Moringa oleifera oil: A possible source of biodiesel

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A B S T R A C T

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 technologically 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; Ramadhas 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
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 (Knöthe 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 determined using the standard EN14112. *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).

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 methanolysis 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% NaOCH$_3$ 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 Na$_2$SO$_4$, 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 mm$^2$/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; C$_{22}$: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 (C$_{18}$:2 and C$_{18}$:3), which is a significant difference compared to other oils such as rapeseed (canola), soybean and sunflower. Besides GC, these results were confirmed by $^1$H NMR using a method described in the literature (Knöthe and Kenar, 2004), which showed a total content of monounsaturated fatty acids (C$_{18}$: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.

#### 3.3.1. Cetane number

The cetane number of *M. oleifera* methyl esters was determined to be 67.07 using an Ignition Quality Tester™ (IQTTM) 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 IQTTM (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, is 40,092 kJ/kg (calculated from data in Lide, 1999). While neither biodiesel standards (ASTM D6751 and EN 14214) contain a specification regarding the heat of combustion, maximum wear scar values of 460 and 520 μm are prescribed in petrodiesel standards EN 580 and ASTM D975.
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 (Dunn, R.O., Bagby, M.O., 1995). 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).

3.3.4. 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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