

Evaluating Esters Derived from Mustard Oil (*Sinapis alba*) as Potential Diesel Additives

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Abstract Biodiesel was produced from mustard oil utilizing transesterification with methanol, ethanol, propanol, and butanol to evaluate the characteristics of mustard biodiesel as an additive to regular diesel. Mustard oil was transesterified with alcohol at 6:1 alcohol to oil molar ratio, using KOH as a catalyst at 1 wt%. The maximum ester content achieved by this method was only 66%. Distillation was then used to purify the ester, raising the ester content to 99.8%. Alternatively, mustard oil methyl ester (MME) can be mixed with esters derived from canola oil or soybean oil to achieve an ASTM quality biodiesel. Biodiesel derived from mustard showed great potential as lubricity additive for regular diesel fuel. With an addition of 1% MME, lubricity of diesel fuel was improved by 43.7%. It is also found that methyl ester is the best lubricity additive among all esters (methyl-, ethyl-, propyl-, and butyl-ester). MME can be used at $-16\text{ }^{\circ}\text{C}$ without freezing whereas monounsaturated compounds (oleic, eicosenoic, and erucic esters) largely present in esters derived from mustard oil can tolerate -42 to $-58\text{ }^{\circ}\text{C}$. Monounsaturated esters derived from higher alcohols such as butyl alcohol demonstrated a superior low temperature tolerance ($-58\text{ }^{\circ}\text{C}$) as compared to that derived from lower alcohol such as methyl alcohol ($-42\text{ }^{\circ}\text{C}$).

Keywords Biodiesel · Transesterification · Mustard oil · Diesel additives

Introduction

Conventional fossil-based fuels are not renewable and are destined to become exhausted. Furthermore, the price of these fuels tends to rise every year, which inspires the use of alternative renewable fuels. Biodiesel, commonly produced from vegetable oils such as canola oil and soybean oil [1, 2], is one of the most promising renewable fuels and use of this fuel is a shift towards sustainable energy. Transesterification, a series of consecutive, reversible reactions as shown in Fig. 1 [3], is commonly used to produce biodiesel from vegetable oils. With rising concerns regarding the use of food crops as feedstock for fuel production, non-food grade oils are gaining tremendous attention from researchers around the world. High erucic acid rapeseed (HEAR) oil or mustard oil is an interesting feedstock for biodiesel production.

Mustard oil can be extracted from *Brassica nigra* (Black Mustard), *Brassica carinata* (Abyssinian Mustard), *Brassica juncea* (Brown, Oriental, and Leaf Mustard), *Sinapis arvensis* (Wild Mustard), and *Sinapis alba* (White Mustard). These seeds can have an oil content of over 40% in which the dominant fatty acids include oleic acid (C18:1), linoleic acid (C18:2), and erucic acid (C22:1). The erucic acid results from the addition of a two-carbon fragment to oleic acid to form eicosenoic acid (C20:1), followed by addition of another two-carbon fragment to eicosenoic acid to form erucic acid [4]. In the case of low erucic acid rapeseed (LEAR) such as *B. napus* (Canola oil or Canadian Brassica), the genetic elongation ability of fatty acids is blocked, leading to the accumulation of the precursor fatty

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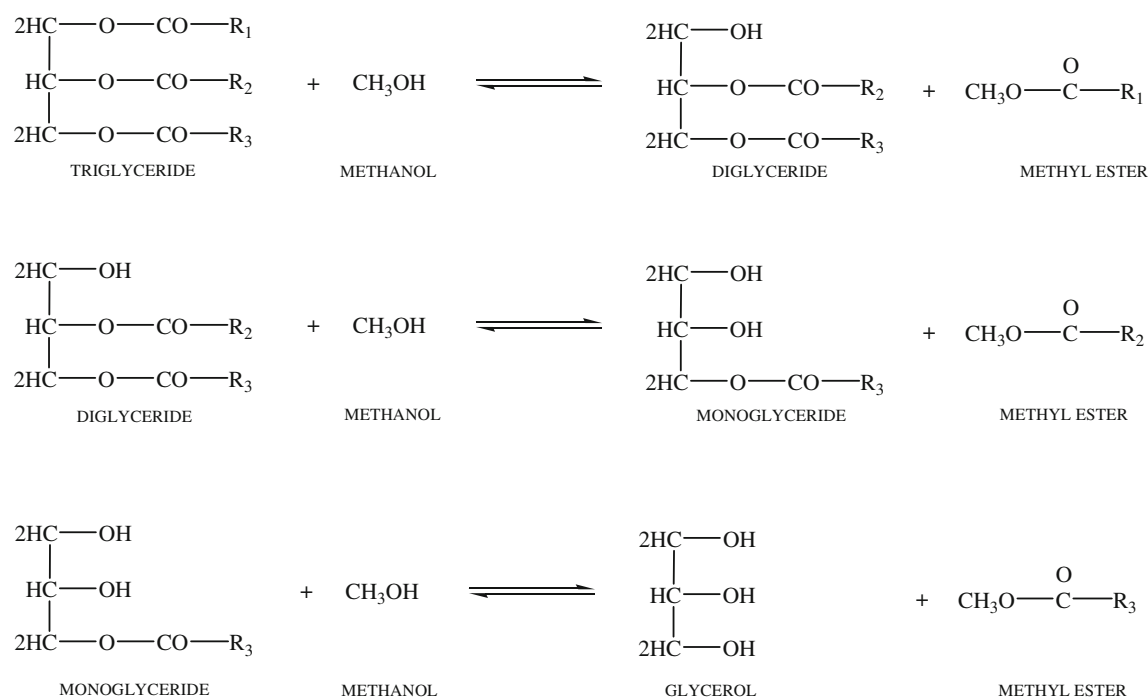


Fig. 1 Transesterification reaction scheme

acid, i.e., oleic acid. The level of erucic acid can be genetically modified ranging from less than 1% to over 60%. A study showed a declining trend in erucic percentage in Canadian LEAR during the 1980s [5].

Many researchers report that cardiac fat infiltration in experimental animals is caused by erucic acid present in HEAR and thus consider erucic acid as being a toxic compound. This compound if fed in large quantities would result in heart lesions [6]. Since there are fewer experiments done on the effects of erucic acid on people compared to the number of experiments on animals, the effects of erucic acid on human health is not fully understood. Historically, the use of rapeseed oil with a high erucic acid level as an edible oil has been objected to by many organizations. The Canadian regulations state that in cooking oil, margarine, salad oil, simulated dairy product, shortening or food that resembles margarine or shortening, the erucic and cetoleic acid may not exceed 5% of the total fatty acid [7]. The advent of low erucic acid rapeseed (LEAR) Has led to a “phase out” of high erucic acid rapeseed (HEAR) from the food market, but HEAR can still be used in other industries such as fuel, lubricating oil, oleochemicals, and biopolymer production.

Canadian mustard seed production has been changing ranging from 105,000 t in 2001–2002 to 306,000 t in 2004–2005. In 2006, the total world mustard exports were 315,000 t, 55% of which were Canadian mustard. In 2006–2007, Saskatchewan dominated Canadian mustard seed production, with 78% of total production. The area

seeded for mustard in 2006 in Saskatchewan was 280,000 acres (113312 ha), which yielded 776 lb per acre (868 kg per ha) [8]. These data show that mustard seed is available in large quantities in Canada. Because it contains a high level of erucic acid, mustard oil does not meet Canadian specifications for edible purposes, but it could be a viable feedstock for biodiesel production. Information related to biodiesel production from mustard oil is necessary for pilot scale production. However, there is no literature available on biodiesel production from vegetable oils of the genus *Sinapis*. Furthermore, the properties of biodiesel derived from mustard oil could be different from those derived from canola oil, due to the difference in fatty acid compositions. In the present work, biodiesel was produced from mustard oil and the resultant fuel was evaluated as a diesel additive using various characterization techniques to demonstrate its distinctive properties as compared to that derived from canola oil.

Materials

Commercial grade canola oil and soybean oil were purchased from a local grocery store. Mustard oil was provided by Mustard Capital Inc., Saskatoon, SK, Canada. Anhydrous methanol (MeOH) (99.8%), anhydrous ethanol (EtOH), and potassium hydroxide (KOH) were purchased from EMD Chemicals Inc., Darmstadt, Germany. Propanol and 1-butanol were purchased from Sigma–Aldrich,

Canada. Diesel fuels were purchased from four gas stations (Esso, Shell, Petro-Canada, Co-op) in Saskatoon, SK, Canada in December 2009. Reference standard chemicals including methyl oleate, triolein, diolein, and monoolein were purchased from Sigma–Aldrich, MO, USA. Fatty acid methyl esters (FAME) mix rapeseed oil reference standard was obtained from SUPELCO, PA, USA. The reference diesel fuel used in lubricity testing of biodiesel was that specified in ASTM D6079-04 and was purchased from Haltermann Products, Hamburg, Germany.

Experimental Procedures

Transesterification of Canola Oil, Soybean Oil and Mustard Oil

In the present work, two types of mustard oil were donated by Mustard Capital Inc. including *S. alba* (White Mustard) and *B. juncea* (Oriental Mustard). The fatty acid compositions and acid values (AV) of these mustard oils were analyzed. *S. alba* was chosen in this study due to its high erucic acid content (see Table 1).

Fatty acid methyl ester was produced from canola oil, soybean oil and mustard oil via the transesterification reaction using KOH as a catalyst. A 100-g sample of the oil was initially placed in a Parr reactor (Parr Instrument Company, IL, USA) and heated to 60 °C. A mixture of methanol (6:1 alcohol to oil molar ratio) and KOH (1 wt% with respect to oil) was added to the reactor. The temperature and stirring speed of the reaction mixture were kept constant for 1.5 h at 60 °C and 600 rpm, respectively. The same procedure was applied to the production of ethyl-, propyl-, and butyl-esters.

Table 1 Fatty acid compositions and AV of *S. alba* and *B. juncea*

Structure	Compound name	<i>S. alba</i> (wt%)	<i>B. juncea</i> (wt%)
C14:0	Myristic ester	0.05	0.06
C16:0	Palmitic ester	2.80	3.01
C16:1	Palmitoleic ester	0.16	0.14
C16:2	Hexadecadienoic ester	0.06	0.03
C18:0	Stearic ester	1.09	1.31
C18:1 z9	Oleic ester	24.98	16.92
C18:1 z11	Vaccenic ester	1.10	1.38
C18:2	Linoleic ester	11.64	20.82
C18:3	Linolenic ester	8.61	12.85
C20:0	Arachidic ester	0.70	0.75
C20:1	Eicosenoic ester	10.44	10.70
C22:0	Behenic ester	0.57	0.43
C22:1	Erucic ester	32.81	25.76
AV (mg KOH/g sample)		0.85	3.1

After the reaction, the glycerol was separated from the ester phase by gravity in a separatory funnel. Heated distilled water was used to remove KOH, soap, and alcohol remaining in the ester phase. A BÜCHI rotavapor was then used to remove the remaining alcohol and water in the ester phase. To remove traces of moisture, the biodiesel was passed through anhydrous sodium sulfate, which had previously been dried in an oven at 100 °C for 1 h. The biodiesel produced from mustard oil was mixed with the purified biodiesel produced from the canola and soybean oils, at various ratios, as shown in Table 2.

Distillation of Transesterification Products

Distillation of the transesterification products of mustard oil was performed as per ASTM D 1160-06. In this step, transesterification products derived from mustard oil were distilled using a spinning band distillation unit (Model: 24/100 A) from B/R Instrument Corp., Easton, MD, USA. For methyl-, ethyl-, and propyl-ester production, the heating unit was set at 14% resulting in 200 °C pot temperature and 170 °C head temperature. The reflux ratio and operating pressure were set at 50 and 667 Pa, respectively. For butyl-ester production, the heater, reflux ratio, and pressure were set at 17%, 50, and 67 Pa, respectively, resulting in 250 °C pot temperature and 180 °C head temperature.

Characterization of Biodiesel

Table 3 summarizes the standard methods used in this study for fuel characterization. The purified methyl ester was analyzed for ester and glyceride content using a

Table 2 Mixtures of biodiesel produced from canola, soybean and mustard oil

Sample	Mustard ME (wt%)	Canola ME (wt%)	Soybean ME (wt%)
CME	0	100	0
MIX1	0.75	99.25	0
MIX2	1.5	98.5	0
MIX3	3	97	0
MIX4	6	94	0
MIX5	12	88	0
MME	100	0	0
SME	0	0	100
MIX6	0.75	0	99.25
MIX7	1.5	0	98.5
MIX8	3	0	97
MIX9	6	0	94
MIX10	12	0	88

ME methyl ester, CME canola oil methyl ester, SME soybean oil methyl ester, MME mustard oil methyl ester, MIX mixture of esters

Table 3 Analysis of transesterification products

Property	Unit	Method
Ester and glycerides content	Mass%	HPLC
Fatty acid compositions	Mass%	AOCS Ce 1-62
Boiling point distribution	°C	ASTM D 6352-04
AV	mg KOH g ⁻¹	AOCS Te 1a-64
Water content	ppm	ASTM D 6304-07
Sulfur content	ppm	ASTM D 5453-09
Phosphorous content	ppm	ASTM D 4951-09
Viscosity	cSt	ASTM D 445-09
Lubricating property	µm, % reduction	ASTM D 6079-04
Oxidative stability	Minutes	EN 14112
Low temperature property	C, J g ⁻¹	DSC

Hewlett-Packard 1100 series (HPLC) with a refractive index detector and two Phenogel 5µ 100A 300 × 7.80 mm 5 micron columns in series protected with a guard column and equipped with a ChemStation for LC 3D, Agilent Technologies. THF was used as a mobile phase at 1 ml/min for 25 min. The operating parameters used were as follows: injection volume 5 µl; column temperature 24 °C; and detector temperature 35 °C. Reference standard chemicals including methyl oleate, triolein, diolein, monoolein, and glycerol were used for the HPLC calibration. Fatty acid compositions of esters were determined using Agilent Technologies 6890 N Network GC System equipped with GC ChemStation software with an FID detector and RESTEK 10638 Stabilwax column. The injection volume was 2 µl and the temperature program was started at 160 °C, held for 1 min, ramped to 240 °C at 4 °C/min and then held for 24 min. The SUPELCO FAME Mix Rapeseed Oil standard was used as a reference for GC calibration.

The lubricating properties of the biodiesel and biodiesel blends were tested by the High-Frequency Reciprocating Rig (HFRR) ASTM D6079-04 method. The test sample was placed in a sample container onto a metal surface. The ball surface was in contact with the metal surface at 50 Hz for 75 min, and the wear scar diameter on the ball surface was then measured using a microscope. A Rancimat instrument was used to determine the oxidation stability of the biodiesel, according to the EN 14112 method (see Table 3). During the Rancimat test, the sample was heated (110 °C in this case) and oxygen was supplied. In the presence of oxygen at high temperatures, the oxidation reaction took place and the oxidation derivatives transferred to a measuring chamber containing Millipore water. As the oxidation derivatives were transferred into the water, an increase in conductivity of the water was detected. The induction time is defined as the time required for conductivity of the water to increase rapidly, and was used as an indication of biodiesel oxidation stability. The low temperature properties of the fuels were

examined by a Differential Scanning Calorimeter (DSC) from PerkinElmer, Inc., CT, USA, equipped with Pyris software thermal analysis and a cryofill filled with liquid nitrogen as a cooling device. After sample encapsulation, the sample chamber was held at 30 °C for 5 min and then cooled from 30 °C to -110 °C at 5 °C/min.

Results and Discussions

Feedstock Analysis

Fatty acid compositions and AV of *S. alba* and *B. juncea* are shown in Table 1. Having a higher erucic acid (32.81%) compared to that of *B. juncea* (25.76%), *S. Alba* was chosen as the feedstock for this study. The AV of this oil was not high (0.85), hence base-catalyzed transesterification was a viable option.

The physical and chemical properties of vegetable oils were evaluated, according to the methods presented in Table 3 Both water content and AV of all three oils were low enough for effective KOH-catalyzed transesterification reactions (water content < 500 ppm and AV < 1). The HPLC analyses of the canola, soybean, and mustard oils suggest that these three oils contain mainly triglycerides and a small amount of diglycerides. In conclusion, all these vegetable oils consist mainly of triglycerides, with a minor percentage of other compounds such as diglycerides, free fatty acids, and water. Table 4.

Transesterification Products of Mustard Oil

Ester obtained from transesterification of mustard oil is discussed in this section. Fig. 2 shows ester formation as well as triglyceride (TG), diglyceride (DG), and monoglyceride (MG) percentages during transesterification of mustard oil. The KOH-catalyzed transesterification

Table 4 AV, water content, ester and glyceride content of vegetable oils

Sample	Canola oil	Soybean oil	Mustard oil
AV (mg KOH g ⁻¹)	0.26	0.28	0.85
Water content (ppm)	288	290	299
Viscosity at 40 °C (cSt)	33.2	29.3	37.5
Phosphorous content (ppm)	n/a	n/a	29.6
Sulfur content (ppm)	1.9	1.2	1.7
TG (wt%)	96.62	99.86	97.04
DG (wt%)	3.25	0	2.54
MG (wt%)	0	0	0
FFA (wt%)	0.13	0.14	0.42

TG triglycerides, DG diglycerides, MG monoglycerides, FFA free fatty acids

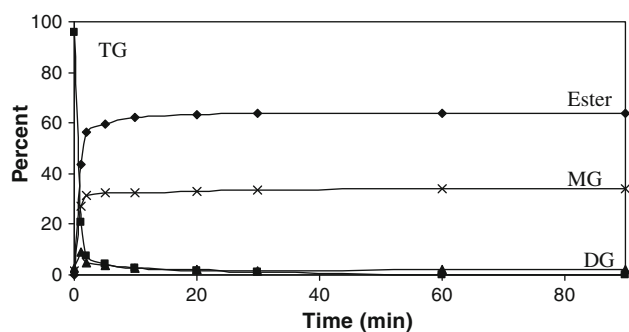


Fig. 2 Ester and glyceride content during the transesterification reaction for MME synthesis

occurred rapidly and the major portion of ester was formed during the first 30 min of the reaction. The reaction was completed within 60 min and only 64% of the ester was formed. TG and DG were observed at negligible amounts; however, there was a high percentage of MG contained in the transesterification products. Transesterification occurs in a series of consecutive, reversible reactions consisting of the conversion of TG to DG, DG to MG, and MG to glycerol (GL) as shown in Fig. 1. The HPLC results implied that TG and DG were smoothly converted to DG and MG, respectively. On the other hand, MG was not able to be converted to form the ester and GL easily, leading to an accumulation of the MG compound in the transesterification products. A product with a high MG percentage was not suitable for use as fuel and required upgrading.

Mixtures of Biodiesel Derived from Canola, Soybean and Mustard Oil

To meet ASTM specifications prior to its use in a diesel engine, the mustard oil methyl ester (MME), was blended

with canola oil methyl ester (CME) and soybean oil methyl ester (SME) at various ratios as shown in Table 2. To discriminate the effects of MME percentage on ester properties, the blend ratios were studied as low as 0.75% MME up to 12% MME. The ester and glyceride content of the mixed and pure esters derived from the canola, soybean, and mustard oils are shown in Table 5. Unlike mustard oil, the canola and soybean oils can easily be transesterified to produce an ASTM-grade biodiesel. All the blended esters showed low values of water content and an AV meeting the ASTM specifications, but the total glycerol content of the higher MME percent blends did not. Total glycerol content can be calculated from the triglyceride, diglyceride, monoglyceride and glycerol contents using the equation: total glycerol content (GL_T) = $GL + 0.26(MG) + 0.15(DG) + 0.1(TG)$ [9]. To meet the ASTM specification of total glycerol content, the MME content of biodiesel blend must not exceed 1.5 wt%. Although, MME can be blended with high purity esters derived from canola and soybean oils, the percentage of MME allowed in a blend was significantly low. An alternate means of using mustard oil as feedstock for biodiesel production has been explored and is discussed in the following sections.

Process Development of Biodiesel Production from Mustard Oil

In an attempt to improve the purity of ester produced from mustard oil, three hypotheses were made related to glycerol formation, catalyst impurity, and high activation energy.

1. *Glycerol formation* It was hypothesized that glycerol was formed during transesterification and the catalyst was transferred into the glycerol phase. As a result, less catalyst was available in the alcohol phase where the reaction took

Table 5 Water content, AV, ester and glyceride content of biodiesel derived from canola, soybean, and mustard oil

Sample	Water content (ppm)	AV	% FFA	%TG	%DG	%MG	%Ester	%Total glycerol
CME	416	0.29	0.15	0	1.39	0	98.46	0.21
MIX1	422	0.24	0.12	0	1.41	0	98.47	0.21
MIX2	460	0.37	0.18	0	1.41	0	98.41	0.21
MIX3	486	0.40	0.20	0	1.43	2.06	96.31	0.75
MIX4	282	0.40	0.20	0	1.40	2.68	95.72	0.91
MIX5	353	0.40	0.20	0	1.41	3.84	94.56	1.21
MME	369	0.60	0.30	0	1.28	33.68	64.75	8.95
SME	443	0.30	0.15	0	0.41	0	99.44	0.06
MIX6	383	0.32	0.16	0	0.41	0	99.43	0.06
MIX7	448	0.36	0.18	0	0.41	0	99.41	0.06
MIX8	416	0.36	0.18	0	0.44	1.68	97.70	0.50
MIX9	460	0.32	0.16	0	0.44	2.25	97.15	0.65
MIX10	467	0.41	0.20	0	0.45	2.97	96.37	0.84
ASTM D6751	500 max	0.5 max	–	–	–	–	–	0.24

See Table 2 for sample legends

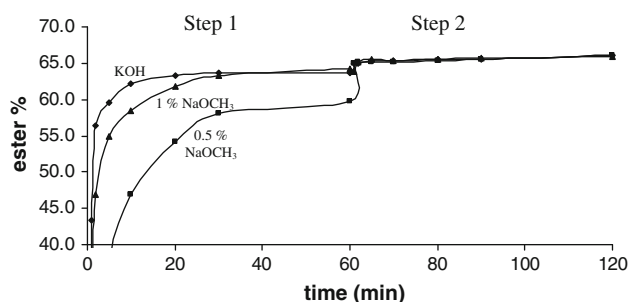


Fig. 3 Ester formation during transesterification reaction for MME synthesis using CH_3ONa and KOH as a catalyst

place, hence hindering the ester yield. In response to this hypothesis, a two-step reaction was performed. After 60 min of the reaction, the glycerol was removed, followed by an addition of a mixture of methanol and KOH (6:1 methanol to oil molar ratio; 1 g of KOH). Addition of methanol/ KOH mixture was expected to compensate the catalyst loss to the glycerol phase. Moreover, it was anticipated that the removal of glycerol would shift the reaction to product side, thereby enhancing the ester yield. The ester formation during this two-step reaction is shown in Fig. 3. The final ester content was 66% which was only 2% higher than the one step process, suggesting that the glycerol formation during transesterification has a minor effect on ester yield.

2. Catalyst impurity KOH , which was purchased from EMD chemicals Inc. and used as a catalyst in this study, contains approximately 15% water. Water, if present in the reaction system, could hydrolyze the ester to form FFA, which intensifies saponification and lowers ester yield. Being anhydrous, sodium methoxide (CH_3ONa) was reported for its high activity towards transesterification of rapeseed, flaxseed, and sunflower oil [10] and was chosen as a catalyst for this study. CH_3ONa loading selected in this study was 0.5 and 1 wt% with respect to mustard oil. Ester formation during transesterification of mustard oil using CH_3ONa compared to that using KOH as a catalyst is shown in Fig. 3. The results suggested that the reaction occurred faster when a higher catalyst loading was used. However, the final ester percentage in both cases was 66%, which was equal to that when KOH was used as a catalyst. This finding indicated that the hydrolysis of the ester during transesterification was insignificant and water contained in the KOH was at an acceptable level for transesterification.

3. Activation energy Based on the HPLC analysis of the final transesterification products derived from mustard oil (see Fig. 2), TG and DG content was negligible, but MG was present in large amounts (33%). It can be assumed that the first two reactions in Fig. 1 (TG to DG and DG to MG) were completed, whereas the conversion of MG to GL was

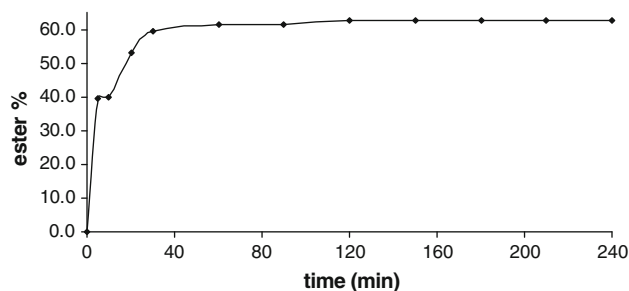


Fig. 4 Ester formation during transesterification reaction for MME synthesis at elevated temperature and pressure (150 °C, 3.4 MPa)

minimal. Based on the principle of activation energy, a minimum energy provided to the reaction must exceed the activation energy of the corresponding reaction to allow it to take place. To provide adequate energy overcoming the activation energy, the reaction was performed at elevated temperature and pressure (150 °C and 3.4 MPa). The reaction was carried out for 4 h. Figure 4 shows the ester formation during elevated temperature and pressure transesterification of mustard oil. The ester percentage at the end of the reaction was only 63%. A high purity biodiesel was not achieved and an alternative means of obtaining high purity ester was required.

Since all three hypotheses could not explain transesterification behavior of *S. alba*, it was believed that the low ester yield obtained from transesterification of *S. alba* was probably due to steric effects of long chain erucic fatty acid hindering the reaction. Figure 5 shows the boiling point distribution of esters derived from canola and mustard oils. It was clear that MME have higher boiling points as compared to CME, due to the high level of a heavy portion. This heavy portion could be either MG or methyl erucate, which boil at a higher temperature than the typical methyl oleate found in CME. To identify the heavy portion, the following reason is given. If the heavy portion in Fig. 5 was erucic ester, this ester would be left out from the rest of the ester portion during distillation. However, results from Table 6 suggest the opposite. It was found that the major ester in MME was methyl erucate (31.57%). Therefore the heavy portion as shown in Fig. 5 is more likely to be MG instead of methyl erucate. The data from Fig. 5 suggest that the ester and MG have a distinctive range of boiling temperature and, therefore, can be separated from each other by means of distillation.

Distillation of Transesterification Products Derived from Mustard Oil

Due to the difference in boiling points between the ester and MG, the transesterification products derived from mustard oil containing mainly ester and MG were distilled following

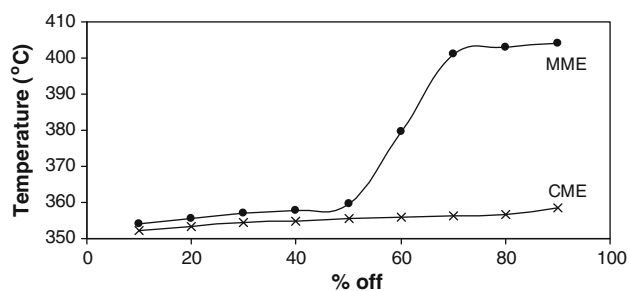


Fig. 5 Boiling point distribution of CME and MME using simulated distillation unit

the method described in the experimental procedures section. The HPLC chromatograms of undistilled MME, distilled MME (DMME), and residuals from distillation of mustard oil butyl ester (MBE) are presented in Fig. 6, and shows that undistilled MME contained mainly esters and MG, whereas MME after distillation contained only the esters. The mustard oil ethyl ester (MEE), mustard oil propyl ester (MPE), and mustard oil butyl ester (MBE) were also distilled, using the method described in the experimental procedures section. The chromatograms of these esters were somewhat similar to that of MME, but the esters were completely separated from monoglycerides and, therefore, high purity esters were achieved. Since the oil samples were exposed to a high temperature (200–250 °C) for a long period of time (~6 h), it was likely that polymerization took place during the distillation process. These polymerized compounds had high molecular weights and were left in the residual portion during distillation (see Fig. 6c).

Characterization of Mustard Biodiesel

Properties from the mustard biodiesel (methyl, ethyl, propyl and butyl esters) and its parent oil are summarized in Table 7. Fatty acid compositions of CME, SME, and MME are shown in Table 6. The results suggested that the major fatty acid in canola, soybean, and mustard were oleic (C18:1), linoleic (C18:2), and erucic acid (C22:1) acids, respectively, in line with those found in literature [3, 11].

The molecular weights of esters and mustard oil (MO) were calculated from the fatty acid compositions corresponding to each sample. The AV of DMME and DMEE met the ASTM specifications, but was higher for butyl-ester synthesis, which was probably due to the severe operating conditions used in the distillation step. At high temperature, it was likely that some ester and monoglyceride degraded into acids resulting in the apparently higher AV. Since esters were separated from glycerides and polymerized compounds during distillation, the total glycerol content of distilled esters was null, hence giving ultra high purity esters. In comparison with the data

obtained from HPLC using RID, DMME was analyzed for free and total glycerol as per ASTM D6584. Free glycerol was not detected in the GC chromatogram; however, total glycerol was measured at 0.121 mass%. These data suggested that the amount of free and total glycerol contained in the distilled ester was trivial and the quality of DMME met the ASTM specification. Water, sulfur, and phosphorous content of all esters were within the range specified in ASTM D6751. Viscosity of esters was reduced significantly from their parent oil (viscosity of MO = 37.5 cSt) due to transesterification and distillation, and met ASTM specifications.

The lubricating property of a fuel is defined as the quality that prevents wear when two moving metal parts come into contact with each other [12]. Oxygen- and nitrogen-containing compounds are responsible for the natural lubricating property of diesel fuel [13]. In petroleum refineries, the processes such as hydrotreating usually utilized to remove sulfur also destroy heterocyclic oxygen and nitrogen containing compounds [14]. Consequently, this typically ultra-low sulfur diesel fuel exhibits poor lubricity. ASTM D6079-04 was used to evaluate lubricating property of biodiesel and diesel fuel by the High-Frequency Reciprocating Rig (HFRR). In this method, the high wear diameter indicates poor lubricating property of the test fluid and vice versa. In the present work, biodiesel samples were blended with the reference diesel fuel and HFRR results were observed. Figure 7 shows that the lubricity of the blended fluid increased with an increase in the biodiesel percentage. The improvement in lubricity was insignificant when the biodiesel percentage exceeds 1% of regular diesel, therefore, it was concluded that a 1% biodiesel blend was the optimum ratio.

The biodiesel derived from canola oil was somewhat superior in its lubricating property as compared to that obtained from mustard oil. However, the biodiesel produced from mustard oil showed great potential as a diesel fuel additive to improve its lubricating property. At 0.1 and 1% distilled mustard oil methyl ester (DMME) blended with diesel fuel, the wear scar diameter was reduced by 11.1 and 43.7%, respectively. The results from Table 7 suggest that the methyl ester was the best lubricity additive among all esters (methyl-, ethyl-, propyl-, and butyl-esters). This is because the lubricity of biodiesel is provided by the polarity-imparting oxygen atoms and the nature of which the oxygen atom is bound in the molecule. It was reported that the order of oxygenated moiety that provides lubricity are $\text{COOH} > \text{OH} > \text{COOCH}_3 > \text{C}=\text{O} > \text{C}-\text{O}-\text{C}$ [15]. In the case of the methyl ester, the lubricity was provided mainly by the COOCH_3 moiety. In contrast, the lubricity of ethyl, propyl, and butyl esters was possibly contributed to by the ketone group ($\text{C}=\text{O}$ moiety), due to the lack of the COOCH_3 moiety in their

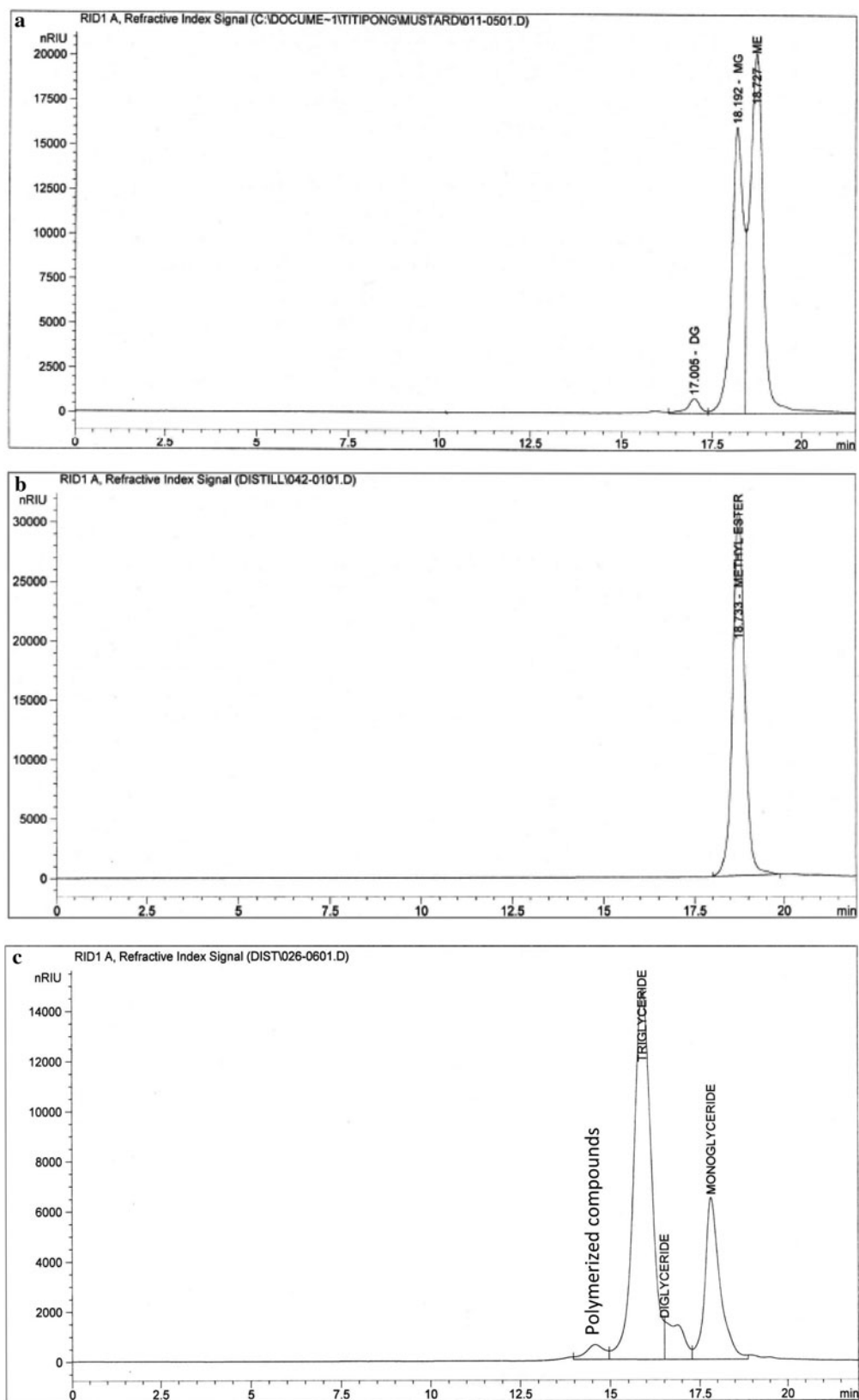


Fig. 6 HPLC chromatograms of **a** undistilled MME, **b** distilled MME, and **c** residuals from distillation of MBE

molecules. Therefore, the methyl ester exhibited a better lubricating property when compared to ethyl, propyl, and butyl esters. In addition, four commercial diesel samples

were purchased from different gas stations (Esso, Shell, Petro-Canada, Co-op) and tested for their lubricity. The viscosity at 40 °C of these commercial diesel fuels were within the range of 2.2–2.4 cSt. The results from Fig. 7 show that DMME/RDF blends had a lubricating property superior to that of the purchased commercial diesel fuels. The lubricity of these commercial diesel fuels can be improved by the addition of DMME.

Table 6 Fatty acid compositions of mustard, canola, and soybean oil methyl ester

Structure	Compound name	MME	CME	SME
C14:0	Myristic ester	0	0.06	0.10
C16:0	Palmitic ester	2.84	4.24	11.56
C16:1	Palmitoleic ester	0.21	0.22	0.15
C16:2	Hexadecadienoic ester	0.04	0.07	–
C18:0	Stearic ester	1.11	2.00	4.32
C18:1 z9	Oleic ester	25.30	61.36	22.82
C18:1 z11	Vaccenic ester	0.93	2.78	1.38
C18:2	Linoleic ester	11.54	18.43	51.93
C18:3	Linolenic ester	8.58	6.72	5.95
C20:0	Arachidic ester	0.68	0.70	0.34
C20:1	Eicosenoic ester	10.34	1.30	0.25
C22:0	Behenic ester	0.48	0.38	0.34
C22:1	Erucic ester	31.57	–	–

Oxidative stability is an important property as it determines stability of biodiesel. It was reported that the oil stability increases with a decrease in the degree of unsaturation [16]. In this study, the rancimat plot of esters derived from mustard oil is presented in Fig. 8. The stability of DMBE was higher than those of DMME, DMEE, and DMPE due to its longer carbon chain length. The longer chain provides a lower double bond concentration per molecule, hence lowering degree of unsaturation and thus increasing stability.

Low temperature property of biodiesel determines how well biodiesel can be operated and stored in a cold environment and therefore is of special importance in cold climate regions. When temperature is reduced to a certain

Table 7 Properties of mustard oil and biodiesel produced from mustard oil

Property	MO	DMME	DMEE	DMPE	DMBE	ASTM D6751
MW cal (g mol ⁻¹)	947	317	331	345	359	n/a
AV (mg KOH g ⁻¹)	0.9	0.4 (0.1)	0.5 (0)	0.6 (0.1)	4.0 (0.2)	0.5
Free fatty acid (mass%)	0.4	0.2	0.3	0.3	2.0	n/a
Triglycerides (mass%)	96.9	0	0	0	0	n/a
Diglycerides (mass%)	2.5	0	0	0	0	n/a
Monoglycerides (mass%)	0	0	0	0	0	n/a
Free glycerol (mass%)	0	0	0	0	0	<0.02
Total glycerol (mass%)	10.1	0	0	0	0	<0.24
Ester (mass%)	0	99.8	99.7	99.7	98.0	n/a
Water (ppm)	241 (58)	231 (44)	62 (45)	187 (10)	345 (30)	<500
Sulfur (ppm)	1.7 (0.2)	0 (0)	14.7 (0.7)	9.5 (0)	10.4 (0.3)	15
Phosphorous (ppm)	30	9	4	10	8	10
Density @40 °C (g ml ⁻¹)	0.9	0.9	0.9	0.9	0.9	n/a
Kinematic viscosity at 40 °C (cSt)	37.5 (0.3)	4.2 (0.2)	4.5 (0.1)	5.0 (0.2)	5.5 (0.2)	1.9–6.0
Wear reduction, HFRR, 1% ester (%)	n/a	43.7 (4.2)	23.2 (5.3)	30.7 (2.4)	30.6 (4.6)	n/a
Induction time, 110 °C (min)	n/a	3	7	7	9	>180
Onset crystallization temperature (°C)						
Saturated compounds	n/a	–16.4 (0.8)	–16.5 (0.1)	–12.3 (1.6)	–16.6 (0)	n/a
Monounsaturated compounds		–42.5 (0.8)	–51.0 (0.2)	–51.9 (0.2)	–58.2 (0)	
Polyunsaturated compounds		–65.4 (0.8)	–93.5 (1.2)	n/a	n/a	
Heat of crystallization (J g ⁻¹)						
Saturated compounds	n/a	8.4 (0.5)	8.9 (0.5)	14.7 (0.7)	3.6 (0.4)	n/a
Monounsaturated compounds		46.7 (2.1)	59.0 (0.5)	48.5 (0.4)	36.8 (0.1)	
Polyunsaturated compounds		23.6 (0.3)	11.6 (0.6)	n/a	n/a	

The numbers in parentheses are the corresponding standard deviation values. *MO* mustard oil, *DMME* distilled mustard methyl ester, *DMEE* distilled mustard ethyl ester, *DMPE* distilled mustard propyl ester, *DMBE* distilled mustard butyl ester

Fig. 7 Lubricity properties of methyl esters derived from mustard oil and canola oil blended with reference diesel fuel using the high frequency reciprocating rig (HFRR) method

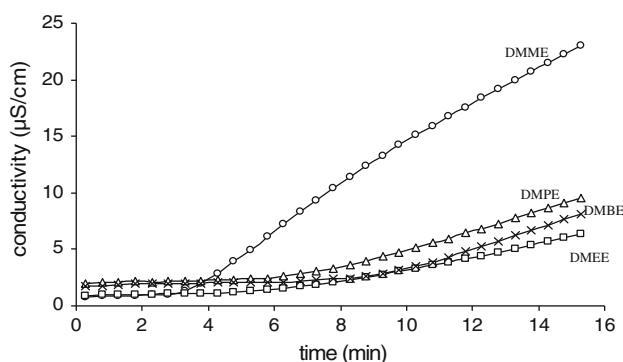
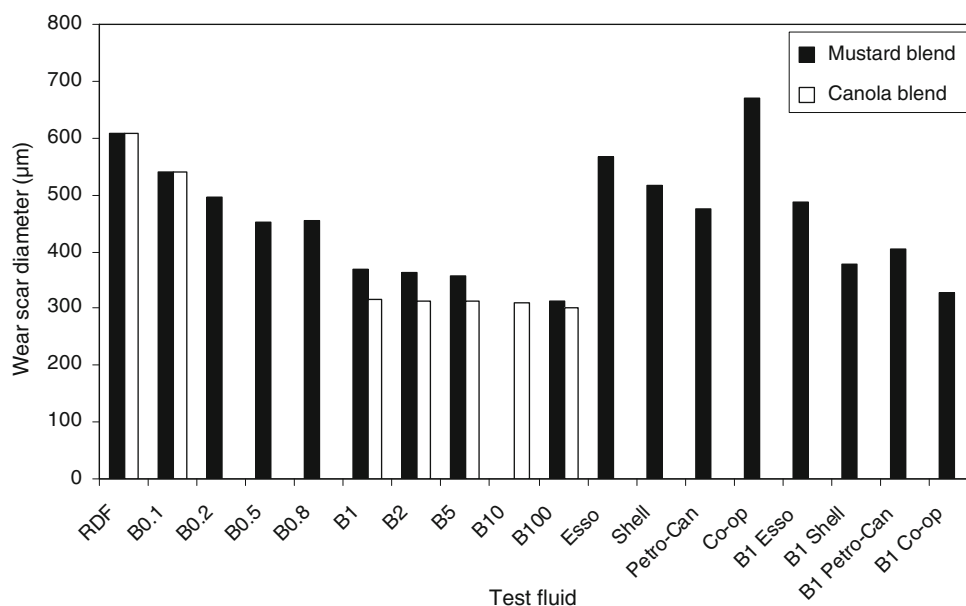


Fig. 8 Rancimat plot of biodiesel derived from mustard oil

point, a portion of the biodiesel or biodiesel blends begins to crystallize, which can create problems with the engine flow system and eventually cause the engine to cease. Differential scanning calorimetry (DSC) is an effective means to determine the low temperature property of esters with good correlation to cloud point and pour point of biodiesel [2, 17]. Figure 9 represents a DSC thermogram of esters derived from mustard oil in this study. The exothermic crystallization of saturated, monounsaturated and polyunsaturated esters appeared as peaks in the corresponding DSC thermogram. Crystallization of saturated compounds occurred at higher temperatures due to the arrangement of the molecules. Saturated compounds are well stacked and hence strengthening the intermolecular attractive forces. On the other hand, the *cis*-formation in unsaturated molecules increases the distance between the molecules and weakens the intermolecular attractive forces, which causes these compounds to crystallize at lower temperatures [2]. The onset crystallization temperatures as

well as heats associated with crystallization of each compound are reported in Table 7. The crystallization temperature of an ester tended to decrease when a higher alcohol was used in transesterification. For unsaturated compounds, if the number of double bonds is the same, a molecule with a higher carbon chain length would have poorer molecular stacking and therefore poorer intermolecular interactions leading to a lower crystallization temperature.

The low temperature property of biodiesel can be improved by using higher alcohols, i.e., cloud point and pour point of the ethyl ester were reported to be lower than those of the methyl ester [17, 18]. Based on this concept, the freezing points of polyunsaturated compounds in propyl- and butyl-esters would be extremely low and lay outside the DSC scan in this study. Heat from the crystallization of monounsaturated compounds was highest as compared to that of saturated and polyunsaturated compounds. This was because the major fatty acids in mustard oil were erucic and oleic acid at 31.6 and 25.3%, respectively (see Table 6). Because they both contain one double bond per molecule, these two compounds were considered as monounsaturated. When a large amount of monounsaturated compounds is present in the oil sample, exothermic heat associated to crystallization of these compounds will be higher, as evidenced from the data in Tables 6 and 7. DSC was also used to study petro-diesel and DMME/petro-diesel blends (1% biodiesel). However, crystallization peaks were not observed on any DSC thermograms in this study. Therefore, it is believed that the crystallization points of these fuels are extremely low and are below the range of DSC scan of 30 °C to −110 °C. This finding suggests that the fuel can be used without freezing in

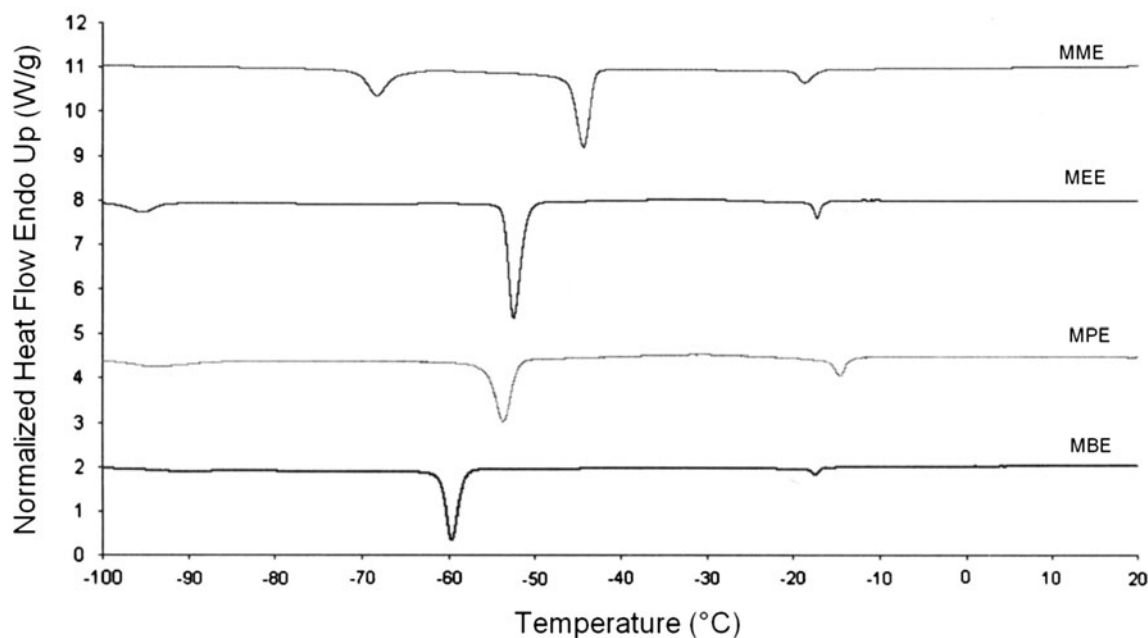


Fig. 9 DSC thermogram of esters derived from mustard oil

winter conditions at the optimum biodiesel–diesel blend (1% biodiesel).

Conclusions

Canola oil and soybean oil can be used as a feedstock to obtain a high quality biodiesel via KOH-catalyzed transesterification, but mustard oil was not suitable for this process. Glycerol formation, hydrolysis and saponification have minor effects on transesterification of mustard oil. Mustard oil methyl ester can be mixed with canola or soybean oil methyl esters up to 1.5 wt% to obtain an ASTM quality biodiesel. Alternatively, distillation can be used to purify esters derived from mustard oil. The distilled esters were extremely pure in ester content. Properties of distilled methyl and ethyl ester satisfy the ASTM specifications. An improvement was required for a specific property of a specific ester such as AV of butyl ester. Esters derived from mustard oil showed great potential as a lubricity additive to diesel fuel. The optimum ester percentage in a biodiesel–diesel blend was 1% by which the wear scar diameter was reduced by 43.7%. Methyl ester was the best lubricity additive among all the esters (methyl-, ethyl-, propyl-, and butyl-esters), and lubricity of the biodiesel–diesel blend was superior to that of commercial diesel fuels. Methyl ester derived from mustard oil did not freeze until the temperature reached -16°C . Monounsaturated compounds (oleic, eicosenoic, and erucic esters) which are largely present in esters derived from mustard oil can

tolerate temperatures of -42 to -58°C . The freezing point of monounsaturated esters can be reduced by using higher alcohols like butyl alcohol as the reactive alcohol. The freezing point of monounsaturated butyl and methyl esters was -58°C and -42°C , respectively. For B1 blend, the fuel can be used at low temperatures without freezing. A detailed study on the oxidative stability is required to improve the stability of esters derived from mustard oil.

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