH) emissions of the ester were higher than those of the US-2D fuel, but the differences were within tolerance limits. The ester fuel was also tested in a Volkswagen Rabbit automobile that was powered by a 1.6-L four-cylinder, four-stroke diesel engine with indirect injection.⁵⁵ A mixture of ester fuel/diesel fuel (1:1) was chosen, and a total of 100 L of ester fuel was consumed. The smoke emissions were extremely low, and only a faint smell of burnt fat was detected. The consumption of fuel was almost the same as diesel fuel. No change in the operation was observed.⁵⁵

Ethyl ester obtained from used palm oil was tested in a single-cylinder direct-injection (DI) diesel engine by blending different proportions of ester with diesel fuel.⁵⁶ The blends included 100% ester (100O); 75:25 ester/diesel (25D), 50:50 ester/diesel (50D), 25:75 ester/diesel (75D), and 100% diesel fuel (100D). All of the blends, including 100% ester, were tested in the engine, and their performance was compared with diesel fuel, in terms of engine performance and exhaust emissions. Engine performance of 100% ester was better than that of the diesel fuel. The blends of ester and diesel fuel burned more efficiently with better fuel economy and generated lower emissions, including lower CO and unburned hydrocarbons. The performances of the 100O and 25D fuels were much better in all aspects, compared to all other blends. However, the 50:50 blend gave better results, in the case of exhaust emissions.⁵⁶ Dorado et al.⁵⁷

used waste olive oil methyl ester in a DI diesel Perkins engine to examine their exhaust emissions under several steady-state operating conditions. Results obtained for the ester fuel were compared with those using No. 2 diesel fuel. The use of biodiesel confirmed the lower emissions of CO, CO₂, NO, and SO₂, with an increase in the emissions of NO₂. There was a slight increase in brake-specific fuel consumption (BSFC), in the case of biodiesel. For both fuels, the combustion efficiency did not vary. However, the exhaust gases had produced slightly different odors, and a slight fried food smell was detected when biodiesel that had originated from waste cooking oil was used.⁵⁷

A biodiesel blend obtained from yellow grease and soybean oil (20% of each) with No. 2 diesel fuel was tested in a four-cylinder turbocharged diesel engine under steady-state engine operating conditions.⁵⁸ A significant reduction in particulates, CO, and unburned hydrocarbons was observed. However, there was an 11% and 13% increase in the oxides of nitrogen when yellow grease and soybean oil methyl esters were used.⁵⁸ Biodiesel blends of methyl esters from waste cooking oil and animal fats (0%, 10%, and 15%) with diesel fuel have been tested in various diesel engines.⁵⁹ When blends were used, the percentage change in air pollutants under idle conditions was from 1.5% to 44%, except for NO, which was slightly reduced under the idle conditions but increased by ~16% at 2500 rpm.⁵⁹ Ulusoy et al.⁶⁰ tested the biodiesel that was prepared from used frying oil in a Fiat Doblo 1.9 DS, four-cylinder, four-stroke 46-kW-power-capacity diesel engine, and its engine performance and emissions were compared with that for diesel fuel No. 2. Biodiesel showed a reduction in wheel force of more than 3.4%, and wheel power also was reduced by more than 2.0%. When biodiesel was used, CO was reduced by 8.6%, hydrocarbons by 30.7%, and particulate emissions by 63.3%. However, CO₂ emissions was increased by 2.6% and NO_x emissions by 5.0% when biodiesel was used.⁶⁰

The engine and road performance tests of biodiesel derived from used cooking oil were evaluated in a Renault Megane automobile and 75 kW Renault Megane diesel engine under winter conditions for 7500-km road tests, and the results were compared with those using No. 2 diesel fuel.⁶¹ The addition of a viscosity improver and pour-point additives showed a significant improvement on the fuel properties of the biodiesel from used cooking oil. The overall performance of the biodiesel was better than that of No. 2 diesel fuel. The condition of the engine injectors was also examined when diesel and ester fuels were used. The distance of 7500 km was divided into two periods, because of the winter conditions. Engine injectors were normally carbonized when No. 2 Diesel fuel was used. However, the carbonization in engine injectors was observed for biodiesel as a result of winter conditions in the first period. In the second period, because of the low viscosity of the biodiesel, the injectors were observed to be cleaner.⁶¹ The combustion performance and emissions of ethyl ester of a waste vegetable oil in a water-cooled furnace was investigated by Tashtoush et al.⁶² At a lower energy rate, biodiesel burned more efficiently with higher combustion efficiency (66%) and exhaust temperature (600 °C), compared to diesel fuel (combustion efficiency of 56% and exhaust temperature of 560 °C). At high energy input, the biodiesel combustion performance deteriorated, because of its high viscosity, density, and low volatility. At both energy levels, the biodiesel emitted fewer pollutants.⁶²

Generators are crucial equipment of industry and are used widely in agriculture. Also, engine performance and the emissions of electric generators are important, because of their indoor applications. The use of biodiesel prepared using waste

Table 7. Conditions for Transesterification of Virgin Oil and Waste Vegetable Oil^a

process	oil	methanol:oil molar ratio	catalyst	temperature (°C)	pressure (kPa)
process I	virgin oil	6:1	1% NaOH	60	400
process II	waste oil (pretreatment)	6:1	1% H ₂ SO ₄	70	
process II	waste oil (transesterification)	6:1	1% NaOH	60	400
process III	waste oil	50:1	1.3:1 H ₂ SO ₄ :oil	80	400
process IV	waste oil (hexane used for extraction of methyl esters)	50:1	1.3:1 H ₂ SO ₄ :oil	80	400

^a Data taken from ref 64.

cooking oil in electric generators has been investigated by Centinkaya and Karaosmanglu.⁶³ The engine performance and emission tests were conducted with a 90-mm-stroke, one-cylinder, and 9-kW 3 LD 510 coded diesel engine, and generator performance tests were performed in a generator set that consisted of a 90-mm-stroke, one-cylinder, 4 LD 640 code and 10.5 kW diesel engine and a 10-kVA-maximum-output, 14.4-A current, and 400-V A 100 LB coded rotating-field three-phase AV generator. Consecutive tests on No. 2 diesel fuel, B100, and B20 were conducted, and the results were compared with each other. Compared to No. 2 diesel fuel, B100 and B20 blends showed improved results, in regard to engine performance and emissions. The use of B100 resulted in lower smoke production than that of B20, whereas the use of B20 resulted in higher power generation and lower BSFC, when compared to B100. However, tests related to the engine noise and measurements of specific emission types (such NO_x, SO_x, CO) are needed to commercialize the use of biodiesel that originated from waste cooking oil in generators.

Overall, the engine performance of biodiesel obtained from waste cooking oil was better than that of diesel fuel, and no change in engine operation was observed during the tests. The emissions produced by the use of biodiesel are less than those using diesel fuels. Only an increase in NO_x was observed when biodiesel obtained from waste cooking oil was used. Generally, the biodiesel fuel consumption is somewhat higher, compared to that observed with regular diesel fuel, because of the lower calorific value of the former. However, the blends of the ester fuel with diesel fuel (75:25 and 50:50) maintains a balance for fuel consumption and emissions. The use of biodiesel that originated from waste cooking oil resulted in a slight fried food smell, when used on a large scale with diesel fuel.

6. Pilot-Plant Designs for Biodiesel Production from Waste Cooking Oil

As discussed previously, there are various methods reported for the production of biodiesel from waste cooking oil. However, the two-step process (acid-catalyzed, followed by alkaline-catalyzed) is one of the better alternatives for the production of biodiesel from waste cooking oil. Based on this, Canackci and Gerpen⁹ have developed a 190-L pilot plant at the Iowa Energy Center's Biomass Energy Conversion Center (BECON) near Ames, IA. The pilot plant can process high-FFA feedstocks, using an acid-catalyzed pretreatment followed by an alkaline-catalyzed (sodium methoxide) transesterification. The study included the pilot-plant-scale production of biodiesel from soybean oil, yellow grease with 9% FFA, and brown grease with 40% FFA.

The estimated costs for biodiesel from soybean oil, yellow grease, and brown grease were \$0.418/L, \$0.317/L, and \$0.241/L, respectively. Twelve-month average prices of the feedstocks and chemicals were taken as a baseline case (over the 1999–

2000 time period). These estimates did not include capital costs or a credit for the value of the co-product glycerine. The capital cost for a plant that processes yellow and brown grease will be somewhat higher than that for soybean oil, because of the need for pretreatment equipment.

Zhang et al.^{13,64} developed four different continuous process flow sheets for biodiesel production from virgin oil or waste vegetable oil using alkaline or acidic conditions. Detailed operating conditions and equipment designs for each process were obtained (see Table 7). The technical benefits and limitations of each process were also evaluated.^{13,64}

A process design with capacity of 8000 tonnes/yr has been developed by Zhang et al.,^{13,64} based on the optimum reaction conditions. A technological analysis, an economic assessment, and a sensitivity analysis of the four processes based on the fixed capital cost, the total manufacturing cost, the after-tax rate of return, and the break-even price of biodiesel were also performed. Some of the important observations made by Zhang et al.^{13,64} are as follows. Process I is good for virgin oil, which requires less process equipment. However, the raw material cost for Process I is very high, because the virgin oil is costly. Thus, Process I has the lowest capital investment but also has a high manufacturing cost. The price of waste cooking oil is less than that of the virgin oil. Hence, the raw material cost of Process II is less than Process I, but Process II must be performed in two steps: pretreatment and transesterification. Process II is more complex than Process I and, hence, requires more equipment than Process I. The pretreatment step in Process II requires extra cost and reduces the economic feasibility of the process. Process III uses only an acidic catalyst for transesterification and requires a higher molar ratio of methanol to oil. To handle such a large amount of methanol, larger reactors and distillation columns are required. Also, because an acidic catalyst is used for the reaction, more process equipment that is composed of stainless steel is required, which would increase the cost of the process. Processes III and IV are similar, except hexane is used for the extraction of fatty acid methyl esters in Process IV, which increases the cost of the process. Process III and IV have lower total manufacturing costs than the alkali-catalyzed (NaOH) process.

Efficient utilization of the byproduct glycerine is expected in reducing the cost of the biodiesel. According to Zhang et al.,^{13,64} based on the after-tax rate of return and break-even price, Processes III and IV are economical, compared to other processes, because of lower production costs. The important factors that affect the economic feasibility of the biodiesel production are plant capacity, the price of waste cooking oil, and the price of biodiesel.

Ultimately, the alkali-catalyzed process using virgin vegetable oil (Process I) is more suitable from the process simplicity point of view; however, from the standpoint of manufacturing cost, the acid-catalyzed process (Process III) is the best alternative to Process I.

7. Conclusions and Future Prospects

Waste cooking oil is an economical choice for biodiesel production, because of its availability and low cost. This oil has many undesirable compounds such as polymers, free fatty acid (FFA), and many other chemicals that are formed during frying, which are of major concern during the transesterification reaction. Pretreatment of the waste cooking oil to remove these undesirable chemicals is not practical. Depending on the water and FFA content of the waste cooking oil, a transesterification method should be selected. If the FFA and water contents are <1 wt % and <0.5 wt %, respectively, then an alkaline catalyst is more suitable for the ester production. If the FFA content of oil is high (>1 wt %), then an acid catalyst is a good choice. However, because of the requirement of high catalyst concentration and high molar ratio, and because of corrosion problems, these catalysts are also not recommended for the transesterification of waste cooking oil. A two-step method (an acid-catalyzed step, followed by an alkaline-catalyzed step) is not feasible, because it requires many steps, which makes the biodiesel process costly. Enzyme-catalyzed transesterification is a very good option to all chemical-catalyzed reactions; however, it must be developed for its commercialization. The catalyst-free supercritical methanol method has great potential for biodiesel production from waste cooking oil; however, the requirements of high temperature (350 °C), high pressure (45 MPa), and high molar ratio of oil to alcohol (1:42) makes the use of this process difficult on an industrial scale. It is recommended that the development of a novel solid acid catalyst that consists of large pores, a moderate to high concentration of strong acid sites, and a hydrophobic surface could be a better choice for the transesterification of waste cooking oil with high FFA. The performances of biodiesel obtained from waste cooking oil as transportation fuel or as an additive are better in all aspects, except for increased NO_x emissions and high Conradson carbon residue (CCR).

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