

Preparation and characterization of bio-diesels from various bio-oils

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Abstract

Methyl, ethyl, 2-propyl and butyl esters were prepared from canola and linseed oils through transesterification using KOH and/or sodium alkoxides as catalysts. In addition, methyl and ethyl esters were prepared from rapeseed and sunflower oils using the same catalysts. Chemical composition of the esters was determined by HPLC for the class of lipids and by GC for fatty acid compositions. The bio-diesel esters were characterized for their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion and volatility. Methyl and ethyl esters prepared from a particular vegetable oil had similar viscosities, cloud points and pour points, whereas methyl, ethyl, 2-propyl and butyl esters derived from a particular vegetable oil had similar gross heating values. However, their densities, which were 2–7% higher than those of diesel fuels, statistically decreased in the order of methyl > 2-propyl > ethyl > butyl esters. Butyl esters showed reduced cloud points (–6°C to –10°C) and pour points (–13°C to –16°C) similar to those of summer diesel fuel having cloud and pour points of –8°C and –15°C, respectively. The viscosities of bio-diesels ($3.3\text{--}7.6 \times 10^{-4}$ Pa s at 40°C) were much less than those of pure oils ($22.4\text{--}45.1 \times 10^{-4}$ Pa s at 40°C) and were twice those of summer and winter diesel fuels (3.50 and 1.72×10^{-4} Pa s at 40°C), and their gross heat contents of approximately 40 MJ/kg were 11% less than those of diesel fuels (~45 MJ/kg). For different esters from the same vegetable oil, methyl esters were the most volatile, and the volatility decreased as the alkyl group grew bulkier. However, the bio-diesels were considerably less volatile than the conventional diesel fuels. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The triglyceride molecules of vegetable oil consist of three long-chain fatty acids that are ester-bonded to a single glycerol molecule. These fatty acids differ by the length of the carbon chains, as well as the number, orientation, and position of double bonds in these chains. The viscosity of vegetable oils is of the order of 10–20 times that of diesel fuel. When used as fuels, they cause injector fouling and other engine problems. Bio-diesels refer to lower alkyl esters of the long-chain fatty acids which are synthesized either by transesterification of vegetable oils with lower alkanols (Sridharan and Mathai, 1974), or by esterification of free fatty acids with lower alkanols. The methyl or ethyl esters of vegetable oils have viscosities approximately twice those of

diesel fuels. Therefore, the bio-diesel esters can be used directly or as blends with diesel fuel in a diesel engine (Peterson et al., 1991). Bio-diesel is a biodegradable and renewable fuel. It contributes no net carbon dioxide or sulfur to the atmosphere and emits less gaseous pollutants than normal diesel. Carbon monoxide, aromatics, polycyclic aromatic hydrocarbons (PAHs) and partially burned or unburned hydrocarbon emissions are all reduced in vehicles operating on bio-diesel.

Bio-diesel, primarily rapeseed methyl ester, has been in commercial use as an alternative fuel since 1988 in many European countries, including France, Austria, Germany, Sweden, Italy, Belgium, Hungary and Czech Republic (Staat and Vallet, 1994; Ahn et al., 1995; Cvangroš and Povazanec, 1996; Connemann, 1997). German bio-diesel standard DIN V 51606 requires a rapeseed ester to have density at 15°C between 0.875 and 0.900 g/ml, viscosity at 15°C between 3.5 and 5.0 mm²/s (cSt), acid number below 0.5 mg KOH/g and iodine value less than 115 g iodine/100 g, among many

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other specifications. A 90% tax deduction proposed by the European Community for the use of bio-diesel enables it to be sold in Europe at prices competitive to conventional diesel fuel. The total European production of bio-diesel for 1997 was estimated at 660,000 tons. In the United States, bio-diesel, primarily made from soybean oils, also is being commercialized. Several demonstration programs use bio-diesel to fuel municipal buses, trucks and construction equipment (Tickell and Tickell, 1999). In Canada, the Canadian Renewable Fuels Association (CRFA), whose members including the Saskatchewan Canola Development Commission and the Ontario Soybean Growers' Marketing Board, promotes renewable bio-fuels (ethanol, bio-diesel) for automotive transportation through consumer awareness and government liaison activities. However, the suggested 20% bio-diesel blended diesel fuel currently costs 10 cents more per blended liter than the conventional diesel due to high feed cost of vegetable oil, thereby preventing its large-scale use in North America.

Much work has been done in the past two decades on the production and real-world market performance of bio-diesel, which has been reviewed recently by Knothe et al. (1997). The most commonly used alcohol for transesterification is methanol because of its lower price than that of other lower alkanols. Rapeseed, canola, sunflower, soybean oils, beef tallow and many other oils have been used for the production of bio-diesel esters (Freedman and Pryde, 1982; Hassett and Hasan, 1982; Kusy, 1982; Freedman et al., 1986; Shay, 1993; Peterson et al., 1996, 1997; Ma and Hanna, 1999). Peterson et al. (1997) reported detailed batch transesterification procedures for methyl and ethyl esters of four lipids using KOH catalyst at room temperature. Use of absolute ethanol was found essential to produce ethyl esters successfully, which was characterized by the production of two liquid phases: ester and denser glycerol phases at the end of the reaction. The specific gravities of the eight bio-diesel esters were 0.87–0.88, while the viscosities were 3.9–6.2 cSt at 40°C. Ahn et al. (1995) carried out methyl ester transesterification of rapeseed oil in two steps and achieved 99% yield. During the soybean methyl ester preparation, Boocock et al. (1996, 1998) added tetrahydrofuran as a co-solvent. The co-solvent transformed the soybean oil/methanol two-phase system into a one-phase system. As a result of improved mass transfer between the reactants, the methanolysis process was rapid and was completed in a few minutes. Lee et al. (1995) prepared esters of vegetable oils and animal fats with C₃–C₅ branched-chain alcohols, and examined their low temperature properties by using differential scanning calorimetry. Compared with the common methyl esters, branched-chain esters greatly reduced the crystallization onset temperature of neat esters and ester diesel fuel blends. They found that 2-propyl and 2-butyl esters of soybean oil crystallized 7–11°C and 2–14°C

lower, respectively, than the soy methyl esters. Sodium alkoxides, which were prepared by dissolving metal sodium in anhydrous alcohol, acted as the catalytic species for the transesterification with branched-chain alcohol. A considerably high alcohol-to-oil ratio of 66:1 was used for the preparation of 2-propyl and 2-butyl esters.

Often, the vegetable oil of choice for bio-diesel production are those which occur abundantly in the region of testing. Therefore, rapeseed oil is the primary bio-diesel source in Europe while in the United States both rapeseed and soybean oils are used. Canola oil is a cultivated version of rapeseed oil, very low in erucic acid content and is now widely produced in Western Canada. In this study, canola oil along with rapeseed, linseed (flax) and sunflower oils, all available in Western Canada, were selected as feedstocks for the synthesis of bio-diesels with methanol, ethanol, 2-propanol and butanol. Selected physical and fuel properties of the bio-diesels were determined and compared with those of conventional diesel fuels.

2. Methods

Rapeseed was purchased from the Saskatchewan Wheat Pool's local supply outlet. The raw edible linseed (flaxseed) was purchased from Early's Farm and Garden, Saskatoon, SK. The rapeseed and linseed oils were then expelled from raw seeds using a small screw press at the Food Science Pilot Plant, University of Saskatchewan, and filtered before transesterification without further treatment. Degummed, refined canola and sunflower oils (Sunfresh Limited, Toronto, Ont.) were purchased locally. OmniSolv grade methanol (99.9%, BDH, Toronto, Ont.), anhydrous ethanol (Commercial Alcohols, Brampton, Ont.), anhydrous 2-propanol and 1-butanol (both from Aldrich Chemical) were used for transesterification reactions. All other reagents were analytical grade or higher.

2.1. Ester preparation

2.1.1. Methyl esters

Canola methyl ester (CME), rapeseed methyl ester (RME), linseed methyl ester (LME) and sunflower methyl ester (SME) were synthesized in a batch type reactor using both potassium hydroxide (KOH) and sodium methoxide (CH₃ONa) as catalysts. The ester preparation involved a two-step transesterification reaction (Ahn et al., 1995; Muniyappa et al., 1996), followed by washing and drying. The two-step reaction utilized a 100% excess methanol, or a total molar ratio of methanol-to-oil of 6:1 with methanol equally divided in the two steps. 200 g of oil (about 0.22 mol) was placed in a dry flask equipped with a magnetic stirrer and thermometer. Dryness is absolutely essential as any water in

the system will consume some of the catalyst and slow the transesterification reaction. In another flask, approximately 23 g of methanol was mixed with 1.0 g of KOH (i.e., 0.5% by the weight of oil), or 0.5 g of CH₃ONa, until all of the catalyst dissolved. This mixture was quickly added to the oil and stirred vigorously for 20 min at 25°C. After separation of glycerol in a separatory funnel, the top ester layer was poured into another flask and transesterified a second time using the same protocol as the first reaction. The crude ester was separated and washed with distilled water to remove the catalyst and unreacted methanol until it became completely translucent. Finally, the ester was dried with anhydrous sodium sulfate.

2.1.2. Ethyl esters

The ethyl esters of canola, rapeseed, linseed (flax) and sunflower oil (abbreviated as CEE, REE, LEE and SEE, respectively) were prepared in much the same way as the methyl esters but only using CH₃ONa catalyst. The transesterification was conducted at 70°C (8°C below ethanol boiling point) for 2 h with vigorous agitation in order to achieve full conversion. As the ethyl esters tended to form emulsions with water, warm (50–60°C) salt water was used as a substitute to reduce emulsification. Tannic acid in water (0.1% w/w) was also an effective washing solution. With mild agitation in a flask, the alcohol and most of the soap could be removed by three washes at 50°C by either solution. After washing, the ethyl esters are dried over anhydrous sodium sulfate.

2.1.3. 2-Propyl esters

Canola 2-propyl ester (CPE) and linseed 2-propyl ester (LPE) were prepared using metal sodium as catalyst precursor and an alcohol-to-oil ratio of 6:1 in a single-step transesterification. 100 g of oil was first heated at 110°C for 1 h to remove trace moisture in the oil. About 170 mg of metal sodium was freshly cut into small pieces from a sodium block and carefully dropped into a flask of anhydrous 2-propanol. The flask was connected to a condenser with a drying tube on the top to prevent moisture from contacting with the alcohol. After all the metal pieces were dissolved, the solution was poured into the oil and the transesterification lasted 3 h with vigorous stirring at 72°C. A small amount of glycerol settled at the bottom of the vessel when the stirring was stopped. After separation of glycerol in a separatory funnel, the crude ester was washed with brine or distilled water, then dried over sodium sulfate.

2.1.4. 1-Butyl esters

Both canola butyl ester (CBE) and linseed butyl ester (LBE) were prepared using the same procedure as their propyl counterpart, except that the transesterification was at 105°C. Since butanol cannot be completely extracted from the ester phase by water-washing, the butyl

esters were further dried in a rotary evaporator at 50°C under vacuum to remove any residual butanol in addition of trace water.

2.2. Ester characterization

The composition of the transesterification products was determined by high performance liquid chromatography (HPLC) using a Waters GPC-Styrigel 0.5 column (7.5 × 30 mm²) with tetrahydrofuran as the mobile phase combined with evaporative light scattering detection (ELSD). The column was operated at 35°C while the ELSD detector at 40°C.

Viscosity of the esters was measured at 40°C using a Brookfield model RVTDCP, cone and plate viscometer (Brookfield Engineering Laboratories, Stoughton, MA). The viscometer was calibrated by Cannon certified viscosity standard. The weight loss of the bio-diesel esters with respect to temperature was measured using a Mettler TA4000 desktop thermal analysis system with a TG50 thermobalance. In the study, about 10 mg of sample was placed in an alumina pan and heated at 5°C/min ramp rate from 30°C to 350°C in 50 ml/min nitrogen purge gas. A separate blank run was conducted using the empty pan under identical conditions, and the data were used for baseline correction during the evaluation of the sample thermogravimetric analysis (TGA) profiles. The corrected TGA data were then stored as temperature versus the corrected sample weight (to 0.1 µg).

The fatty acid composition, and the properties of bio-diesel such as density, cloud point, pour point, acid value, iodine value, and gross heat of combustion were measured according to the standard methods as given in Table 1. The properties of bio-diesel esters derived from canola oil and various alcohols were evaluated in triplicate, and are reported in various data tables in this paper. Since the variations in data were less significant, evaluation of properties for other esters was only performed once unless otherwise stated.

Table 1
Standard methods applied for ester characterization

| Characterization tests | Standard methods |
|--------------------------|--|
| Fatty acid composition | AOCS official method Ca 5a-40 (AOCS, 1997a) |
| Density | ASTM D5002 (ASTM, 1998d) |
| Cloud point | ASTM D2500 (ASTM, 1998c) |
| Pour point | ASTM D97 (ASTM, 1998a) |
| Acid values | AOCS official method Te 2a-64 (AOCS, 1997c) |
| Iodine value | AOCS Recommended Practice Cd 1c-85 (AOCS, 1997b) |
| Gross heat of combustion | ASTM D240 (ASTM, 1998b) |

3. Results and discussion

3.1. Bio-diesel ester preparation

Both KOH and CH₃ONa were used as base catalysts for the synthesis of methyl esters. The overall catalyst usage in the two-step transesterification was 1% and 0.5% for KOH, and CH₃ONa based on oil weight, respectively. The use of two catalysts resulted in two methyl ester samples from each of the four oils. When comparing each pair of the methyl esters from the same oil, it was found that their yields were close, and their HPLC chromatograms were identical. Therefore, both catalysts were equally effective for methyl ester syntheses. When using either KOH or CH₃ONa as base catalyst for methyl ester transesterification, the active catalytic species was the same, CH₃O⁻, methoxide anion (Shirley, 1964), which was formed by the reaction between hydroxide and methanol if KOH was the catalyst, or by dissociation if sodium methoxide was used. In both catalyst cases, the yields of the methyl esters were 95–97% relative to the theoretical yields. Since KOH is more economical, it is the preferred choice for large-scale methyl ester production.

In this research, a two-step process was adapted for methyl ester preparation in which glycerol formed during the first step was separated from the reaction mixture before the second step. This facilitated the reaction to nearly complete conversion in the second step. It was found that two 20 min periods were sufficient for the completion of the transesterification with methanol. It has been reported that in a commonly used single-stage process, a period of 1 h is required to achieve 98% conversion of rapeseed oil to methyl esters at 25°C (Peterson et al., 1991). This longer period was due to the fact that vegetable oil transesterification with alkanols is a reversible chemical reaction. Also, since the by-product, glycerol, was less volatile than the alkanols, the reaction equilibrium cannot be shifted to high product yield during one-stage process by simple distillation. Therefore, a two-stage process would work better than a one-stage process. For simplicity, we have applied an equal amount of methanol in each step in the present study. Use of other alcohol-to-oil ratios (3.5:1 in the first step, then 0.95:1 in the second step) also has been reported in the literature (Cvengroš and Povazanec, 1996).

Potassium hydroxide has been reported as a catalyst for rapeseed oil ethyl ester transesterification (Korus et al., 1993). During preliminary tests of making CEE, an ethanol-to-oil molar ratio 5.1:1 (70% excess) and 1.3 wt% KOH were used at 70°C, and no phase separation was observed after 2 h, indicating lower conversion to ester. However, with CH₃ONa catalyst, the reaction was continued for only 1 h and higher conversion was achieved. The KOH was less effective than methoxide as

a catalyst for ethyl ester synthesis from vegetable oils. This is because ethanol (pK_a = 15.9) and other primary alcohols are somewhat weaker acids compared to water (pK_a = 15.7), while methanol (pK_a = 15.5) is a slightly stronger acid. Branched-chain alcohol such as 2-propanol is even less acidic. Therefore, the reaction of KOH with methanol may favor the formation of methoxide ion, the reactivity between KOH and other alcohols, especially 2-propanol, to form respective alkoxide anion would be very low. Although KOH was an excellent base catalyst for methyl esters, it became less effective for ethyl, butyl and 2-propyl esters.

2-Propyl and butyl esters were prepared by using sodium metal as a catalyst, which reacted with the corresponding anhydrous alcohol to produce active butoxide and 2-propoxide anions. At the end of transesterification with oil, glycerol was easily settled out, forming two phases. The yields of linseed butyl ester and 2-propyl ester were 96% and 87%, respectively. The lower yield in the latter case could have been due to less reactivity of the branched-chain alcohol, probably because of its lower acidity and stronger steric hindrance towards transesterification. In a recent Canadian patent (Stoldt and Dave, 1998), elemental sodium and potassium also were claimed as the catalysts for making propyl, butyl or other longer-chain alkyl esters of vegetable oils.

3.2. HPLC analyses

HPLC was used to analyze the purity of the bio-diesel ester samples. The HPLC method employed was the low molecular weight gel permeation chromatograph, which separated different components according to their solvated molecular size, with the larger one eluting first. Therefore, any unreacted triglycerides (TGs) will first elute, followed by diglycerides (DGs), monoglycerides (MGs), and finally alkyl esters (bio-diesels). The chromatogram of a crude, unwashed CEE sample after its separation from glycerol is shown in Fig. 1(a). It can be seen that the classes of lipids were efficiently separated and trace residual glycerides were readily detected in the crude esters. The retention times of tri- (around 5.6 min), di- (5.9 min) and monoglycerides (6.3 min) and alkyl esters were well resolved. The majority (over 90%) of the fatty acids in the canola, linseed and sunflower oils were those containing 18 carbons and included stearic, oleic, linoleic and linolenic acids in the order of increasing unsaturation. Their alkyl esters emerged as a single peak in the gel permeation chromatogram because of similar molecular sizes. On the other hand, rapeseed oil contained approximately 7% eicosenoic and 54% erucic acids, which were a 20 and 22 carbon monounsaturated fatty acid, respectively. Subsequently, the alkyl esters of rapeseed oil yielded two peaks in the chromatogram as shown in Fig. 1(b), for RME. The

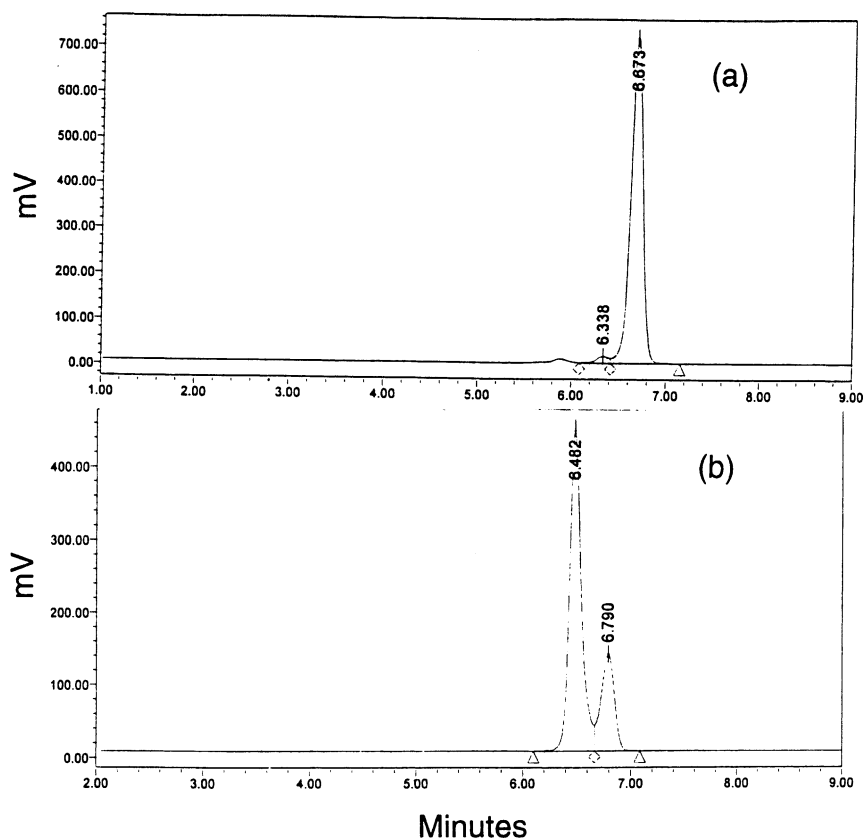


Fig. 1. HPLC chromatograms of: (a) crude canola ethyl ester; (b) purified rapeseed methyl ester.

earlier and larger one at 6.5 min represented the bulkier C_{20} and C_{22} fatty acid esters while the latter one at 6.8 min was for esters of the C_{18} fatty acids. All samples of methyl, ethyl and butyl esters exhibited only the ester peaks in the chromatograph, demonstrating the high purity of these samples. Small mono- and diglycerides peaks were detected in the chromatograms of CPE and LPE samples, indicating trace impurities in the 2-propyl esters.

3.3. Fatty acid composition

The fatty acid compositions of the 12 bio-diesel esters are presented in Table 2. The error in the analysis of fatty acid compositions is within 5%. A total of seven different fatty acids were found in the esters. As expected, similar fatty acid compositions were observed in the different alkyl esters originating from the same vegetable oil source. The dominant fatty acid in canola

Table 2
Fatty acid composition (wt%) of the bio-diesel esters

| Fatty acid | CME | CEE | CPE | CBE | LME | LEE | LPE | LBE | RME | REE | SME | SEE |
|-------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Palmitic (16:0) | 4.2 | 4.4 | 4.5 | 4.4 | 5.2 | 5.1 | 5.1 | 5.3 | 3.1 | 3.1 | 6.5 | 6.3 |
| Stearic (18:0) | 2.2 | 2.3 | 2.3 | 2.3 | 3.2 | 3.1 | 3.1 | 3.2 | 0.0 | 0.0 | 4.9 | 4.7 |
| Oleic (18:1) | 67.2 | 69.4 | 67.3 | 67.8 | 14.5 | 13.7 | 14.2 | 13.8 | 13.9 | 13.2 | 20.5 | 21.0 |
| Linoleic (18:2) | 18.9 | 18.0 | 19.4 | 18.9 | 15.3 | 15.2 | 15.1 | 15.2 | 13.3 | 13.3 | 68.0 | 68.0 |
| Linolenic (18:3) | 7.4 | 5.9 | 6.5 | 6.7 | 61.9 | 62.9 | 62.5 | 62.6 | 9.4 | 9.2 | 0.0 | 0.0 |
| Eicosenoic (20:1) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 6.8 | 6.9 | 0.0 | 0.0 |
| Erucic (22:1) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 53.5 | 54.4 | 0.0 | 0.0 |
| Total saturated | 6.4 | 6.7 | 6.8 | 6.7 | 8.4 | 8.2 | 8.2 | 8.5 | 3.1 | 3.1 | 11.4 | 11.0 |
| Total unsaturated | 93.6 | 93.3 | 93.2 | 93.3 | 91.6 | 91.8 | 91.8 | 91.5 | 96.9 | 96.9 | 88.6 | 89.0 |
| Calculated Iodine Value | 115.0 | 111.2 | 113.5 | 113.4 | 210.0 | 211.7 | 210.9 | 211.0 | 108.0 | 107.3 | 141.6 | 141.9 |

Note: CME: canola methyl ester; CEE: canola ethyl ester; CPE: canola 2-propyl ester; CBE: canola butyl ester; LME: linseed methyl ester; LEE: linseed ethyl ester; LPE: linseed 2-propyl ester; LBE: linseed butyl ester; RME: rapeseed methyl ester; REE: rapeseed ethyl ester; SME: sunflower methyl ester; SEE: sunflower ethyl ester.

oil esters was oleic acid (18:1) averaging at 68 wt%. In the sunflower oil esters it was linoleic acid (18:2) at 68 wt%, and in linseed oil esters it was linolenic acid (18:3) at 62 wt%. These three fatty acids all have an 18 number carbon chain with the number of double bonds increasing from 1 to 3, respectively. Erucic acid (22:1) was the most common fatty acid found in rapeseed oil esters at average 54 wt%. All the vegetable oil esters had very highly unsaturated fatty acid content, ranging from about 88% (sunflower esters) to 97% (rapeseed esters). Palmitic (16:0) and stearic (18:0) were the only two saturated fatty acids, in minor amount, found in these esters.

3.4. Density

The densities of the four pure oils and their 12 bio-diesel esters at 25°C and arranged by the sources of vegetable oils and alcohols are presented in Table 3. The densities of the esters were significantly lower than that of the source oil and varied from 0.86 to 0.89 g/ml. For the different alkyl esters made from the same vegetable oil, the density decreased in the order of methyl ~ iso-propyl > ethyl > 1-butyl esters. The density of a No. 1 Canadian winter diesel fuel (LSD-43 Diesel Light) was 0.82 g/ml (Munson et al., 1999), while that of a No. 2 summer diesel fuel (C-5 Seasonal Diesel) was 0.86 g/ml (Galbraith and Hertz, 1997). Both diesel fuels (DFs) were not additized, and have been used as reference fuels in the related studies of bio-diesel ester as fuel lubricity additive. It may be noted that the density of the diesel fuel is influenced by the original crude oil and the refining steps to make the product. Also, the densities of the fuel during transitional period in spring and the end of summer are different when the refiner switches from

one product to the other. In comparison, the bio-diesel esters had on average 7% and 2% higher specific weight than the reference Nos. 1 and 2 DFs, respectively.

3.5. Viscosity

The dynamic viscosities at 40°C of the four vegetable oils and their esters are given in Table 4. The viscosity of the pure vegetable oils used in this study ranged from 2.24×10^{-3} Pa s (linseed oil) to 4.51×10^{-3} Pa s (rapeseed oil). After transesterification, the viscosity of their lower alkyl esters was reduced to the lowest value of 3.32×10^{-4} Pa s for LME to the highest viscosity of 7.60×10^{-4} Pa s for REE. For linseed and canola esters, the viscosity increased as the size of the alkyl group increased from methyl to butyl ester. Both 2-propyl esters of linseed and canola oils had higher viscosity, which in part could be due to the glyceride impurities in these two esters. For the same alkyl esters, their differences in viscosity were dependent on those of the vegetable oils. For example, the rapeseed oil was the most viscous one among the four oils; consequently, the viscosities of its methyl and ethyl esters were the highest in their respective series. The viscosities of the Nos. 1 and 2 DFs were 1.75 and 3.50×10^{-4} Pa s at 40°C, respectively. The bio-diesel esters had viscosity 1.9–4.2 times that of No. 1 DF and 0.95–2.2 times that of No. 2 DF.

3.6. Iodine value

Since the iodine value was only dependent on the origin of the vegetable oil, the bio-diesel esters made from the same oil showed similar iodine values, as shown in Table 2. The average iodine values of the bio-diesels were calculated to be 108, 113, 142, and 211

Table 3
Density of the vegetable oils and their esters

| Oils | Density at 25°C (g/ml) | | | | |
|-----------|------------------------|---------------|---------------|-------------------|-------|
| | Pure oil | Methyl | Ethyl | 2-Propyl | Butyl |
| Linseed | 0.925 | 0.887 | 0.884 | 0.888 | 0.877 |
| Canola | 0.912 | 0.875 ± 0.001 | 0.869 ± 0.001 | 0.874 | 0.861 |
| Sunflower | 0.914 | 0.882 | 0.876 | n.d. ^a | n.d. |
| Rapeseed | 0.908 | 0.877 | 0.873 | n.d. | n.d. |

^a Not determined.

Table 4
Viscosity of the vegetable oils and their esters

| Oils | Dynamic viscosity at 40°C (10^{-4} Pa s) ^a | | | | |
|-----------|--|-------------|-------------|-------------|-------|
| | Pure oil | Methyl | Ethyl | 2-Propyl | Butyl |
| Linseed | 22.4 | 3.32 | 3.64 ± 0.07 | 4.88 | 4.06 |
| Canola | 33.4 | 3.79 ± 0.06 | 3.91 | 6.24 ± 0.04 | 4.39 |
| Sunflower | 28.9 | 4.24 | 4.40 | n.d. | n.d. |
| Rapeseed | 45.1 | 5.18 | 7.60 | n.d. | n.d. |

^a 1×10^{-4} Pa s = 1 cP.

for rapeseed, canola, sunflower and linseed esters, respectively. The linseed esters had the highest iodine value because its major constituent was linolenic acid, a triple double-bond fatty acid. The iodine value of the conventional diesel fuel was approximately 10 (Peterson et al., 1997). Therefore, the bio-diesels had significantly higher degree of unsaturation than diesel fuel. When heating unsaturated fatty acids, polymerization of glycerides will occur, which may lead to the gum formation. This problem could be worse with the increase in the number of double bonds in the fatty acid chain. To ensure the quality of bio-diesel as alternative fuel, Mittelbach (1996) proposed to limit the unsaturated fatty acid in bio-diesel specifications, especially the content of higher unsaturated fatty acids, like linolenic acid.

3.7. Acid value

The acid value is defined as the milligrams of potassium hydroxide necessary to neutralize the free acids in 1 g of sample. The suggested ASTM standard for pure bio-diesel sets the maximum acid value (acid number) at 0.80 mg KOH/g while the German standard DIN V 51606 sets it at 0.5 mg KOH/g (Knothe et al., 1997). The acid values of various bio-diesel esters are listed in Table 5. Their numbers varied from low 0.15–0.16 mg KOH/g for REE and CME to highest 0.61 for SEE. Conventional diesel fuel possessed a very low acid value of 0.002.

3.8. Cloud point and pour point

The cloud point of any petroleum fuel oil is defined as the temperature at which a cloud of wax crystals first appears in the oil when it is cooled at a specific rate. The pour point is the lowest temperature at which the oil

specimen can still be moved. Both quantities are often used to specify cold temperature usability of fuel oils.

The cloud point and pour point of various bio-diesel esters of the four vegetable oils are shown in Table 6. The cloud points for ethyl esters were approximately 2°C lower than those of the corresponding methyl esters, while butyl esters of linseed and canola oil were 10°C and 7°C lower, respectively, than their methyl esters. The cloud points of the two branched-chain esters were rather high. Cloud formation was observed at the bottom of the test jar at 3°C and 7°C for LPE and CPE, respectively. In preparing the 2-propyl esters for cloud point determination, some crystals were separated from the samples by centrifuging before the measurements. These crystalline materials were shown by HPLC as mono- and diglycerides. Even after such pretreatment, the remaining impurities interfered with the observation, resulting in higher readings of cloud point. When Lee et al. (1995) measured the cloud and pour points for different branched-chain esters of soybean oil, they also observed similar interference of monoglyceride impurities with the cloud point of 2-butyl ester. However, they found that these impurities did not interfere with pour point measurement. Among all the bio-diesels, CBE had the lowest pour point of -16°C, while SEE had the highest of -5°C. Among the eight methyl and ethyl esters, the two rapeseed esters, RME and REE, showed much lower pour point of -15°C in comparison with the other ones. The primary fatty acid in the rapeseed oil/ester was erucic acid, having a *cis* double bond in its long carbon chains. This double bond hampered crystal packing thus resulted in a lower melting fatty acid, and consequently a lower pour point of its esters.

The cloud and pour points of No. 1 Canadian winter DF were -50°C and -51°C, respectively, which were much lower than those of all the bio-diesel esters. The No. 2 summer DF had cloud and pour points of -8°C

Table 5
Acid value of the bio-diesel esters

| Oils | Acid value (mg KOH/g) | | | |
|-----------|-----------------------|---------------|----------|-------|
| | Methyl | Ethyl | 2-Propyl | Butyl |
| Linseed | 0.335 | 0.324 | 0.586 | 0.254 |
| Canola | 0.163 ± 0.015 | 0.265 ± 0.028 | 0.469 | 0.280 |
| Sunflower | 0.179 | 0.610 | n.d. | n.d. |
| Rapeseed | 0.430 | 0.152 | n.d. | n.d. |

Table 6
Cloud point and pour point of the bio-diesels from vegetable oils

| Oils | Cloud point (°C) | | | | Pour point (°C) | | | |
|-----------|------------------|-------|----------|-------|-----------------|-------|----------|-------|
| | Methyl | Ethyl | 2-Propyl | Butyl | Methyl | Ethyl | 2-Propyl | Butyl |
| Linseed | 0 | -2 | 3 | -10 | -9 | -6 | -12 | -13 |
| Canola | 1 | -1 | 7 | -6 | -9 | -6 | -12 | -16 |
| Sunflower | 1 | -1 | n.d. | n.d. | -8 | -5 | n.d. | n.d. |
| Rapeseed | 0 | -2 | n.d. | n.d. | -15 | -15 | n.d. | n.d. |

Table 7

Gross heat of combustion of the vegetable oils and their esters

| Oils | H_g (MJ/kg) | | | | |
|-----------|---------------|--------------|--------------|----------|-------|
| | Pure oil | Methyl | Ethyl | 2-Propyl | Butyl |
| Linseed | 39.51 | 40.00 | 39.65 | 39.56 | 40.38 |
| Canola | 39.78 | 40.07 ± 0.16 | 40.41 ± 0.21 | 40.04 | 40.24 |
| Sunflower | 39.46 | 39.71 | 39.80 | n.d. | n.d. |
| Rapeseed | 40.27 | 40.43 | 40.97 | n.d. | n.d. |

and -15°C , respectively. These values were close to the cloud and pour points of LBE (-6°C and -16°C , respectively) and CBE (-10°C and -13°C , respectively). Using butyl alcohol, the cold flow properties of the bio-diesel were improved as the summer diesel fuel. Also, the pour points of RME and REE were comparable to those of the summer DF.

3.9. Heat of combustion

Heat of combustion measures the energy content in a fuel. It is an important property of the bio-diesels that

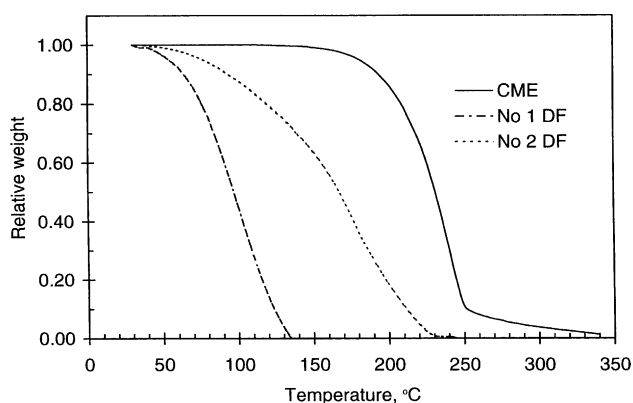


Fig. 2. TGA curves of the canola methyl ester and the reference diesel fuels. Conditions: ramp rate – $5^{\circ}\text{C}/\text{min}$; purge gas – N_2 at $50\text{ ml}/\text{min}$.

determines the suitability of these materials as alternative to diesel fuels. The gross heat of combustion of the four pure vegetable oils and the corresponding 12 esters is listed in Table 7. The values of the gross heat of combustion ranged from 39.56 (CPE) to 40.97 MJ/kg (REE) for various esters. These values were the same or slightly higher than those of the pure vegetable oils. The heat content of the diesel fuel was approximately 45 MJ/kg. The vegetable oil and their esters contained approximately 11% less heat energy on a mass basis. Since the densities of the bio-diesel esters were 2–7% higher than those of diesel fuels, the heat energy of the bio-diesels therefore was about 4–9% lower on a volume basis.

3.10. Thermogravimetric analysis

The TGA technique has been employed to yield information on the volatility of the bio-diesels since the volatility influences the ignition quality of the fuels in a compression ignition engine. A typical TGA profile of bio-diesel esters (CME) along with that of the two reference diesel fuel samples is shown in Fig. 2. The No. 1 winter DF was highly volatile even at room temperature. Its 5% distillation temperature, which is an indication of the potential onset of combustion, was 54.7°C (see Table 8). It rapidly evaporated when heated to 70°C and completely volatilized at approximately 135°C (Fig. 2).

Table 8

Volatilization and distillation temperatures from TGA

| Samples | Onset of volatilization ($^{\circ}\text{C}$) ^a | Distillation temperature ($^{\circ}\text{C}$) | | |
|-----------------|---|---|-------------|-------------|
| | | 10% | 50% | 90% |
| CME | 181.1 ± 5.2 | 194.1 ± 8.4 | 231.5 ± 6.0 | 251.7 ± 3.2 |
| CEE | 182.3 | 197.1 | 237.5 | 264.7 |
| CPE | 190.5 | 206.6 | 247.4 | 328.4 |
| CBE | 149.2 | 197.8 | 251.1 | 285.0 |
| LME | 176.1 | 188.8 | 229.5 | 246.7 |
| LEE | 178.4 | 191.9 | 231.7 | 298.6 |
| LPE | 178.7 | 192.6 | 234.6 | 326.1 |
| LBE | 173.2 | 197.1 | 249.6 | 332.8 |
| SME | 178.2 | 192.9 | 236.1 | > 350 |
| SEE | 187.3 | 202.3 | 247.3 | 320.3 |
| RME | 192.7 | 206.9 | 251.8 | 293.6 |
| REE | 203.2 | 220.5 | 274.4 | > 350 |
| No. 1 winter DF | 54.7 | 64.0 | 97.3 | 123.5 |
| No. 2 summer DF | 76.8 | 94.1 | 168.3 | 211.4 |

^a At 5% weight loss.

The No. 2 summer DF, being twice more viscous than the No. 1 DF, vaporized more slowly and lost 95% of its initial weight when heated up to 220°C. The onset of volatilization and distillation temperatures estimated from the TGA data for the 12 bio-diesel esters and the two diesel fuels are presented in Table 8. The data in Table 8 indicate that the bio-diesel esters were considerably less volatile in comparison to the diesel fuels. Taking CME as an example, it showed negligible weight loss when heated below 150°C. It only began rapid evaporation around 180°C. At 250°C, the volatile components in the CME, which accounted for approximately 90% of the weight, had been lost (see Fig. 2 and Table 8). The remaining 10% were much more viscous and a portion of it stayed in the pan until 350°C. The residue was completely burnt out after heating to 800°C when cleaning the pan. The TGA curves of other esters were similar to those of CME shown in Fig. 2, with varying onset and distillation temperatures depending on the composition of the esters. For different esters from the same vegetable oil, methyl esters were the most volatile ones. The volatility decreased as the alkyl group grew bulkier. The high content of long-chain unsaturated fatty acids in the bio-diesel contributed to its poor volatility and tendency to form a deposit at high temperature.

4. Conclusions

Alkali hydroxide and methoxide were equally capable as base catalysts for methyl ester synthesis from vegetable oils even at the ambient temperature. Only the sodium alkoxides were effective in the production of ethyl, 2-propyl and butyl esters, because of weaker acidity of the relevant alkanols in comparison to water.

HPLC analysis showed that the methyl, ethyl and butyl esters from four vegetable oils were free from impurities. Only trace amounts of impurities, mainly mono- and diglycerides were presented in 2-propyl esters.

Based on GC analysis, seven types of fatty acids in the vegetable oil esters were identified and quantified, and all these esters were about 90% unsaturated. The esters made from different vegetable oils had a unique dominant fatty acid compound. The difference in fatty acid composition apparently affected various fuel properties of the esters such as viscosity and pour point. The physical and fuel properties of ethyl esters in general were comparable to those of methyl ester from the same oil. The two butyl esters showed improved cold flow properties than both their methyl and ethyl counterparts. The heat of combustion of the vegetable oil esters was approximately 40 MJ/kg. Since the esters were denser, the energy content of a full tank of bio-diesel fuel would be only 4–9% less than the diesel fuel.

The esters were found to be considerably less volatile than the diesel fuels. Some residue was left from bio-diesels at 350°C, which could cause coke deposit on injectors in engines. However, compression ignition (diesel) engines generate a nonfiring temperature of about 800°C as air is compressed inside the combustion chamber (Heywood, 1988). Therefore, compression ignition of the esters as an alternative fuel should not be a problem.

Bio-diesels made from different vegetable oils and alcohols have compatible properties as conventional diesels, thus can be used as neat or blended fuels in diesel engines when economic condition permits. Some anti-gelling additives may be needed to improve the cold flow property if bio-diesels are used under severe winter conditions.

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