

Synthesis and characterization of vegetable oil derived esters: evaluation for their diesel additive properties

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Abstract

Trans-esterification of four vegetable oils; canola oil, greenseed canola oil from heat-damaged seeds, processed waste fryer grease and unprocessed waste fryer grease, was carried out using methanol, and KOH as catalyst. The methyl esters of the corresponding oils were separated from the crude glycerol, purified, and characterized by various methods to evaluate their densities, viscosities, iodine values, acid numbers, cloud points, pour points and gross heat of combustion, fatty acid and lipid compositions, lubricity properties, and thermal properties. The fatty acid composition suggests that 80–85% of the ester was from unsaturated acids. Substantial decrease in density and viscosity of the methyl esters compared to their corresponding oils suggested that the oils were in their mono or di glyceride form. The lubricity of the methyl esters, when blended at 1 vol% treat rate with ISOPAR[®] M reference fuel, showed that the canola methyl ester enhanced the fuel's lubricity number. From the analyses performed, it was determined that the ester with the most potential for being an additive or a substitute for diesel fuel is the canola methyl ester, whose physical and chemical characteristics are similar to diesel fuel.

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1. Introduction

Diesel fuels play an important role in the industrial economy of a country. These fuels run a major part of the transport sector and their demand is increasing steadily, requiring an alternative fuel which is technically feasible, economically competitive, environmentally acceptable, and readily available (Srivastava and Prasad, 2000; Bej, 2002). Vegetable oils are widely available from various sources, and the glycerides present in the oils can be considered as a viable alternative for diesel fuel (Shay, 1993; Ali et al., 1995). Biodiesel, which is synthesised from bio-oil, is a realistic alternative of diesel fuel because it provides a fuel from renewable resources and has lower emissions than petroleum diesel. It is biodegradable and contributes a minimal amount of net greenhouse gases or sulfur to the atmosphere. More specifically, biodiesel cuts down on the amount of carbon dioxide, hydrocarbons, and par-

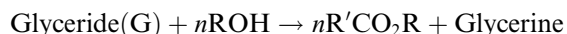
ticulate matter released into the environment (Karaosmanoglu et al., 1996; Dunn, 2001).

The heating value of vegetable oils is similar to that of diesel fuel. However, their use in direct injection diesel engines is restricted by some unfavourable physical properties, particularly their viscosity. The viscosity of vegetable oil is approximately ten times higher than the diesel fuel. Therefore, use of vegetable oil in direct injection diesel engines creates poor fuel atomisation, incomplete combustion, carbon deposition on the injector, and fuel build up in the lubricant oils resulting in serious engine fouling (Sridharan and Mathai, 1974; Encinar et al., 2002). This necessitates improvement in viscosity of the bio-oil. The possible treatments employed to improve the oil viscosity includes dilution with a suitable solvent, emulsification, pyrolysis, and trans-esterification (Peterson et al., 1991; Otera, 1993).

Trans-esterification is a process of displacement of an alcohol group from an ester by another alcohol. In vegetable oil almost 90–95% is glycerides, which are basically esters of glycerol and fatty acids (Quick et al., 1983). The nature of the fatty acid components of

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glycerides plays an important role in determining the physico-chemical properties of bio-oil. In the process of trans-esterification of bio-oil, in particular the glyceride, an alcohol is used to replace the glycerine to obtain esters of the fatty acids, however, with lower molecular weight. The process can be presented as:



where, R' and R are hydrocarbon chain of the fatty acid group and alcohol, respectively. The number of moles of the alcohol is represented by *n*, which can be 1, 2 or 3 depending upon the nature of glyceride, i.e., whether the glyceride is mono, di or tri. The glycerine produced in this process is a valuable byproduct due to its numerous applications in various industrial processes.

The alcohols employed in the trans-esterification are generally short chain alcohols such as methanol, ethanol, propanol, and butanol. It was reported that when trans-esterification of soybean oil using methanol, ethanol and butanol was performed, 96–98% of ester could be obtained after an hour of reaction (Freedman et al., 1986). Although use of different alcohols present few differences with regards to the kinetic of reaction, the final yield of esters remains more or less unchanged. Therefore, selection of the alcohol is based on cost and performance consideration.

Alkoxides and hydroxides of potassium and sodium are often used as a catalyst in trans-esterification. However, acid catalysts are also used. It was reported that using acid and base catalysts in this reaction base catalysts performed better than the acid catalysts (Formo, 1954). The reaction can be performed at lower temperature, even at room temperature, with the base catalysts, whereas acid catalysis required higher temperature (100 °C) and longer reaction time. Therefore, the objectives of this work were to prepare, and analyze biodiesel produced from 100% canola oil, greenseed canola oil and waste vegetable cooking oils, and to determine which type of oil will generate the highest quality product for blending with diesel fuel.

2. Methods

Four types of oils/fats samples, which included canola oil, greenseed canola oil, processed waste fryer grease, and unprocessed waste fryer grease, were used to prepare biodiesel. Each of these oils was reacted with methanol to produce methyl esters of the oils/fats, also known as bio-diesel. The detail procedure for the synthesis of different esters and the determination of their properties is described below.

2.1. Materials

The canola oil used in this process was purchased at a local store. Mr. Roy Button of Canodev Research Inc., Canada supplied the greenseed canola oil. Both the processed and unprocessed waste fryer grease was supplied by Saskatoon Processing Co. (Saskatoon, Canada). The difference between the processed and unprocessed waste fryer grease is that the processed grease has citric acid added to it to remove most of the solids.

2.2. Synthesis of esters

2.2.1. Canola methyl ester

For the synthesis of methyl ester, a two-stage process was chosen as it removes the majority of the mono-, di-, and tri-glycerides in the first stage and those remaining could be taken out in the second stage (Lang et al., 2001a), resulting in a more purified product. The amount of canola oil used in the reaction was 100 g. A 6:1 molar ratio of methanol to oil was used in order to utilize 100% stoichiometric excess of methanol (Lang et al., 2001a). Therefore, 22.64 g of methanol was used for the entire procedure, and 11.32 g was used per stage. The amount of potassium hydroxide used was 1.0 wt.% of the vegetable oil.

In the first stage, 0.5 g of KOH was added to 11.32 g of methanol and stirred until the catalyst was completely dissolved. Canola oil (100 g) was placed in an Erlenmeyer flask and the methanol/KOH solution was added to the oil. This mixture was stirred for 20 min at 25 °C, and then poured into a separatory funnel. After about an hour separation had occurred, and the glycerol was removed from the separatory funnel as a dark brown coloured liquid from the bottom of the flask. Another 0.5 g of KOH was added to 11.32 g of methanol, and stirred until the KOH dissolved. This was then added to the canola methyl ester obtained from the first stage, and was again stirred for 20 min. Afterwards, the mixture was added to a separatory funnel and allowed to separate overnight.

Once the glycerol was removed by gravity settling, the canola methyl ester was washed to remove alcohol and catalyst remaining in the ester phase. Based on past experiments water washing was found to be an inefficient method, because of the amount of water used, and the soap emulsions were difficult to remove. Therefore, a cleaner, easier method was used which involved washing the biodiesel with silica gel. The methanol was removed with the help of a Rota-Evaporator (R-114, Buchi, Switzerland) from the ester before the silica gel treatment. The ester was added to the sample flask, and this flask was immersed in water at a temperature of 60 °C while constantly rotating. Cold water was flowing through the condenser at a rate of approximately 40 l/h,

and the system was connected to a vacuum. After about 30 min the entire methanol had boiled off. The canola methyl ester was removed from the sample flask and transferred to an Erlenmeyer flask, to which silica gel was added. This mixture was stirred for approximately 20 min, and then filtered to remove the silica gel from the canola methyl ester. A layer of sodium sulfate crystals was added to a vacuum filtration funnel, and the ester was filtered through it to remove any traces of water present. The dried canola methyl ester was then bottled and kept for characterization studies.

2.2.2. Methyl esters of processed and unprocessed waste fryer grease

For greenseed methyl ester synthesis the procedure was the same as that described for canola methyl ester. The procedure used for the preparation of methyl esters from processed and unprocessed waste fryer greases was similar to the one described for canola methyl ester (Lang et al., 2001a). The only difference was that 1.75 g of KOH was used instead of 1.0 g. Therefore, 0.825 g of KOH was used per stage. It may be noted here that a titration was performed to estimate the amount of KOH required to keep the pH of 100g of the oil in the range 8–9 (Tickel and Tickel, 1999). In the case of processed and unprocessed waste fryer greases it was 1.75 g.

2.3. Methyl esters characterizations

Using standard procedures as listed in Table 1, physical and chemical properties such as density, viscosity, heat of combustion, cloud and pour points, acid value, and iodine value were determined. The gas chromatography (GC, Hewlett Packard, 5890 series) and high performance liquid chromatography (HPLC, Agilent 1100) were used to determine the ester's fatty acid and lipid compositions. Also, the differential scanning calorimeter, DSC 2010 with a TA 2100 PC-based controller, was used to determine the low temperature behaviour of the esters. The results from each of these characterization techniques are reported in Section 2.4.

The lipid composition of the methyl esters was determined using HPLC with a Waters GPC-Styragel 0.5

column (7.5×300 mm). The mobile phase was tetrahydrofuran, and an evaporative light scattering detector (ELSD) was used. The column was operated at 35 °C and the ELSD was maintained at 40 °C. The HPLC method used was the low molecular weight gel permeation chromatograph.

The fatty acid compositions of the methyl esters were measured by gas chromatography using a GC (Hewlett Packard, Model 5890) equipped with a DB-FFAP column and flame ionization detector. The densities of the methyl esters were determined using a density meter (Parr, Model DMA 35, USA) at 30 °C. The viscosities of the methyl esters were determined at 40 °C using a (Brookfield, Model LVTDVCP-II, Brookfield Engineering Laboratories, Stoughton, MA) digital cone and plate viscometer. Each of the experiments was performed thrice to obtain the density and viscosity data. The heats of combustion of the methyl esters were measured using an Oxygen Bomb Calorimeter (Parr 1341, USA). In order to ensure complete combustion after firing, approximately 50 wt.% benzoic acid powder was mixed with the sample liquids. The cloud point was defined as the temperature at which a cloud of wax crystals first appeared in a liquid when it was cooled under certain conditions. The pour point was defined as the lowest temperature at which a liquid can be moved (Lang et al., 2001b). The acid value was defined as the 'mg' of potassium hydroxide necessary to neutralize the free acids in 1 g of sample, but as a result of the acid values for bio diesel typically being less than 1 mg KOH/g, 20 g of methyl ester samples were used for the analysis. To obtain acid value data each experiment was repeated thrice. The iodine value, expressed as grams of iodine absorbed/100 g sample, represents a description of the unsaturation of oils and their fatty acid derivatives, and was determined directly from fatty acid compositions and corresponding acid factors given in the standard method. Acid factors are the reacting ratios of I₂ to the individual fatty acids. The calculation used to determine the iodine value is:

$$\text{Iodine value} = \sum (\% \text{ of Fatty acid} \times \text{Acid factor})$$

where 'Σ' represents the summation of the product of all the fatty acids and their corresponding acid factors.

The differential scanning calorimetry (DSC) method was used to study the low temperature properties of the biodiesel esters. For each scan approximately 5.00 mg of sample was weighed and sealed into an aluminum pan. Samples were equilibrated at 30 °C and then cooled at 5.0 °C/min to -70 °C for 5 min and then heated to 30 °C at 5.0 °C/min. The cooling curves were analyzed for freezing points of the esters as well as the latent heats. The potassium levels in the methyl esters were analyzed by Fluid Life Corporation in Edmonton, AB using inductively coupled plasma (ICP).

Table 1
Standard test methods used to characterize methyl esters

Properties	Method
Fatty acid composition	AOCS method Ca 5a-40
Density	ASTM D5002-94
Heat of combustion	ASTM D240-92
Cloud point	ASTM D 2500
Pour point	ASTM D 97
Acid value	AOCS Te 2a-64
Iodine value	AOCS Cd 1c-85

2.4. Experimental design for lubricity measurement

Lubricity tests of the biodiesel esters were carried out in the Department of Mechanical Engineering, University of Saskatchewan, Saskatoon, Canada using a Munson Roller on Cylinder Lubricity Evaluator (M-ROCLE). The M-ROCLE bench test applies a constant load of 24.62 N to a stationary steel bearing roller. This roller rubs against a fuel-lubricated rotating steel bearing race or cylinder. The situation that occurs in diesel injection pumps is imitated by crossing the roller and cylinder axes to develop a high theoretical 897 MPa Hertzian stress at the point of contact. To determine the coefficient of friction developed with the fuel and methyl ester blends, the computer interfaced steady state motor frictional torque was measured during an individual 3 min run. In order to control ambient temperature, fuel temperatures and room humidity at 24 °C, 25 °C, and 45% respectively, an environmental chamber was used. At least six runs were conducted on each fuel/ester sample to check for its reproducibility. The elliptically shaped wear scars produced on the test rollers during each run were microscopically measured using a computer video system. The wear area stress was calculated based on the ratio of applied load to wear area. A dimensionless lubricity number (LN), indicating the lubricating property of the test fuel, was calculated after determining the unlubricated Hertzian contact stress, using the following equation:

$$LN = \frac{\sigma_{ss}}{\sigma_H \times \mu_{ss}}$$

and

$$\sigma_{ss} = \frac{P}{A}$$

where σ_{ss} is the steady state ROCLE contact stress (MPa), σ_H is Hertzian theoretical elastic contact stress (MPa), μ_{ss} is the steady state coefficient of friction, P is the applied load (N), A is the roller wear scar area (m²).

A LN of 1.0 or greater was determined to be the passing value for a diesel fuel of sufficient lubricity. The type of fuel used in the lubricity evaluation was ISO-PAR[®] M Solvent supplied by Imperial Oil, Canada. The density of this fuel is 793 kg/m³, and its kinematic viscosity is 2.3 mm²/s (cSt) at 40 °C.

The four samples of biodiesel esters were combined at 1 vol% with the reference diesel fuel and the lubricity evaluation was performed. At least six runs were conducted on each fuel/ester sample to check for its reproducibility. These data were used to calculate average and standard deviation and are discussed in the following section.

3. Results and discussion

The chromatograms of the canola methyl ester are shown in Fig. 1. From the results of the high performance liquid chromatography it can be seen that the canola methyl ester is the only biodiesel sample produced that is impurity free (cf. Fig. 1). Each of the other three methyl esters contains a small amount of triglycerides indicating that esterification in these cases was slower than that in the case of canola oil. In each of the four biodiesel esters, the most common fatty acid was oleic acid, at approximately 65% of the total fatty acid composition. Linoleic acid was the next common fatty acid in the esters. The third most common fatty acid in the canola and greenseed methyl esters was linolenic acid, while in the processed and unprocessed methyl ester it was palmitic acid (Table 2).

The densities, viscosities, cloud points, pour points, and gross heat of combustion are given in Table 3. The densities of the canola oil, greenseed oil, and waste fryer greases ranged from 909 ± 1.0 to 911 ± 1.2 kg/m³. The densities of their methyl esters were in the range of 872 ± 1.0–877 ± 1.0 kg/m³ and decreased in the order of greenseed methyl ester > processed grease methyl ester > canola methyl ester > unprocessed grease methyl ester. The densities of the no. 1 Canadian winter diesel fuel (LSD-43 Diesel Light) and the no. 2 summer diesel fuel (C-5 Seasonal Diesel) were 820 and 860 kg/m³, respectively. The viscosities of the canola and greenseed oils and waste fryer grease ranged from 29.8 ± 0.7 to 39.2 ± 0.4 cP. The canola oil yielded the lowest viscosity, followed by the greenseed oil, the processed waste fryer grease, and the unprocessed waste fryer grease. The viscosities of the methyl esters were much lower than their respective oils and grease. They ranged from 4.23 ± 0.05 to 5.69 ± 0.12 cP. For this group it was expected that the viscosity would increase in the same order as it did for the oils and waste fryer grease. This is not the case, however. The canola methyl ester had the lowest viscosity, but the next lowest was the unprocessed grease methyl ester, followed by the greenseed methyl ester and then the processed grease methyl ester. The viscosities of the nos. 1 and 2 diesel fuels were 1.75 and 3.50 cP at 40 °C, respectively.

The heat of combustion (Table 3) of the canola and greenseed oils and the processed and unprocessed grease ranged from 23.89 ± 0.26 to 25.22 ± 0.64 MJ/kg. The heat of combustion of the methyl esters was slightly lower than their respective oils and waste fryer greases, except for the canola methyl ester, which was similar. The heat of combustion of the methyl esters ranged from 20.95 ± 0.20 to 25.11 ± 0.29 MJ/kg. The greenseed methyl ester had the lowest heat of combustion, followed by the processed grease methyl ester, the unprocessed grease methyl ester, and finally the canola methyl ester. The heat of combustion of the diesel fuel was

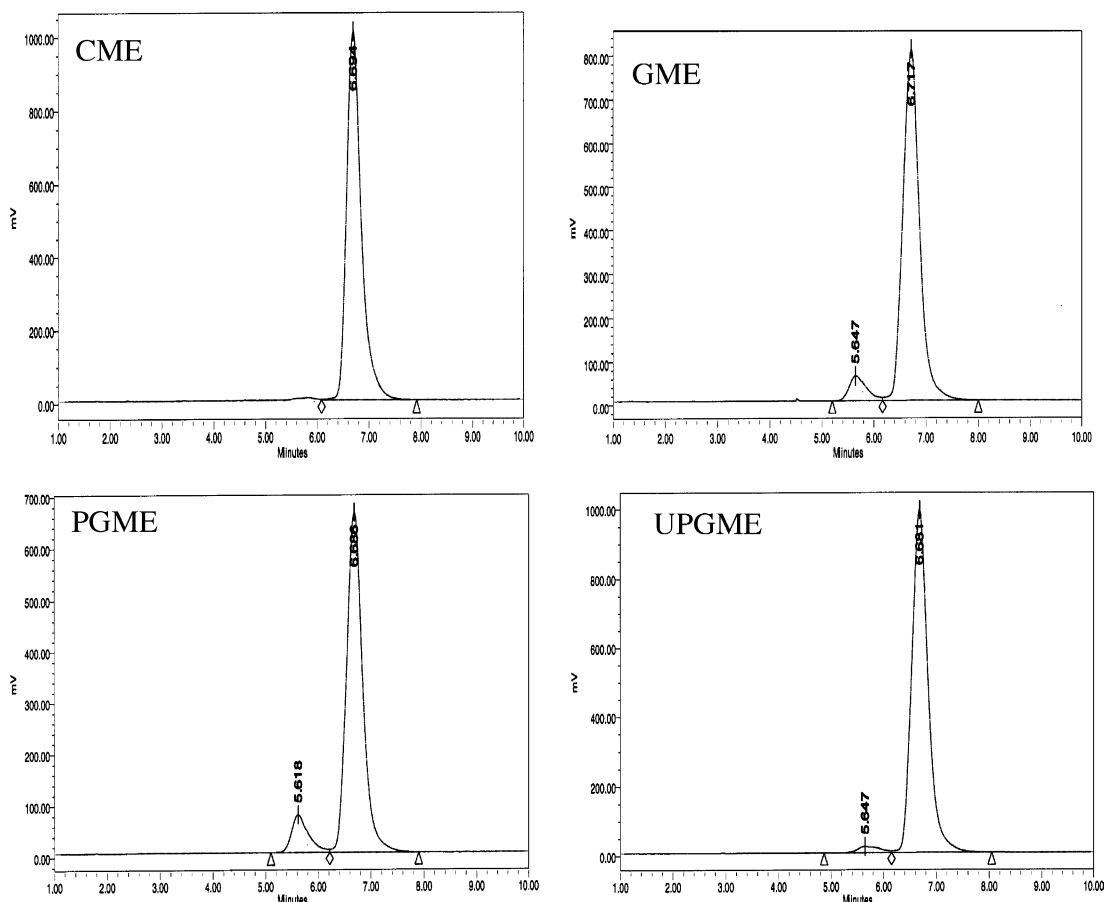


Fig. 1. Chromatograms of the methyl Esters of various vegetable oils.

Table 2

Fatty acid composition of methyl esters

Fatty acid	CME	GME	PGME	UPGME
Palmitic	4.21	4.38	10.00	9.5
Stearic	2.03	1.98	6.44	7.16
Oleic	62.33	62.74	65.98	69.15
Linoleic	19.13	19.99	13.29	10.55
Linolenic	9.18	9.6	3.03	2.51
Eicosenoic	1.26	0	0	0
Erucic	1.87	1.31	1.26	1.15
Total	100.01	100.00	100.00	100.02

CME: canola methyl ester, GME: greenseed methyl ester, PGME: processed grease methyl ester, UPGME: unprocessed grease methyl ester.

approximately 45 MJ/kg. Therefore, the oils and esters contained approximately 48% less heat energy on a mass basis.

The cloud point (Table 3) of the various methyl esters ranged from 1 to 5 °C. The canola methyl ester had the lowest cloud point and the unprocessed waste fryer grease methyl ester had the highest. The pour point of the methyl esters ranged from –12.0 to 1.0 °C. The greenseed methyl ester had the lowest pour point, and the unprocessed grease methyl ester had the highest. The canola and greenseed methyl esters had relatively lower

pour points than the processed and unprocessed waste fryer grease methyl esters. The cloud and pour points of the no. 1 diesel fuel were –50 and –51 °C, respectively. These values were much lower than that of the esters. The no. 2 diesel fuel had cloud and pour points of –8 and –15 °C, respectively. The pour points for the diesel fuel was much lower than those of processed and unprocessed waste fryer grease methyl esters and was somewhat lower than those of the canola and greenseed methyl esters. DSC analysis also shows that the processed and unprocessed grease methyl esters have poor

Table 3
Densities of oils and methyl esters

Sample	Density (kg/m ³)	Viscosity (cP)	Cloud point (°C)	Pour point (°C)	Gross heat of combustion (MJ/kg)
Pure canola oil	911 ± 1.2	29.8 ± 0.7	nd	nd	25.14 ± 0.13
Greenseed oil	910 ± 0.6	30.9 ± 0.8	nd	nd	23.89 ± 0.26
Processed waste fryer grease	910 ± 1.2	37.8 ± 0.7	nd	nd	25.22 ± 0.64
Unprocessed waste fryer grease	909 ± 1.0	39.2 ± 0.4	nd	nd	24.67 ± 0.55
Canola methyl ester	875 ± 0.6	4.23 ± 0.05	1.0–2.0	–8.0 to –10.0	25.11 ± 0.29
Greenseed methyl ester	877 ± 1.0	4.70 ± 0.11	1.0–3.0	–10.0 to –12.0	20.95 ± 0.20
Processed grease methyl ester	877 ± 0.6	5.69 ± 0.12	2.0–3.0	–2.0 to –3.0	21.26 ± 0.24
Unprocessed grease methyl ester	872 ± 1.0	4.63 ± 0.10	4.0–5.0	–1.0 to 1.0	21.37 ± 0.79

nd: not determined.

Table 4
Acid values of methyl esters

Sample	Acid value	Iodine value (g iodine absorbed/100 g sample)	Potassium level (ppm)
Canola methyl ester	0.154 ± 0.010	127	227
Greenseed methyl ester	0.162 ± 0.021	124	114
Processed grease methyl ester	0.324 ± 0.023	103	228
Unprocessed grease methyl ester	0.191 ± 0.016	98	78

low temperature characteristics. The canola and greenseed methyl esters did not freeze until –50 °C, but the processed and unprocessed grease methyl esters began freezing at around –10 °C. Therefore, in regions with a cold climate, processed and unprocessed grease methyl esters would be a poor choice to use as a transportation fuel source.

The acid values (cf. Table 4) ranged from 0.154 ± 0.010 to 0.324 ± 0.023 mg KOH/g of oil. The lowest acid value was that of the canola methyl ester. The highest acid value belonged to the processed waste fryer grease methyl ester. The acid factors were 0.9976 for palmitoleic acid, 0.8986 for oleic acid, 1.810 for linoleic acid, 2.735 for linolenic acid, 0.8175 for eicosenoic acid, and 0.7497 for erucic acid. The measured acid value was low for the canola and greenseed methyl esters, somewhat high for the unprocessed grease methyl ester, and very high for the processed grease methyl ester. Therefore, the unprocessed and processed grease methyl esters have considerable free fatty acid present. The high value for the processed grease methyl ester might be a result of the citric acid that is added when the waste fryer grease is processed. This citric acid may potentially increase the acid value of the processed grease methyl ester.

The iodine values of various esters (cf. Table 4) ranged from approximately 98–127 grams of iodine absorbed/100 g sample. The unprocessed grease methyl ester had the lowest iodine number, followed by the processed grease methyl ester, the greenseed methyl ester, and the canola methyl ester. These data show that the canola and greenseed methyl esters have a greater degree of unsaturation than the processed and unpro-

cessed grease methyl esters. The unprocessed grease methyl ester contained the least amount of potassium with 78 ppm, while the processed grease methyl ester contained the most potassium, about 228 ppm (cf. Table 4). Because the allowable potassium level is not specified in ASTM standards for biodiesel, the amount of potassium contained in the biodiesel samples cannot be deemed as overly excessive or limited. However, the high amount could be attributed to ineffective washing, or perhaps not washing long enough. Also, although sodium hydroxide was not used as a catalyst, levels of greater than 1 ppm of sodium were found in the methyl esters.

The thermograms of four methyl esters; the canola methyl ester, greenseed methyl ester, processed waste fryer grease methyl esters, and unprocessed waste fryer grease methyl esters are presented in Fig. 2. Only one long, sharp peak is found in both canola methyl and greenseed methyl esters, representing the major component. The processed waste fryer grease methyl ester has a small peak starting at –9 °C and lasting over a range of 55 °C. This peak could be small trace amounts of glycerol in the ester sample. The second peak at –62.35 °C represented the major component. The unprocessed waste fryer grease methyl ester also has a long peak that began at –5 °C and lasted over a range of 35 °C. A second peak appeared after this and was retained over a range of 10 °C. The first peak may also be due to trace amounts of glycerol in the sample, but the second peak is an unknown. The third peak is long and sharp and is a representation of the major component.

The major peak temperatures and the latent heat of the cooling curves are given in Table 5. The values in the

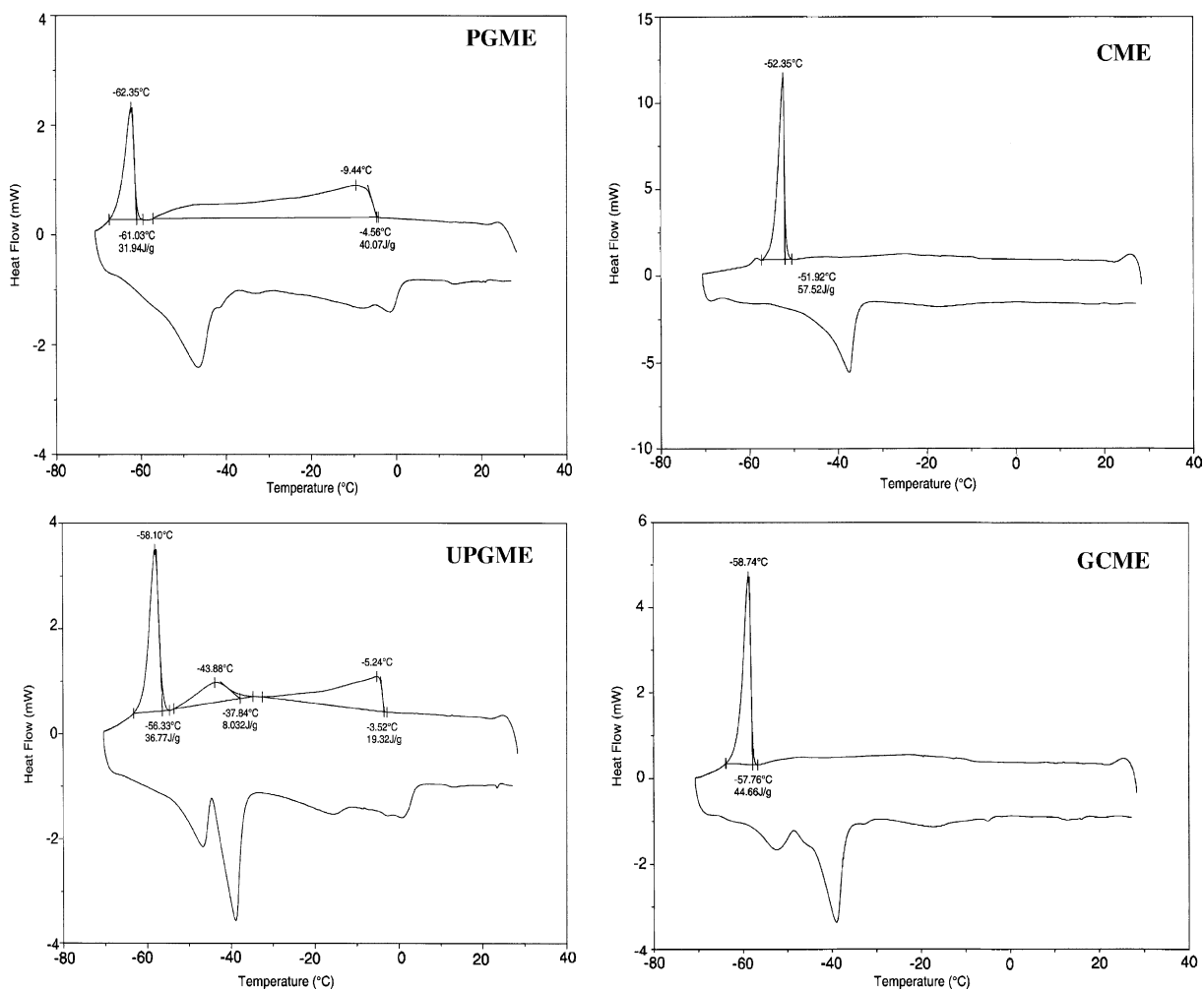


Fig. 2. DMC thermogram of methyl esters of various oils.

Table 5
Major peak temperatures and latent heat of methyl esters

Sample	Major peak temperature (°C)	Heat of transition (kJ/kg)
Canola methyl ester	-52.3	57.5
Greenseed methyl ester	-58.7	45.0
Processed grease methyl ester	-9.5	41.2
	-62.3	30.2
Unprocessed grease methyl ester	-5.2	19.7
	-43.8	8.2
	-58.1	36.4

Table 6
Ester and glycerol yields

Feed	Product		Ester yield relative to theoretical yield (%)
	Ester (g)	Glycerol (g)	
Canola oil	86.1	21.7	87
Greenseed canola oil	75.3	21.4	75
Processed waste fryer grease	50.8	32.3	51
Unprocessed waste fryer grease	58.7	49.0	58

Table 7
M-ROCLE test conditions

Fuel temperature	25 ± 1.5 °C
Fuel capacity	63 ml
Ambient temperature	24 ± 1.0 °C
Ambient humidity	45 ± 5%
Applied load	24.6 N
Load application velocity	0.25 mm/s
Hertzian contact stress	896.9 MPa
Test duration	3 min
Race rotational velocity	600 rpm
Race surface velocity	1.10 m/s
Test specimens	
Falex test cylinder	F-S25 Test Rings, SAE 4620 Steel, Outer diameter = 35.0 mm, Width = 8.50 mm
Falex tapered test rollers	F-15500, SAE 4719 Steel, Outer diameter = 10.18 mm, 10.74 mm, Length = 14.80 mm

Table 8
Wear area, coefficient of friction, and lubricity number data from average of six M-ROCLE replicate evaluations

Sample	Average wear area (mm ²)	Coefficient of friction	Lubricity number (LN)
Canola methyl ester	0.1996 ± 0.0113	0.1068 ± 0.0017	1.2916 ± 0.0711
Greenseed methyl ester	0.2991 ± 0.0342	0.1095 ± 0.0009	0.8437 ± 0.0999
Processed grease methyl ester	0.3278 ± 0.0176	0.1100 ± 0.0005	0.7600 ± 0.0376
Unprocessed grease methyl ester	0.3226 ± 0.0156	0.1103 ± 0.0004	0.7699 ± 0.0352
ISOPAR [®] M reference diesel fuel	0.2984 ± 0.0078	0.1084 ± 0.0006	0.8453 ± 0.0213

table were averaged from two scans. The latent heat values for the major component peaks ranged from 30.2 to 57.5 kJ/kg.

From the trans-esterification reactions performed, the amount of glycerol removed and methyl ester produced are given in Table 6. The ester yield relative to the theoretical yield for each of the four methyl esters is also given in this table. The yields of both the canola methyl ester and greenseed canola methyl ester would be considered satisfactory. For both the processed and unprocessed grease methyl esters, the ester yield relative to the theoretical yield was quite low, and the amount of glycerol removed was quite high. This might be due to the first stage of the reaction. After the mixture sat for a few hours, in this stage there was still no clear separation. Though precautions were taken in separating biodiesel from glycerol, in these cases, some of the methyl ester was probably removed when the glycerol was drained leading to the lower yield of the ester.

The lubricity evaluations conducted using the M-ROCLE bench test (cf. Tables 7 and 8, and Fig. 3a and b) showed that the only biodiesel sample that enhanced the reference fuel was the canola methyl ester (cf. Fig. 4). It increased the LN above the specified minimum value of 1.0 required for diesel fuels. Also, the greenseed methyl ester, processed grease methyl ester, and unprocessed grease methyl ester caused pitting on the rollers.

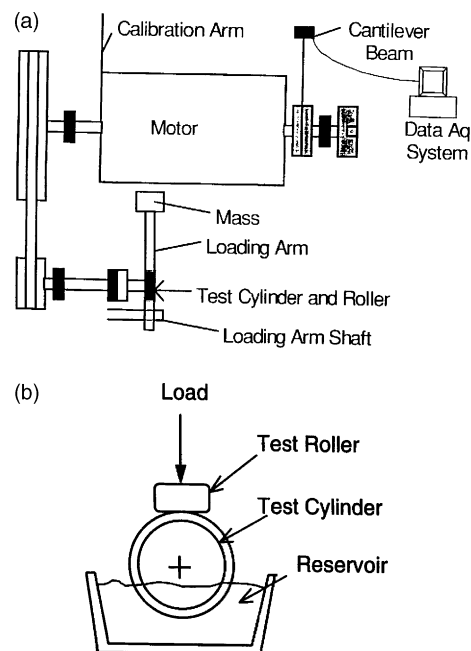


Fig. 3. (a) The schematics of the M-ROCLE test apparatus and (b) actual contact between the test roller and the test cylinders.

Thus these samples were corroding the rollers during the tests.

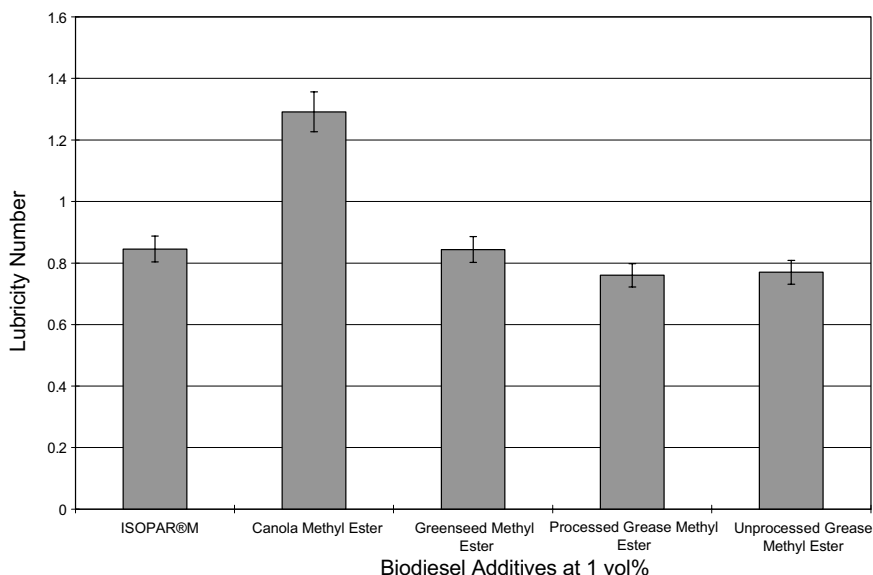


Fig. 4. M-ROCLE lubricity number results for 1 vol% biodiesel additives.

From the results, it can be concluded that pure canola oil is the best choice amongst the four oil/fats to produce biodiesel. Greenseed oil from heat-damaged seeds could also be a good alternative. The amount of triglycerides that the greenseed methyl ester contains is quite small, however, and most other properties compare well with the canola methyl ester. Therefore, the greenseed methyl ester is also a realistic alternative, with some further work on its synthesis to obtain better lubricity results. The processed and unprocessed grease methyl esters do not compare well to the canola and greenseed methyl esters. They too contained small amounts of triglycerides, and they have poor cold temperature properties and LNs, making them less attractive.

4. Conclusions

From the analysis performed it is determined that all four types of oils can be used to produce biodiesel. Overall, the best ester yield relative to the theoretical yield was the canola methyl ester. The greenseed methyl ester had a yield that was also satisfactory. Both the canola methyl ester and the greenseed methyl ester had similar physico-chemical properties, which compared well to diesel fuel. Due to a low LN, the greenseed methyl ester does not compare well to diesel fuel, and should not be used as an additive until further modifications to the production procedure are performed. Therefore, from the four methyl esters produced, the best choice to use as a fuel or as an additive would be the canola methyl ester.

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