Moringa oleifera oil: A possible source of biodiesel

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Abstract

Biodiesel is an alternative to petroleum-based conventional diesel fuel and is defined as the mono-alkyl esters of vegetable oils and animal fats. Biodiesel has been prepared from numerous vegetable oils, such as canola (rapeseed), cottonseed, palm, peanut, soybean and sunflower oils as well as a variety of less common oils. In this work, Moringa oleifera oil is evaluated for the first time as potential feedstock for biodiesel. After acid pre-treatment to reduce the acid value of the M. oleifera oil, biodiesel was obtained by a standard transesterification procedure with methanol and an alkali catalyst at 60 °C and alcohol/oil ratio of 6:1. M. oleifera oil has a high content of oleic acid (>70%) with saturated fatty acids comprising most of the remaining fatty acid profile. As a result, the methyl esters (biodiesel) obtained from this oil exhibit a high cetane number of approximately 67, one of the highest found for a biodiesel fuel. Other fuel properties of biodiesel derived from M. oleifera such as cloud point, kinematic viscosity and oxidative stability were also determined and are discussed in light of biodiesel standards such as ASTM D6751 and EN 14214. The 1H NMR spectrum of M. oleifera methyl esters is reported. Overall, M. oleifera oil appears to be an acceptable feedstock for biodiesel.

1. Introduction

Biodiesel is defined as the fatty acid alkyl esters of vegetable oils, animal fats or waste oils. It is a technically competitive and environmentally friendly alternative to conventional petrodiesel fuel for use in compression-ignition (diesel) engines (Knothe et al., 2005; Mittelbach and Remschmidt, 2004). Biodiesel is biodegradable, renewable, non-toxic, possesses inherent lubricity, a relatively high flash point, and reduces most regulated exhaust emissions in comparison to petrodiesel. The use of biodiesel reduces the dependence on imported fossil fuels, which continue to decrease in availability and affordability.

Vegetable oils for biodiesel production vary considerably with location according to climate and feedstock availability. Generally, the most abundant vegetable oil in a particular region is the most common feedstock. Thus, rapeseed and sunflower oils are predominantly used in Europe; palm oil predominates in tropical countries, and soybean oil and animal fats in the USA (Knothe et al., 2005; Mittelbach and Remschmidt, 2004). However, biodiesel production from conventional sources (soybean, rapeseed, palm, etc.) increasingly has placed strain on food production, price and availability (Torrey, 2007). Therefore, the search for additional regional biodiesel feedstocks is an important objective. Some recent examples, studies of biodiesel from less common or unconventional oils include tobacco (Usta, 2005), Pongamia (Karmee and Chadha, 2005), Jatropha (Foidl et al., 1996) and rubber seed (Ikwuagwu et al., 2000; Ramadas et al., 2005) oils.

The Moringaceae is a single-genus family of oilseed trees with 14 known species. Of these, Moringa oleifera, which ranges in height from 5 to 10 m, is the most widely known and utilized (Morton, 1991; Sengupta and Gupta, 1970). M. oleifera, indigenous to sub-Himalayan regions of northwest India, Africa, Arabia, Southeast Asia, the Pacific and Caribbean Islands and South America, is now distributed in the Philippines, Cambodia and Central and North America (Morton, 1991). In Pakistan, M. oleifera is widely grown in the Punjab plains, Sindh, Baluchistan, and in the Northwestern Frontier Province (Qaiser, 1973). It thrives best in a tropical insular climate and is plentiful near the sandy beds of rivers and streams (Council of Scientific and Industrial Research, 1962). The fast growing, drought-tolerant M. oleifera can tolerate poor soil, a wide rainfall range (25 to 300+ cm per year), and soil pH from 5.0 to 9.0 (Palada and Changl, 2003). When fully mature, dried seeds are round or triangular shaped, and the kernel is surrounded by a lightly wooded shell with three papery wings (Council of Scientific and Industrial Research, 1962; Sengupta and Gupta, 1970; Qaiser, 1973). M. oleifera seeds contain between 33 and 41% w/w of vegetable oil (Sengupta and Gupta, 1970). Several...
authors investigated the composition of M. oleifera, including its fatty acid profile (Anwar and Bhanger, 2003; Anwar et al., 2005; Sengupta and Gupta, 1970; Somali et al., 1984) and showed that M. oleifera oil is high in oleic acid (>70%). M. oleifera is commercially known as “ben oil” or “behen oil,” due to its content of behenic (docosanoic) acid, possesses significant resistance to oxidative degradation (Lalas and Tsaknis, 2002), and has been extensively used in the enfeeble process (Council of Scientific and Industrial Research, 1962). M. oleifera has many medicinal uses and has significant nutritional value (Anwar et al., 2007). A recent survey conducted on 75 indigenous (India) plant-derived non-traditional oils concluded that M. oleifera oil, among others, has good potential for biodiesel production (Azam et al., 2005).

The objective of the present study was to explore the utility of M. oleifera methyl esters (MOME) as a potential source of biodiesel fuel. The important fuel properties of MOME were determined and are compared with other biodiesel fuels.

2. Experimental section

2.1. Materials

M. oleifera seeds were obtained from the University of Agriculture (Faisalabad, Pakistan). Pure standards of FAME were purchased from Sigma Chemical Company (St. Louis, MO). All other chemicals and reagents (methanol, n-hexane, sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide and anhydrous sodium sulfate) were analytical reagent grade and purchased from Sigma-Aldrich (St. Louis, MO, USA). All chemicals and reagents were used as received.

2.2. Property determination

Cetane numbers were determined as derived cetane numbers using the standard ASTM D6890 as described previously (Knouthe et al., 2003). ASTM D6890 is now approved as an alternative to the traditional cetane number standard (ASTM D613) in the biodiesel standard ASTM D6751. Kinematic viscosity was obtained with Cannon–Fenske viscometers employing the standard ASTM D445. Oxidative stability measurements were carried out with a Rancimat (Metrohm, Herisau, Switzerland; equipped with software for statistical evaluation) using the standard EN14112. Lubricity was investigated utilizing a high-frequency reciprocating rig (HFRR) lubricity tester following the method ASTM D6079 as described in the literature (Knouthe and Steidley, 2005). Cloud and pour point determinations were conducted with a Phase Technology (Richmond, BC, Canada) cloud, pour and freeze point analyzer. Acid values were determined with AOCS (American oil chemists’ society), method Cd3d-63, free and total glycerol by a slightly modified method ASTM D6584 and Na, K, P, S, Ca and Mg with an inductively-coupled plasma atomic emission spectroscopy (ICP-AES) instrument (Plasma 400; Perkin–Elmer Corp. Norwalk, CT).

The fatty acid profile was determined by gas chromatography using a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA, USA), equipped with a flame-ionization detector and a Supelco (Bellefonte, PA, USA) SP-2560 capillary column, (100 m × 0.25 mm i.d., 0.2 µm film thickness). The oven temperature ramp program was 175 °C for 5 min, 175–250 °C at 4 °C/min, and held for 20 min at 250 °C. Retention times were verified against authentic samples of individual pure fatty acid methyl esters. All relative percentages determined by GC for each fatty acid methyl ester sample are the means of triplicate runs. Additional determination of the fatty acid profile by 1H NMR spectroscopy was performed on a Bruker (Billerica, MA) Avance 500 spectrometer operating at 500 MHz with CDCl3 as solvent.

2.3. Extraction of M. oleifera oil

M. oleifera seeds (500 g) were crushed and placed in a Soxhlet extractor fitted with a 2-L round-bottomed flask and a reflux condenser. After extraction for 6 h with 0.80 L of refluxing n-hexane, the solvent was removed at 45 °C under vacuum using a rotary evaporator to afford crude M. oleifera oil (35% w/w). The acid value of the crude M. oleifera oil was 2.9, necessitating acid pre-treatment before transesterification.

2.4. Transesterification of M. oleifera oil

After acid pre-treatment using a literature procedure (Canakci and Van Gerpen, 2001) of M. oleifera oil reduced its acid value to 0.953, further methanolation of M. oleifera oil was conducted by a standard procedure employing a 6:1 molar ratio of methanol to vegetable oil (scale: 100 g M. oleifera oil) for 1 h at 60 °C with 1 wt% NaOCH3 as catalyst. After completion of the reaction, the mixture was cooled to room temperature without agitation, leading to separation of two phases. The upper phase consisted primarily of MOME and the lower phase contained glycerol, excess methanol and catalyst, soaps formed during the reaction, some entrained MOME and partial glycerides. After separation of the two phases by decantation, most excess methanol was removed from the upper MOME layer at 80 °C. The remaining catalyst was then removed by successive washes with distilled water. Finally, residual water was removed by treatment with Na2SO4, followed by filtration.

3. Results and discussion

3.1. M. oleifera oil

After extraction, Moringa seeds were found to contain 35% w/w oil, which is in agreement with previous literature (Anwar et al., 2005). Earlier studies describe the sterol, tocopherol and flavonoid content of crude M. oleifera oil. (Anwar et al., 2005; Lalas and Tsaknis, 2002).

The M. oleifera oil had an acid value of 2.9, necessitating acid pre-treatment prior to base-catalyzed transesterification. The kinematic viscosity of the parent oil was 29.63 mm2/s. The cloud point of M. oleifera oil was 5 °C and the pour point was 4 °C. The oxidative stability per Rancimat test was 15.32 h (standard deviation = 1.29 h), which is consistent with the presence of antioxidants occurring naturally in this oil (Lalas and Tsaknis, 2002) and the very low amount of polysaturated fatty acids.

3.2. Fatty acid profile of M. oleifera oil and its methyl esters

The fatty ester profile of the M. oleifera oil used here as determined by GC is given in Table 1 and agrees with prior literature on M. oleifera oil (Anwar and Bhanger, 2003; Anwar et al., 2005; Sengupta and Gupta, 1970; Somali et al., 1984). Also listed in Table 1 for comparison purposes are the fatty acid profiles of palm, rapeseed (canola), soybean and sunflower oils. As indicated by Table 1, oleic acid (72.2%) is the predominate fatty acid in M. oleifera oil. Also significant is the disproportionately high content (7.1%) of behenic (docosanoic; C22:0) acid in M. oleifera oil compared to other more conventional oilseed crops. M. oleifera oil contains a low amount (1.0% or less) of polysaturated fatty acid methyl esters (C18:2 and C18:3), which is a significant difference compared to other oils such as rapeseed (canola), soybean and sunflower. Besides GC, these results were confirmed by 1H NMR using a method described in the literature (Knouthe and Kenar, 2004), which showed a total content of monounsaturated fatty acids (C18:1...
and C20:1) of 74.5% with about 0.7% C18:2 and the remaining 24.8% comprised of saturated fatty acids. The 1H NMR spectrum is shown in Fig. 1, with one of the most notable features being the virtual absence of the signals of bis-allylic protons at approximately 2.8 ppm, which agrees with the low amount of polyunsaturated fatty acids present in M. oleifera oil. In summary, the fatty ester profile of M. oleifera oil differs from that of other common vegetable oils used as biodiesel feedstocks, which is also reflected in the fuel properties discussed below. It may be also noted that oils with high oleic acid content are being developed which would give biodiesel fuels with a reasonable balance of fuel properties, although other fatty acids may be even more advantageous with regards to specific fuel properties such as cold flow (Knothe, 2008).

3.3. Properties of M. oleifera methyl esters

The properties of MOME as largely determined by the esters are summarized in Table 2 together with the relevant specifications from the biodiesel standards ASTM D6751 and EN 14214 and discussed below for each individual property. Other properties as influenced by production or similar factors are briefly summarized below the discussion of the properties caused by the esters.

### Table 1

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Moringa oleifera</th>
<th>Palm&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Rapeseed&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Soybean&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Sunflower&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16:0</td>
<td>6.5</td>
<td>44.1</td>
<td>3.6</td>
<td>11</td>
<td>6.4</td>
</tr>
<tr>
<td>C18:0</td>
<td>6.0</td>
<td>4.4</td>
<td>1.5</td>
<td>4</td>
<td>4.5</td>
</tr>
<tr>
<td>C18:1</td>
<td>72.2</td>
<td>39.0</td>
<td>61.6</td>
<td>23.4</td>
<td>43.9</td>
</tr>
<tr>
<td>C18:2</td>
<td>1.0</td>
<td>10.6</td>
<td>21.7</td>
<td>32.2</td>
<td>63.8</td>
</tr>
<tr>
<td>C18:3</td>
<td>–&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.3</td>
<td>9.6</td>
<td>7.8</td>
<td>–&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>C20:0</td>
<td>4.0</td>
<td>0.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C20:1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.0</td>
<td>–</td>
<td>1.4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C22:0</td>
<td>7.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>other</td>
<td>1</td>
<td>1.1% C14:0</td>
<td>0.2% C22:1</td>
<td>Traces</td>
<td>Traces</td>
</tr>
</tbody>
</table>

<sup>a</sup> Data from Gunstone and Harwood, 2007. These values constitute averages of numerous samples.

<sup>b</sup> This may indicate traces (<1%) or absence of these fatty acids.

<sup>c</sup> Eicosenoic acid.

### Table 2

<table>
<thead>
<tr>
<th>Property</th>
<th>M. oleifera methyl esters</th>
<th>ASTM D6751</th>
<th>EN 14214</th>
</tr>
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<tbody>
<tr>
<td>Cetane number</td>
<td>67.07</td>
<td>47 min</td>
<td>51 min</td>
</tr>
<tr>
<td>Kinematic viscosity (mm²/s; 40 °C)</td>
<td>4.83</td>
<td>1.9–6.0</td>
<td>3.5–5.0</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>18</td>
<td>Report</td>
<td>–&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>17</td>
<td>–&lt;sup&gt;a&lt;/sup&gt;</td>
<td>–&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Oxidative stability (h)</td>
<td>3.61</td>
<td>3 min</td>
<td>6 min</td>
</tr>
<tr>
<td>Lubricity (HFRR; μm)</td>
<td>135, 138.5</td>
<td>–&lt;sup&gt;c&lt;/sup&gt;</td>
<td>–&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Not specified.

<sup>b</sup> Not specified. EN 14214 uses time- and location-dependent values for the cold-filter plugging point (CFPP) instead.

<sup>c</sup> Not specified. Maximum wear scar values of 460 and 520 μm are prescribed in petrodiesel standards EN 580 and ASTM D975.

3.3.1. Cetane number

The cetane number of M. oleifera methyl esters was determined to be 67.07 using an Ignition Quality Tester<sup>™</sup> (IQT<sup>™</sup>) described previously (Knothe et al., 2003). The cetane numbers of methyl oleate, methyl palmitate and methyl stearate are 59.3, 85.9 and 101, respectively, in the IQT<sup>™</sup> (Knothe et al., 2003). Considering that the other saturated fatty acid methyl esters (C20:0 and C22:0) in MOME as well as C22:1 likely have high cetane numbers, the high cetane number of MOME is well-explained. MOME appears to be a biodiesel fuel with one of the highest cetane numbers ever reported for a biodiesel fuel. M. oleifera-derived biodiesel easily meets the minimum cetane number requirements in both the ASTM D6751 and EN 14214 biodiesel standards, which are 47 and 51, respectively.

It may be noted that the heat of combustion of MOME (not determined experimentally during the course of this work) is well within the range of other biodiesel fuels. The heat of combustion of methyl oleate, the major component of MOME as well as C22:1 likely have high cetane numbers, the high cetane number of MOME is well-explained. MOME appears to be a biodiesel fuel with one of the highest cetane number requirements in both the ASTM D6751 and EN 14214 biodiesel standards, which are 47 and 51, respectively.

![Fig. 1. 1H NMR spectrum of M. oleifera methyl esters. The strong singlet peak at approximately 3.7 ppm is indicative of methyl esters. The signals of the olefinic protons can be found at about 5.4 ppm. The spectrum shows the virtual absence of polyunsaturated fatty acids as discussed in the text.](image-url)
heat of combustion, the European standard EN14213 for use of biodiesel as heating oil prescribes a minimum heat of combustion of 35,000 kJ/kg.

3.3.2. Cold flow

MOME displayed a cloud point 18 °C and a pour point of 17 °C (see also Table 2). These values are rather high and resemble those for palm oil which also contains even higher amounts of saturated fatty acids. However, the relatively high content of C22:0, which possesses an even higher melting point than C16:0 or C18:0, in *M. oleifera* oil likely has the effect of compensating for the higher amounts of saturated fatty acids in palm oil. The reason is that the cold flow properties of biodiesel are determined by the amounts of higher-melting components (usually the saturated esters) and not their nature (Imahara et al., 2006). Thus, decreasing the amounts of higher-melting saturated fatty esters is the only method for improving cold flow properties. The cloud point is the parameter contained in the biodiesel standard ASTM D6751, while the European standard EN 14214 prescribes the cold-filter plugging point (CFPP). The cloud point can be correlated with tests such as the CPPP and is more stringent as it relates to the temperature at which the first solids form in the liquid fuel (Dunn and Bagby, 1995).

3.3.3. Kinematic viscosity

The kinematic viscosity at 40 °C of MOME was determined to be 4.83 mm²/s at 40 °C. The kinematic viscosity values of methyl oleate, methyl palmitate and methyl stearate are 4.51, 4.38 and 5.85 mm²/s, respectively, at 40 °C (Knothe and Steidley, 2005a). The contributions of the C20:0, C22:0 and C20:1 esters, with the saturated esters being solids at 40 °C, would lead to high viscosity values. Thus, this result agrees well the viscosity values of the individual fatty ester components. *M. oleifera* methyl esters thus meet the requirements of both the ASTM D6751 and EN 14214 biodiesel standards, which prescribe viscosity ranges of 1.9–6.0 and 3.5–5.0 mm²/s, respectively.

3.3.4. Oxidative stability

The oxidative stability of MOME was determined by the Rancimat method EN 14112, which utilizes 3 g of material per test. The average of three tests was 3.61 h (standard deviation = 0.079 h). Thus, MOME met the oxidative stability requirement in the ASTM D6751 standard, which prescribes a minimum of 3 h but did not meet the minimum prescribed in the EN 14214 standard, which is 6 h. The oxidative stability of MOME is considerably reduced compared to the parent oil (see data discussed above). Possible explanations are that the antioxidants naturally present in *M. oleifera* oil are either deactivated through the transesterification process and/or removed by the subsequent purification or separation procedures.

3.3.5. Lubricity

Two tests of MOME using the high-frequency reciprocating rig (HFRR) lubricity tester gave ball wear scars of 135 and 138.5 μm. These values are well below the maximum values prescribed in the petrodiesel standards ASTM D975 and EN 590. Thus, MOME displays excellent lubricity, which is in accordance with the results on lubricity for biodiesel derived from other oils or fats (Knothe and Steidley, 2005b).

3.3.6. Other analyses

Other analyses do not deal with the fuel properties imparted by the major fatty ester components; rather they are a measure of issues such as the completeness of reaction, presence of contaminants and proper storage. However, minor components or contaminants analyzed by these methods can significantly the properties discussed above. The acid value of MOME synthesized in this work was 0.3914, well within the maximum of 0.5 set in the ASTM and EN biodiesel standards. Furthermore, the fuel met the free (0.015%) and total (0.22%) glycerol specifications set in the ASTM and EN biodiesel standards (0.02 for free glycerol and 0.24% and 0.25% for total glycerol in the ASTM and EN standards, respectively). Analyses by ICP-AES for a total of six other elements gave the following results for the *M. oleifera*-derived biodiesel fuel produced here: Na 0.4 ppm, K 1 ppm, P 0.2 ppm, S 2.4 ppm, Ca 0.1 ppm and Mg 0.02 ppm. Thus, extraneous elements should not pose a problem with *M. oleifera*-derived biodiesel fuel.

4. Conclusions

Biodiesel was prepared from *M. oleifera* oil by alkali-catalyzed transesterification with methanol after acid pre-treatment. Fuel properties such as cetane number, kinematic viscosity, oxidative stability and others were determined. The most conspicuous property of biodiesel derived from *M. oleifera* oil is the high cetane number of approximately 67, which is among the highest reported for a biodiesel fuel. The oxidative stability of *M. oleifera* based biodiesel fuel is also enhanced compared to other biodiesel fuels, although the cloud point is rather high. Thus, biodiesel derived from *M. oleifera* oil is an acceptable substitute for petrodiesel, also when compared to biodiesel fuels derived from other vegetable oils.

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References


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