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Biodiesel production from mixtures of canola oil and used cooking oil

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Abstract

Used cooking oil (UCO) was mixed with canola oil at various ratios in order to make use of used cooking oil for production of biodiesel and also lower the cost of biodiesel production. Methyl and ethyl esters were prepared by means of KOH-catalyzed transesterification from the mixtures of both the oils. Water content, acid value and viscosity of most esters met ASTM standard except for ethyl esters prepared from used cooking oil. Canola oil content of at least 60% in the used cooking oil/canola oil feedstock is required in order to produce ethyl ester satisfying ASTM specifications. Although ethanolysis was proved to be more challenging, ethyl esters showed reduced crystallization temperature (−45.0 to −54.4 °C) as compared to methyl esters (−35.3 to −43.0 °C). A somewhat better low-temperature property of ester was observed at higher used cooking oil to canola oil ratio in spite of similar fatty acid compositions of both oils.

Keywords: Biodiesel; Transesterification; Canola oil; Used cooking oil

1. Introduction

Biodiesel is a well known alternative, renewable fuel which provides less harmful emissions when compared with the conventional fossil-based diesel fuel. The most common method to produce biodiesel is transesterification of vegetable oils or animal fats with a short-chain alcohol [1]. High purity methyl ester can be achieved by transesterification of fresh vegetable oils with methanol in presence of an alkaline catalyst [2,3]. Transesterification of canola oil (CO) produces ester whose properties are comparable with those of conventional diesel fuels [3]. It has also been reported that the lubricity of diesel fuel can be enhanced by 60% with the addition of 1 vol.% canola-derived methyl ester [4].

However, the main drawback of this fuel is the high cost of feedstock which leads to the high price of the product biodiesel. A comparison of biodiesel price with that of diesel fuel can be used to depict severity of economic barrier of biodiesel. According to S&T Consultants Inc. and Meyers Norris Penny LLP [5], the price of biodiesel in the United States, on average, was 2.22 US$/US gallon while diesel fuel cost at 1.21 US$/US gallon. This economical factor has been undermining biodiesel business for decades.

In more recent years, attempts to utilize used cooking oil (UCO) as a feedstock for biodiesel production have been made to overcome the economic problem. This is because the cost of yellow grease, which is 16.5 ¢/lb, is lower than that of canola oil, which is 34 ¢/lb [6]. However, due to high free fatty acids (FFA) and water content in used cooking oils, they cannot be directly transesterified using an alkaline catalyst, which otherwise, gives low yield and low quality of biodiesel. This is because the side saponification reaction consumes catalyst and generates soap which causes problems in producing high quality biodiesel. Transesterification of used cooking oils with an alkaline catalyst can be done only when the FFA and water content have been removed through different pre-treatment processes [7,8]. Alternatively, acid catalyst can be used instead to prevent the emergence of this saponification [9]. However, this approach

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requires a longer reaction time, a higher operating temperature, and an acid-resistible reactor. It is obvious that exploitation of used cooking oils requires a more sophisticated technology and a more complicated process, which increase the cost of biodiesel production process.

Even though several attempts have been made to produce biodiesel from various fresh vegetable oils and used cooking oils, the combination of these two sources as feedstock for biodiesel production is relatively unexplored. It was anticipated that the addition of fresh vegetable oil, i.e., canola to used cooking oil would improve yield and quality of biodiesel produced from direct alkali-catalyzed transesterification. The purpose of this study was to optimize canola to used cooking oil ratio to produce high yield and quality biodiesel while maintaining a simple and low-cost alkali-catalyzed transesterification process. This study could provide an alternative means to make use of UCO for a low-cost biodiesel production process.

2. Materials and method

2.1. Materials

UCO was obtained from the campus cafeteria, University of Saskatchewan, Saskatoon, Canada. Commercial grade canola oil (CO) was purchased from a local grocery store. Anhydrous methanol (MeOH) (99.8%) and potassium hydroxide (KOH) were purchased from EMD Chemicals Inc., Darmstadt, Germany. Anhydrous ethanol (EtOH) was obtained from Commercial Alcohol Inc., Brampton, Ont., Canada. Sulfuric acid (H_2SO_4) was procured from EM Science, Darmstadt, Germany. Reference standard chemicals including methyl oleate, triolein, diolein, and monoolein were purchased from Sigma–Aldrich, MO, USA.

2.2. Method

Canola oil methyl ester (CME), canola oil ethyl ester (CEE), used cooking oil methyl ester (UME), and used cooking oil ethyl ester (UEE) were produced by means of KOH-catalyzed transesterification from a 100 g of feedstock. The same method was also used for the production of methyl and ethyl ester from mixed feedstock. In the present work, 80:20, 60:40, 40:60, 20:80 ratio of UCO and CO was used to produce 80UME (methyl ester produced from 80 g of UCO and 20 g of CO), 60UME (methyl ester produced from 60 g of UCO and 40 g of CO), 40UME (methyl ester produced from 40 g of UCO and 60 g of CO), and 20UME (methyl ester produced from 20 g of UCO and 80 g of CO), respectively. Ethyl esters were also produced from the same set of feedstock. The feedstock was initially placed in a Parr reactor (Parr Instrument Company, IL, USA) and heated to 50 °C. A mixture of alcohol (methanol or ethanol at 6:1 alcohol to oil molar ratio) and KOH (1 wt.% with respect to oil) was then added to the reactor. The temperature and stirring speed of the reaction mixture were maintained constant for 2 h at 50 °C and 600 rpm, respectively.

After the reaction, the transesterification product was allowed to stand in a separating funnel for glycerol separation. Due to a strong emulsion in the case of ethanolysis products, glycerol was not separated only by gravity. In order to separate glycerol from ethyl ester phase, approximately 10 g of pure glycerol was added into the transesterification product and the separatory funnel was shaken vigorously and the product was allowed to stand. Glycerol layer separated from ester layer within an hour.

To avoid the formation of emulsion, tannic acid solution (0.1 wt.%) was used in the washing step, thereby neutralizing the excess base catalyst. The pH of washing water was measured by pH-indicator strips from EMD Chemicals Inc., Gibbstown, NJ throughout the washing process. The pH of washing water was initially very high at approximately 10 due to dissolved KOH. After seven to eight times of washing, the washing water became clear and its pH was approximately 7.7. The washing process was continued until the approximate pH of 7 was achieved.

Unreacted methanol and water was removed using BÜCHI rotavapor. The process was continued until the constant weight was observed. Biodiesel was finally passed through the anhydrous sodium sulphate, which was previously dried in an oven at 100 °C for 1 h, to remove traces of moisture.

The percentage of triglyceride, diglyceride, monoglyceride, and ester were analyzed by gel permeation chromatography (GPC) using a Hewlett-Packard 1100 series (HPLC) with refractive index detector and two Phenogel (5 μ 100A 300 × 7.80 mm) columns in series protected with guard column. The data were collected by ChemStation software, Agilent Technologies. Tetrahydrofuran (THF) was used as a mobile phase at 1 ml/min for 25 min. The operating parameters were as follows: injection volume 5 μl; column temperature 24 °C; and detector temperature 35 °C. Reference standard chemicals including methyl oleate, triolein, diolein, and monoolein were used for the calibration. The esters were extensively characterized for their properties such as water content (AOCS Ca 2e-84), acid value (AOCS Te 1a-64), heating value (ASTM D240-92), density (ASTM D5002-94), viscosity (ASTM D2500), and fatty acid compositions (AOCS Ce 1-62).

Thermal analysis of biodiesel esters was performed by a differential scanning calorimeter (DSC) from Perkin-Elmer, Inc., CT, USA equipped with Pyris software thermal analysis and a cryofill filled with liquid nitrogen as a cooling device. The rate of cooling and heating can cause major differences in calorimetric peaks and traces in a DSC thermogram. This is because different shape of biodiesel crystal, thus different peak position can be formed as a result of different cooling rate. In the present work, a standard cooling rate of 5 °C/min [4,10] was used. The program used for thermal analysis was set as follows: (1) hold at 30 °C for 5 min; (2) cool from 30 °C to −80 °C at 5 °C/min; (3) hold at −80 °C for 5 min; and (4) heat from −80 °C to 30 °C at 5 °C/min.

3. Results and discussion

3.1. Analysis of feedstock

The saponification value of CO and UCO was 193.0 and 178.4, respectively. Based on saponification value, molecular weight of feedstock with 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100 UCO to CO ratio were 943, 929, 915, 900, 886, and 872 g/mol, respectively. It is believed that the higher molecular weight value of UCO was due to the formation of polymerized compounds such as polymerized triglycerides during the frying process [11]. The frying process contributed to the formation of FFA, which can be demonstrated in terms of acid value (AV). The acid value of UCO was 2.5 mg KOH/g while that of CO was significantly lower (0.4 mg KOH/g). Fig. 1a and b show HPLC chromatograms of CO and UCO, respectively. It can be seen that CO composed mainly of triglyceride (16.2 min) and trace amounts of diglyceride (16.9 min) while UCO composed of triglyceride, diglyceride, and monoglyceride (18.4 min). Diglyceride and monoglyceride were probably products of triglyceride decomposition during the frying process. In addition, a small peak at 14.7 min in UCO chromatogram indicates existence of molecules with higher molecular weight than that of triglyceride. Such compounds might be polymerized compounds. These compounds affect overall properties of UCO such as molecular weight and viscosity. The higher molecular weight, AV, viscosity, and the presence of polymerized compounds suggest that the quality of UCO is lower compared to fresh CO.

3.2. Analysis of the transesterification products

Feedstock for this study were various mixtures of UCO and CO with UCO to CO weight ratio of 100:0, 80:20, 60:40, 40:60, 20:80, 0:100. All feedstock were transesterified with methanol and ethanol. Fig. 1c and d show HPLC chromatograms of CME and UME, respectively. The chromatogram of CME (Fig. 1c) does not show a peak of triglyceride at 16.1 min. The disappearance of triglyceride peak in chromatogram of CME indicates the complete conversion of triglyceride to an ester. However, a peak of triglyceride is present in UME chromatogram (Fig. 1d) indicating incomplete transesterification due to interference of saponification. The saponification occurred due to the reaction of free fatty acid present in feedstock with base catalyst producing soaps. These soaps interfere with the separation of glycerol and also induce emulsion afterward. Glycerol is not detected in biodiesel indicating complete glycerol separation from esters. Ester percentages in the biodiesel as analyzed by the HPLC are shown in Fig. 2. The ester percentage in both methyl and ethyl ester tend to increase with CO percentage in feedstock mixture. These results strengthen our hypothesis that the addition of CO would help to improve biodiesel yield.

The amounts of ester collected from each experiment are shown in Fig. 3a. Reproducibility of the recovery of esters is

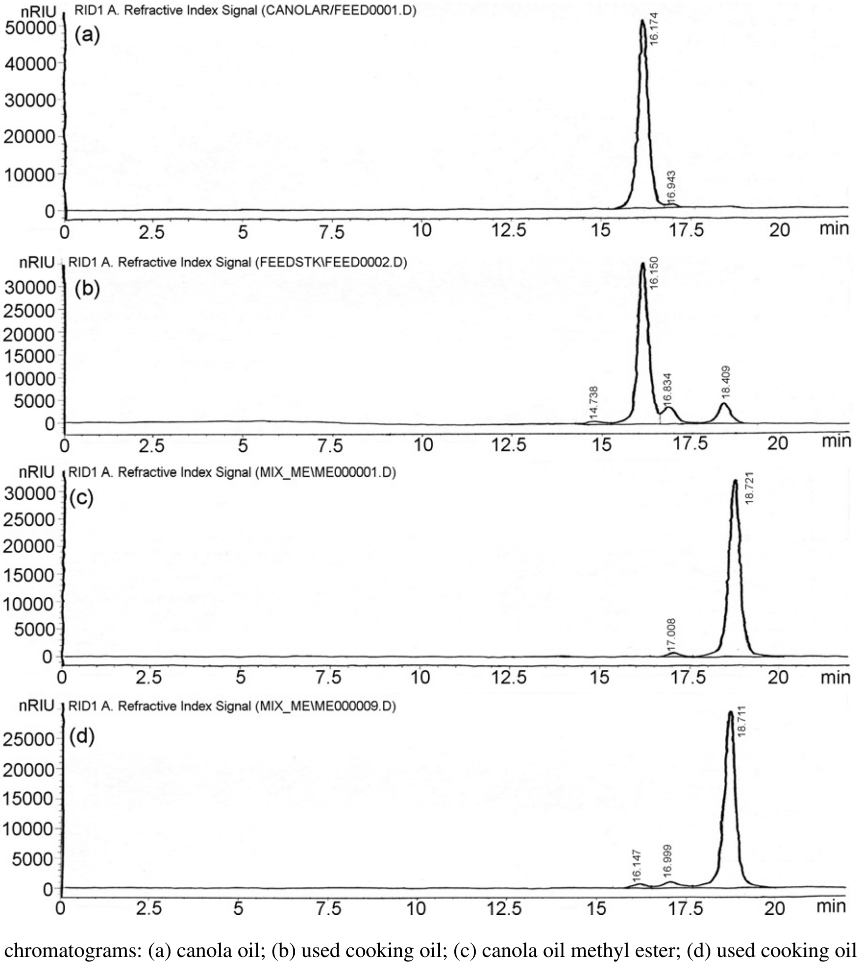

Fig. 1. HPLC chromatograms: (a) canola oil; (b) used cooking oil; (c) canola oil methyl ester; (d) used cooking oil methyl ester.

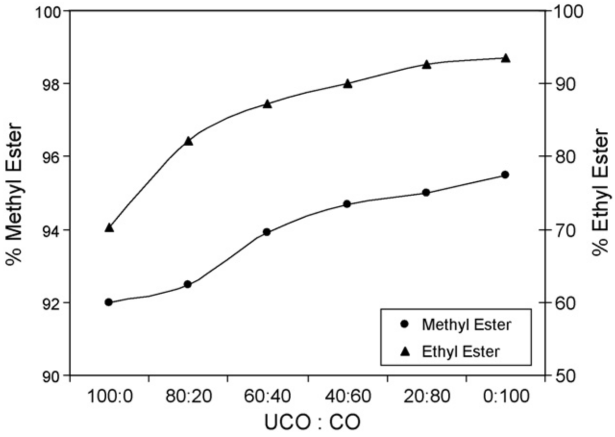

Fig. 2. Ester percentage as analyzed by HPLC analysis: (●) methyl ester; (▲) ethyl ester (reaction condition: alcohol to oil ratio 6:1, reaction temperature 50 °C).

~5%. In comparison with methyl ester yield obtained from pure UCO feedstock, the higher methyl ester yield was obtained with the addition of CO to the feedstock mixture. In case of ethyl ester, a higher amount of CO (at least 60 wt.%) was required to improve ethyl ester yield. Considering UCO, the lower ester yield was observed due to the fact that UCO was a compilation of various compounds such as triglyceride, diglyceride, and monoglyceride. Therefore, a 100 g of UCO contains less moles of triglyceride when compared to a 100 g of CO. Diglyceride and monoglyceride contained in UCO have higher glycerol to acyl-group molar ratio than triglyceride (glycerol to acyl-group molar ratio of triglyceride, diglyceride, and monoglyceride are 0.33, 0.5, and 1, respectively). As a result, the same amount of feedstock containing mainly triglyceride (CO) would have more moles of acyl-group than that containing a mixture of triglyceride, diglyceride and monoglyceride (UCO). Theoretically, one mole of acyl-group gives one mole of biodiesel ester, therefore the higher yield of esters was observed at a lower UCO to CO ratio. Dmytryshyn et al. [2] also reported a low ester yield (approximately 50–60%) when UCO was used as a feedstock.

Fig. 3b displays the amount of glycerol collected at different UCO to CO ratios. Although less ester yield was obtained at higher UCO to CO ratio, the glycerol recovery was opposite to this trend. Based on the concept of glycerol to acyl-group molar ratio in feedstock, a 100 g of UCO would have more moles of glycerol group than a 100 g of CO. Therefore, glycerol was collected at a larger amount when a higher UCO to CO ratio was used as a feedstock.

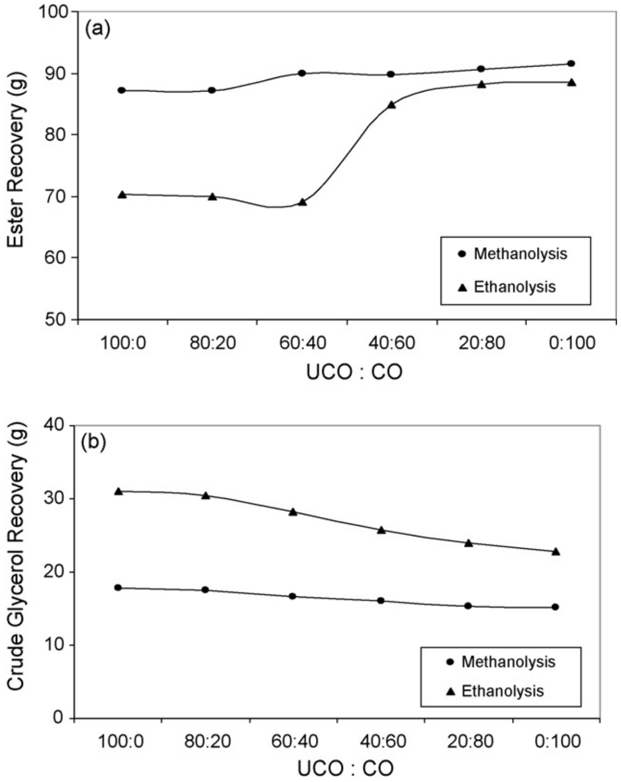

Fig. 3. Amounts of ester and glycerol collected from transesterification of a 100 g of feedstock: (a) ester recovery; (b) glycerol recovery; (●) methanolysis; (▲) ethanolysis (reaction condition: alcohol to oil ratio 6:1, reaction temperature 50 °C).

The percentage of triglyceride, diglyceride, and monoglyceride in each ester are presented in Table 1. The percentage of these acylglycerols in ester phase increased as amount of UCO in feedstock increased. This observation is predictable as Table 2 shows that UCO has higher acid value thus higher free fatty acid content compared to CO. Alkali catalyst (KOH) was consumed by reacting with free fatty acid to

Table 1
Triglyceride, diglyceride, and monoglyceride percentage in esters

Type of ester	Triglyceride (wt.%)	Diglyceride (wt.%)	Monoglyceride (wt.%)	Total glycerin (wt.%)
UME	1.6	3.4	1.3	1.0
80UME	1.3	3.1	1.2	0.9
60UME	0.3	2.5	1.1	0.7
40UME	0.0	2.5	1.1	0.7
20UME	0.0	2.1	1.1	0.6
CME	0.0	1.7	0.9	0.5
UEE	8.5	11.3	9.3	5.0
80UEE	3.9	7.1	6.5	3.1
60UEE	2.5	5.4	5.5	2.5
40UEE	1.3	3.9	4.6	1.9
20UEE	0.6	2.9	3.6	1.4
CEE	0.0	2.3	3.1	1.2

Table 2
Characteristics of esters

Type of ester	Water content (ppm)	Heating value (MJ/kg)	Density (g/cm^3)	Viscosity @40 °C (mm^2/s)	Acid value (mg KOH/g)
UME	290	39.1	0.86	4.9	0.5
80UME	338	39.2	0.86	4.9	0.4
60UME	212	39.6	0.86	4.8	0.4
40UME	329	39.5	0.86	4.6	0.4
20UME	350	40.0	0.86	4.6	0.4
CME	480	39.1	0.86	4.4	0.5
UEE	720	39.3	0.87	8.8	1.5
80UEE	437	39.6	0.86	6.4	1.2
60UEE	327	39.8	0.86	5.8	1.0
40UEE	341	39.7	0.86	5.5	0.5
20UEE	357	40.2	0.86	5.1	0.4
CEE	420	40.3	0.86	4.9	0.5
Canola oil	–	39.7	0.90	38.2	0.4
Used cooking oil	200	–	0.90	44.7	2.5
Summer diesel fuel	–	45.5	–	–	0.002
ASTM	0.05 max (% volume)	–	–	1.9–6.0	0.5 max

form soap resulting in the higher level of acylglycerols. The higher amount of these glycerides in ethyl esters compared to methyl esters indicates lower glyceride conversions in case of ethanolysis than that of methanolysis. This is due to the higher reactivity of methanol as compared to ethanol towards transesterification [12]. Total glycerin content (GL_T) is defined as $GL_T = GL + 0.26(MG) + 0.15(DG) + 0.1(TG)$ [13]. GL_T of the prepared esters are above the ASTM limit (0.24% max) suggesting that purification of these esters is required. The purification process will be discussed in Section 3.4.

3.3. Characterizations of the esters

The esters obtained from transesterification were characterized and their properties are presented in Table 2. Water content of all esters met ASTM standard except for ethyl ester prepared from UCO. The densities of all esters were considerably lower than those of their parent oils and were not highly related to UCO to CO ratio. Acid value of all methyl esters met the ASTM standard. In contrast, acid value of UEE was very high at 1.5 mg KOH/g and did not meet the ASTM standard. This might be due to the unreacted FFA in UCO. However, with the addition of CO up to 60% in the feedstock, the acid value of ethyl ester was reduced to 0.5 mg KOH/g, which meets the ASTM standard. The viscosities of both CO and UCO were very high at 38.2 and 44.7 mm^2/s, respectively. Viscosities of esters were significantly lower when compared to their parent oils and met the ASTM standard (with an exception of some esters). Viscosity of esters decreased with a decrease in UCO to CO ratio as UCO itself was more viscous than CO. The viscosity of UEE was very high and did not meet the standard. This is due to lower reactivity of ethanol as compared to methanol [12] resulting in the presence of unconverted acylglycerols, thereby increasing viscosity. Low ester percentage in UEE as shown in Fig. 2 helps to strengthen this concept. The ester content can be improved by the addition of CO in the feedstock. By adding CO up to 40%, an ethyl ester with a satisfiable level of viscosity at 5.8 mm^2/s was obtained. The further reduction of viscosity can be accomplished if more CO was used in the feedstock. Heating values of all esters were approximately the same value, which are roughly

Table 3
Boiling point distribution (°C) of esters

% off	10	20	30	40	50	60	70	80	90
UCO	610.3	617.5	625.2	635.3	648.1	664.3	683.6	704	726.9
CO	599.7	606.3	608.8	611.8	615	619	624.8	635.2	654.2
UME	355.7	358.2	359.9	361.2	362.3	363.2	364.2	365.9	409.3
80UME	357.5	361.2	363.6	365.5	367.1	368.6	369.8	370.9	372.1
60UME	357	360.7	363.2	365.1	366.8	368.2	369.5	370.6	371.8
40UME	355.5	358	359.5	360.7	361.7	362.6	363.5	364.3	365.6
20UME	355	357.6	359.2	360.5	361.6	362.6	363.5	364.3	365.2
CME	354	355.7	356.7	357.6	358.4	359	359.6	360.2	365.3
UEE	363.9	365.3	366.4	367.3	370.8	515.7	600.6	611	639.4
80UEE	363.8	365.6	366.8	367.8	368.6	369.3	370	389	542.7
60UEE	363.3	364.9	365.9	366.8	367.5	368.1	368.7	369.6	426.1
40UEE	364.8	367.3	368.9	370.2	371.3	372.2	373.1	374.6	416.9
20UEE	364.4	366.6	368.1	369.3	370.2	371.1	371.9	372.6	373.6
CEE	364.3	366.3	367.7	368.8	369.7	370.5	371.2	371.9	372.8
Diesel fuel	175	185	195	218	242	260	285	320	365

10% lower than that of the reference diesel fuel. These results are in substantial agreement with those reported in the literature [3].

Table 3 shows boiling points of each biodiesel esters, their corresponding feedstock, and a reference diesel fuel. The boiling points at 90% off of feedstock were very high (654.2 °C for CO and 726.9 °C for UCO). The boiling points of UCO were higher than that of CO due to its high molecular weight constituent such as polymerized acylglycerols. When transesterification was carried out, it is possible for these polymerized compounds to give rise to polymerized esters which have a higher molecular weight and boiling point than a monomer ester. Table 3 also showed that esters derived from UCO have higher boiling point than those derived from CO. The boiling points of esters have a tendency to decrease when more CO was used in the feedstock. As expected, boiling points of ethyl esters were obtained at higher value when compared to the corresponding methyl ester. For example, boiling point at 90% off of CME was 365.3 °C while the corresponding boiling point for CEE was observed at higher level of 372.8 °C. This is because ethyl ester generally has higher molecular weight and boiling point as compared to methyl ester. The unusual high boiling point of UEE is due to presence of unconverted acylglycerols as a result of incomplete transesterification as discussed earlier.

3.4. Ester purification

The ester percentages in ethyl esters are less than those of methyl esters as shown in Fig. 2. The ethyl esters were purified by means of column chromatography as described by Meher et al. [14]. After purification, ethyl esters showed improvement in ester percentage with decrease in total glycerin content (GL_T) as presented in Table 4. The acid values and viscosities of the purified esters reduced significantly. This is due to the improvement of the purity of ethyl esters after purification of the esters.

3.5. Thermal analysis by differential scanning calorimetry (DSC)

The low-temperature flow property of biodiesel is very important for its use in a cold-climate country. This is because when a blended diesel fuel is used at a low temperature, the biodiesel portion of the blend crystallizes and separates out from diesel fuel. This crystal can create problems to engine flow system, undermine engine operation, and eventually cause engine to stop running. Therefore, a satisfactory attribute of biodiesel low-temperature properties should be warranted prior to its commercial use. Such property is conventionally characterized by cloud point (CP) and pour point (PP).

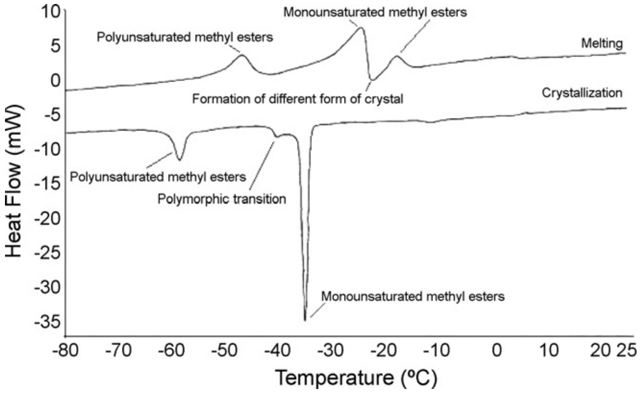

Fig. 4. Typical DSC thermogram of canola oil methyl ester.

More recently, DSC have been used to determine the low-temperature property of biodiesel [4]. Each fatty acid ester such as palmitic methyl ester, stearic methyl ester, oleic methyl ester, etc. is miscible with each other at room temperature and therefore shows no heat change when mixed. However, crystallization or polymorphic transition (a change in structural geometry when solid) of a given ester could exhibit heat change, which is possible to monitor using a DSC. It is reported in the literature that enthalpy of crystallization of triglycerides can be measured using a DSC [15]. In addition, it has been also reported that polymorphic transition of triglyceride usually occurs after a melting of the first habit (a shape of crystal). Lee et al. [10] reported that branched-chain esters have lower crystallization temperature than that of conventional straight-chain esters. They reported a good correlation between crystallization temperature measured by a DSC and CP and PP of the biodiesel samples.

In this study, a typical DSC thermogram of CME is shown in Fig. 4 and fatty acid compositions of CME and UME are presented in Table 5. The top and bottom curves in Fig. 4 are heating and cooling curves, respectively. The initial concentration of a given fatty acid methyl ester (palmitoleic methyl ester, oleic methyl ester, linoleic methyl ester, etc.) in CME was lower than its saturated concentration at 30 °C, thus crystallization is not possible. When the sample temperature was reduced, the saturated concentration and solubility of each component was also reduced. At certain point, the saturated concentration reduced to the point lower than its actual concentration, thereby making crystallization of the corresponding component possible [16]. The major peak at −35.3 °C appeared as a result of exothermic crystallization of monounsaturated fatty acid methyl esters. These esters were a major portion of CME

Table 4
Characteristics of purified ethyl esters

Type of ester	Ester content (wt.%)	Total glycerin (wt.%)	Acid value (mg KOH/g)	Viscosity @40 °C (mm^2/s)
UEE	89.4	1.18	0.5	3.1
60UEE	95.7	0.54	0.5	2.0
40UEE	97.7	0.35	0.6	2.7
CEE	96.5	0.47	0.5	2.5

Table 5
Fatty acid compositions of canola oil methyl ester and used cooking oil methyl ester

Structure	Compound name	Percentage in canola oil methyl ester	Percentage in used cooking oil methyl ester
C14:0	Myristic methyl ester	0.05	0.08
C16:0	Palmitic methyl ester	4.23	5.31
C16:1 *z*7	Hexadecenoic methyl ester	0.03	0.04
C16:1 *z*9	Palmitoleic methyl ester	0.23	0.36
C16:2	Hexadecadienoic methyl ester	0.07	0.06
C16:3	Hexadecatrienoic methyl ester	0.11	0.10
C18:0	Stearic methyl ester	1.89	2.76
C18:1 *z*9	Oleic methyl ester	57.75	56.94
C18:1 *z*11	Vaccenic methyl ester	3.58	2.17
C18:2	Linoleic methyl ester	19.09	19.03
C18:3	Linolenic methyl ester	8.71	6.54
C20:0	Arachidic methyl ester	0.67	0.67
C20:1 *z*5	Eicosenoic methyl ester	0.04	0.10
C20:1 *z*11	Eicosenoic methyl ester	1.37	1.42
C20:2	Eicosadienoic methyl ester	0.14	0.16
C22:0	Behenic methyl ester	0.36	0.36
C24:0	Lignoceric methyl ester	0.04	0.14
C24:1 *z*15	Tetracosenoic methyl ester	0.18	0.17
C26:0	Hesacosanoic methyl ester	0.04	0
	Total saturated fatty acid	7.27	9.32
	Total monounsaturated fatty acid	63.17	61.20
	Total polyunsaturated fatty acid	19.41	19.34

as GC analysis showed a result of 63.2%. The small peak right after exothermic crystallization of monounsaturated fatty acid methyl ester at −40.7 °C was probably due to its polymorphic transition. It is well known that unsaturated ester crystallized at lower temperature than saturated ester. This is because they have different three-dimensional conformations. Saturated ester molecules are in its minimum energy when fully extended and are well stacked, thereby strengthening intermolecular attraction force [17]. Unlike saturated ester, especially *cis*-formation, unsaturated ester molecules have weaker intermolecular interactions and therefore crystallize at a lower temperature. This explains exothermic crystallization of polyunsaturated fatty acid methyl esters at lower temperature of −58.6 °C. These observations are consistent with those reported in the literature in which crystallization temperature of saturated compounds were higher that that of unsaturated compounds [4]. Endothermic peaks on the heating curve at −47.0 and −24.6 °C represent melting point of polyunsaturated and monounsaturated fatty acid methyl ester crystals, respectively. These crystals melted at temperature above their corresponding crystallization temperature. This finding confirm with those found in the literature indicating that the melting temperature is higher than crystallization temperature of the same component [4,15]. After the melting of monounsaturated fatty acid methyl ester crystal, a different crystal shape of the same component can be formed. This behavior is shown by exothermic crystallization peak at −22.6 °C on the heating curve. Another endothermic peak at −17.8 °C is due to melting of the recently formed crystal of methyl ester. A similar behavior has been reported in the literature [15].

Fig. 5 displays comparative cooling DSC thermograms of UME, 40UME, and CME, respectively. The major crystallization temperature of UME (−43 °C) is lower than that of CME (−35.3 °C). As discussed earlier, these peaks represent monounsaturated fatty acid methyl ester of each UME and CME. The literature suggests that crystallization temperature of linear, long-chain esters decrease with increase in the carbon chain length if number of double bond is the same [4]. The comparison has been made for samples with different fatty acid compositions (esters from canola oil and rapeseed oil) and the difference of the peak temperature was obvious (>20 °C). In this study, the chain length difference between monounsaturated fatty acid methyl ester of UME and CME is trivial and so does the peak temperature difference. Polymerized methyl ester in UME is another possible reason contributed to this difference. It is possible for a polymerized methyl ester to form a crystal shape such that is having a poor molecular stacking and poor intermolecular interactions. A detailed study is required to acquire a better understanding on this phenomenon. The major peak temperature of 40UME fell between those of UME and CME. This is because 40UME was produced from a mixture of UCO and CO.

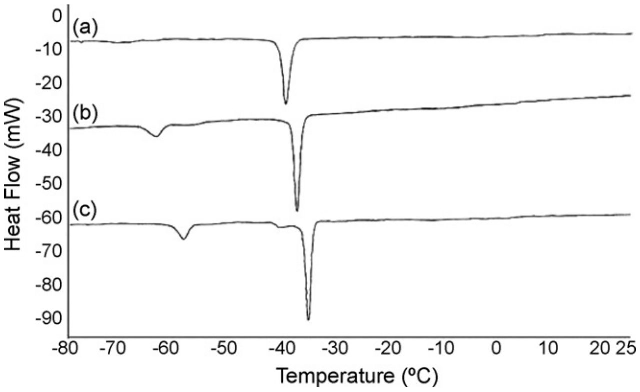

Fig. 5. Cooling curves of DSC thermogram: (a) used cooking oil methyl ester; (b) 40:60 UCO:CO methyl ester; (c) canola oil methyl ester.

Table 6
Major peak temperature and heat associated to crystallization and melting of esters

Ester	Major crystallization peak temperature (°C)	Major melting peak temperature (°C)	Total heat associated with crystallization of ester (kJ/kg)	Total heat associated with melting of ester (kJ/kg)
UME	−43.0	−27.8	49.6	55.0
80UME	−41.1	−27.4	70.4	74.4
40UME	−37.4	−26.4	71.4	77.4
20UME	−36.8	−26.2	76.1	78.9
CME	−35.3	−24.6	84.0	88.8
UEE	−54.4	−30.0	38.1	30.6
80UEE	−51.3	−25.8	48.1	44.6
40UEE	−45.6	−19.5	51.3	49.0
20UEE	−45.7	−20.6	58.5	56.1
CEE	−45.0	−19.6	60.2	58.1

Table 6 summarizes major peak temperature and total heat associated with melting and crystallization of esters. As expected, ethyl esters have lower major peak temperature than methyl esters. This is a typical observation as ethyl esters are known to have a lower cloud point than methyl ester [3]. The heat associated with crystallization of esters prepared from UCO was lower than that of esters prepared from CO. This might be due to polymerized esters prepared from UCO, which cause an increase in average molecular size of the ester, thereby affecting its total heat of crystallization. The heat associated with crystallization is approximately equivalent to the heat associated with crystal melting. The difference between heat associated with melting and crystallization might be because some polymorphs crystallized or melted during the period of time outside DSC scan. However, those polymorphs are habits of minor components as the calorimetric peaks of major components are presented within the range of DSC scan and the total heat differences were trivial. These findings show that DSC provided an accurate means of monitoring crystallization of biodiesel esters.

4. Conclusions

Used cooking oil is an economical feedstock for the production of biodiesel. However, the production process using this feedstock is usually more complicated than that using fresh oil feedstock. Nevertheless, the utilization of used cooking oil for a single step KOH-catalyzed transesterification is possible with addition of a certain amount of canola oil. Methyl and ethyl esters were prepared at different used cooking oil to canola oil ratio and were characterized extensively for their properties. Methanolysis products showed satisfactory properties. In contrast, canola oil of at least 60% was required to achieve a high quality ethyl ester (UCO:CO ratio of 40:60). Based on the feedstock cost discussed in the earlier part, if the feedstock consists of 40% UCO instead of pure canola oil, the feedstock cost will be reduced by ∼20%. Due to the reduction of feedstock cost and economical operating cost of a single step transesterification, production of biodiesel from mixture of canola and used cooking oil is a promising alternative.

Although ethanolysis was proved to be more challenging, ethyl ester showed a better low-temperature property. The low-temperature property difference between esters derived from used cooking oil, canola oil and mixtures of both oils were trivial as fatty acid compositions of both oils were similar.

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References

[1] F. Ma, M.A. Hanna, Biodiesel production: a review, Bioresour. Technol. 70 (1999) 1–15.

[2] S.N. Dmytryshyn, A.K. Dalai, S.T. Chaudhari, H.K. Misha, M.J. Reaney, Synthesis and characterization of vegetable oil derived esters: evaluation for their diesel additive properties, Bioresour. Technol. 92 (2004) 55–64.

[3] X. Lang, A.K. Dalai, N.N. Bakhshi, M.J. Reaney, P.B. Hertz, Preparation and characterization of bio-diesels from various bio-oils, Bioresour. Technol. 80 (2001) 53–62.

[4] X. Lang, A.K. Dalai, M.J. Reaney, P.B. Hertz, Biodiesel esters as lubricity additives: effects of process variables and evaluation of low-temperature properties, Fuels Int. (2001) 207–227.

[5] S&T Consultants Inc., Meyers Norris Penny LLP, Economic, Financial, Social Analysis and Public Policies for Biodiesel: A Report, 2004.

[6] B. Chorney, Canadian Canola Growers Association Presentation to Agri-Energy Opportunities in Manitoba, Retrieved February 7, 2007, from Manitoba Canola Growers Association Web site: http://www.mcgacanola.org/documents/ BrianChorneyCCGABiodieselpresentationApril182006.pdf.

[7] M. Canakci, J.V. Gerpen, Biodiesel production from oils and fats with high free fatty acids, Trans. ASAE 44 (2001) 1429–1436.

[8] J. Cvengroš, Z. Cvengrošová, Used frying oils and fats and their utilization in the production of methyl esters of higher fatty acids, Biomass Bioenergy 27 (2004) 173–181.

[9] J.U. Obibuzor, R.D. Abigor, D.A. Akiy, Recovery of oil via acid-catalyzed transesterification, J. Am. Oil Chem. Soc. 80 (2003) 77–80.

[10] I. Lee, L.A. Johnson, E.G. Hammond, Use of branched-chain esters to reduce the crystallization temperature of biodiesel, J. Am. Oil Chem. Soc. 72 (1995) 1155–1160.

[11] M. Mittelbach, H. Enzelsberger, Transesterification of heated rapeseed oil for extending diesel fuel, J. Am. Oil Chem. Soc. 76 (1999) 545–550.

[12] R. Sridharan, I.M. Mathai, Transesterification reactions, J. Sci. Ind. Res. 33 (1974) 178–186.

[13] W. Zhou, D.G.B. Boocock, Phase behavior of the base-catalyzed transesterification of soybean oil, J. Am. Oil Chem. Soc. 80 (2006) 1041–1045.

[14] L.C. Meher, M.G. Kulkarni, A.K. Dalai, S.N. Naik, Transesterification of karanja (*Pongamia pinnata*) oil by solid basic catalysts, Eur. J. Lipid Sci. Technol. 108 (2006) 389–397.

[15] D.M. Small, The Physical Chemistry of Lipids: from Alkanes to Phospholipids, Plenum Press, New York, USA, 1986.

[16] P.J. Lawler, P.S. Dimick, Crystallization and polymorphism of fats, in: C.C. Akoh, D.B. Min (Eds.), Food Lipids, Mercel Dekker Inc, New York, USA, 2002, pp. 275–297.

[17] S. Norris, Trans Fats: The Health Burden, Parliamentary Information and Research Service from Library of Parliament, Retrieved February 7, 2007, from the parliament of Canada Web site: http://www.parl.gc.ca/information/library/ PRBpubs/prb0521-e.pdf.