JATROPHA CURCAS SEED OIL AS A VIABLE SOURCE FOR BIODIESEL

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Abstract

The purpose of the present study was to explore the utility of Jatropha (*Jatropha curcas*) seed oil for biodiesel production. The preliminarily evaluated Jatropha oil was transmethylated under optimized set of reaction conditions: methanol/oil molar ratio (6:1), sodium methoxide catalyst concentration (1.00%), temperature (65°C) and mixing intensity (600 rpm) providing 94.00% yield of Jatropha oil methyl esters (JOMEs)/biodiesel. The gas chromatographic (GC) analysis showed that JOMEs mainly comprised of six fatty acids: linoleic (49.75%), stearic (16.80%), oleic (13.00%), palmitic (12.15%), arachidic (5.01%) and gadoleic (2.00%) acids. ^{1}H-NMR spectrum of JOMEs was also recorded. The thermal stability of the JOMEs produced was assessed by thermogravimetric analysis (TGA). The fuel properties of the biodiesel produced were found to be within the standards specifications of ASTM D 6751 and EN 14214.

Introduction

Currently, fossil fuels are the main resources of energy meeting the world requirements. The fossil-based resources, such as gasoline, petro-diesel and natural gas are limited and insufficient for the future world's energy demands. In this connection there is much concern for search of renewable fuels.

"Biodiesel" is well known chemically as the mono-alkyl esters of long-chain fatty acids and is produced from several types of conventional and non-conventional vegetable oils and animal fats including those of used oils from the frying industry, soybean oil, rapeseed oil, tallow, rubber seed oil and palm oil (Tomasevic & Siler-Marinkovic, 2003; Shah *et al*., 2004; Ramadhas *et al.*, 2005; Ahmed *et al*., 2007). In the situation of rapidly growing energy requirements, the contribution of new and especially some non-food oils has to play a significant role (Chitra *et al*., 2005; Rashid *et al*., 2008; Chakrabarti & Ahmad, 2008; Rashid *et al*., 2009; Harun & Ahmed, 2009).

Jatropha curcas (Linnaeus), belonging to *Euphorbiaceae* family and the genus Jatropha is commonly known as Jamalghota (Soomro & Memon, 2007). Jatropha, a crop native to North American region is now distributed in several regions (Africa, India, South East Asia and China) across the World (Chitra *et al*., 2005).

It is reported that Jatropha seeds contain about 30 to 40% of oil (Kandpal & Madan, 1995). The presence of some anti-nutritional factors such as toxic phorbol esters and a high content of stearic acid (*ca* 17%) render Jatropha oil unfit for edible purposes (Shah *et al*., 2004). The most abundant fatty acid in Jatropha oil is linoleic (47.3%) followed by stearic (17.0%), oleic (12.8%), palmitic (11.3%) and arachidic (4.7%) acids (Adebowale & Adedire, 2006). Jatropha oil is looked up on as one of the most appropriate renewable alternative sources of biodiesel in terms of availability and cost.

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Houfang *et al*., (2009) investigated a two-step process consisting of pre-esterification and transesterification to produce biodiesel from crude *Jatropha curcas* L., oil. The yield of biodiesel by transesterification was higher than 98% in 20 min using 1.3% KOH as catalyst and a molar ratio of methanol to oil 6:1 at 64°C (Houfang *et al*., 2009). As a part of our systematic investigations of exploring indigenous vegetable oil resources for biodiesel production, efforts were made to evaluate the utility of Jatropha seed oil for biodiesel production. Biodiesel was characterized by GLC and ^{1}H-NMR. In addition the thermal stability and fuel properties of Jatropha oil biodiesel were appraised.

Materials and Methods

Materials: The seeds of *Jatropha curcas* harvested at botanical garden at University of Agriculture, Faisalabad (UAF) during 2007 were procured from Department of Botany, UAF, Faisalabad, Pakistan. Methanol, *n*-hexane, sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide and anhydrous sodium sulfate were purchased from Merck (Darmstadt, Germany). All the chemicals used were analytical reagent grade. Pure standards of fatty acid methyl esters were obtained from Sigma Chemical Co. (St. Louis, MO).

Extraction of oil: The crushed seeds (500 g) of each batch of Jatropha were extracted using a Soxhlet extractor on a water bath for 6 h with 0.8 L of *n*-hexane. After oil extraction, the excess solvent was distilled off reduced vacuum using a rotary evaporator (Eyela, N-N Series, Rikakikai Co. Ltd. Tokyo, Japan) at 45°C.

Transesterification reaction: The transesterification was carried out in a lab scale biodiesel reactor following the reaction conditions of our previous study (Rashid & Anwar, 2008). Briefly, 100 g of Jatropha oil, specified amount of $NaOCH_3$ were placed in a 250 mL round bottom flask. Mixture was stirred (600 rpm) at a temperature of 65°C for 120 min., for completion of transesterification reaction. Then the reaction mixture was transferred to a separating funnel for separation of two phases. Of the two separated phases; the upper phase consisted of methyl esters with small amounts of impurities such as residual alcohol, glycerol and partial glycerides, while the lower was the glycerol. The upper methyl esters layer collected was further purified by distilling residual methanol at 80°C (external bath temperature). Some traces of impurities such as remaining catalyst, residual methanol and glycerol were removed by successive rinses with distilled water. Residual water was then removed by drying esters with Na_2SO_4, followed by filtration using Whatman filter paper No.42. The yield of methyl esters was calculated using the following formula;

$$\text{Yield of methyl esters (\%)} = \frac{\text{grams of methyl esters produced}}{\text{grams of oil used in reaction}} \times 100$$

Fatty acid profile by GC: The analysis of the JOMEs/biodiesel was accomplished using a SHIMADZU gas chromatograph, model 17-A, fitted with a flame ionization detector (FID) and a methyl-lignocerate-coated polar capillary column SP-2330 (30 m × 0.32 mm × 0.25 μm; Supelco, Inc., Bellefonte, PA., USA.). The column temperature was programmed from 180 to 220°C at a linear flow rate of 5°C/min. The initial and final holds up time were 2 and 10 min, respectively, while the injector and detector were set at 230°C and 240°C, respectively. A sample volume of 1.0 μL was injected onto the column

in split mode (split ratio 1:75). All the quantitative measurements were made by Chromatography Station for Windows (CSW32) software (Data Apex Ltd. CZ-158 00 Prague 5, the Czech Republic). The fatty acid composition was reported as a relative percentage of the total peak area.

^{1}H-NMR verification of Jatropha oil methyl esters (JOMEs): ^{1}H-NMR spectrum of JOMEs was obtained using a Bruker (Billerica, MA) AV-500 spectrometer operating at 500 MHz with a 5-mm broadband inverse Z-gradient probe in CDCl3 (Cambridge Isotope Laboratories, Andover, MA, USA) as solvent and reference.

Thermal stability of JOMEs: The thermogravimetric (TG) data of the JOMEs were recorded using TGA apparatus (Gateway Airgas, St. Louis, MO). Dry nitrogen was flushed over balance chamber at a flow of 40 ml/min, while dry air was used over sample at flow of 60 ml/min. Using platinum pans, 10 μL of sample was taken. The thermo balance temperature was equilibrated at 50°C, and then increased to 600°C at a ramp rate of 10°C/min.

Fuel properties of JOMEs: The fuel properties of the biodiesel/JOMEs produced were determined following ASTM and EU specifications (ASTM, 2003; EN 14214, 2003). The determinations of density, kinematic viscosity, lubricity, flash point, cloud point, pour point, sulfur content, copper strip corrosion, ash content, acid value, ester contents, free and bound glycerol, mono, di and triglycerides were made in accordance with ASTM D 5002, ASTM D 445, ASTM D 6079, ASTM D 93, ASTM D 2500, ASTM D 97, ASTM D 4294, ASTM D 130, ASTM D 874, ASTM D 664, EN 14103 and ASTM D 6584, respectively. All the analysis was performed in triplicate and the data reported as mean ± standard deviation.

Results and Discussion

Quality of produced biodiesel: Table 1 depicts the fatty acid composition (FAC) of JOMEs (Fig. 1). Linoleic, stearic, oleic, palmitic, arachidic and eicosanoic acids were the main component of JOMEs with contribution present at 49.75, 16.80, 13.00, 12.15, 5.01 and 2.00%, respectively. Small amount (0.58%) of minor fatty acid C22:0 was also detected. The concentration of C18:2 of the investigated JOMEs/biodiesel were in close agreement with that of cottonseed oil methyl esters (COME). The content of stearic acid was quite high (16.80%). JOMEs has highest amount (35%) of saturated fatty acids (SFA) as compared to other vegetable oils methyl esters (Rashid & Anwar 2008; Rashid *et al*., 2009a; Rashid *et al*., 2009b).

    ^{1}H-NMR spectrum of methyl esters in general should present a signal in δ 3.7 that is characteristic of oxymethylic hydrogen referent to methylic esters and shouldn't present signals between δ 4.0-4.3 and δ 5.3, referent to hydrogen of CH$_2$ and CH glycerol group (Fig. 2). When compared ^{1}H-NMR spectrum of Jatropha oil with ^{1}H-NMR spectrum of JOME sample, it can be verified that there is a singlet in δ 3.64 that is characteristic of oxymethylic hydrogen, and this signal was attributed to esters (biodiesel), multiplet in δ 4.12-4.24 and δ 5.30-5.34 attributed to oxymethylic hydrogen that are characteristic of triglycerides from Jatropha oil. From the NMR data it could be verified that Jatropha oil conversion into biodiesel was quite complete.

Table 1. Fatty acid (FA) composition (g/100g of FA) of Jatropha oil methyl esters/JOMEs.

FA	JOMEs
$C_{16:0}$	12.15 ± 0.24
$C_{18:0}$	16.80 ± 0.60
$C_{18:1}$	13.00 ± 0.26
$C_{18:2}$	49.75 ± 0.87
$C_{20:0}$	5.01 ± 0.10
$C_{20:1}$	2.00 ± 0.04
$C_{22:0}$	0.58 ± 0.01
SFA	34.54
MUFA	15.00
PUFA	49.75

Values are mean ± SD of triplicate determinations
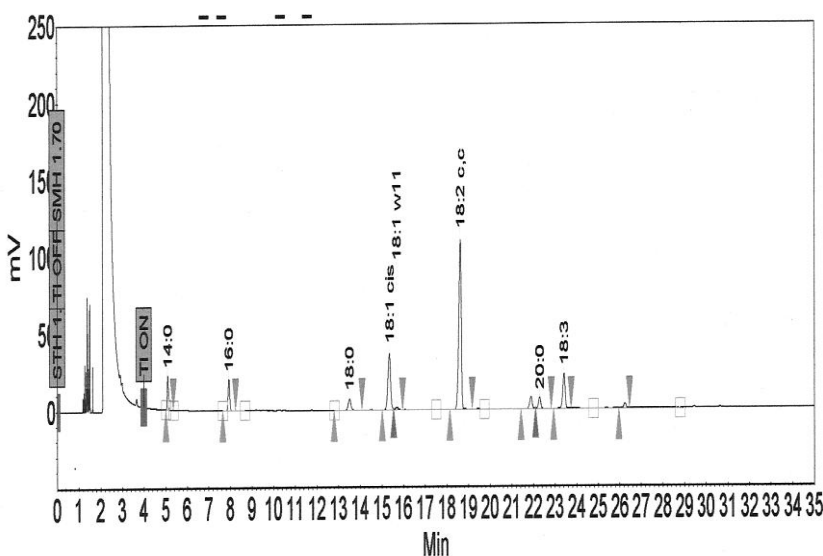SFA = Saturated fatty acids; MUFA = Mono unsaturated fatty acids; PUFA = Poly unsaturated fatty acids

Fig. 1. Gas chromatography (GC) chromatogram of Jatropha oil methyl esters (JOMEs).

Thermo-gravimetric analysis (TGA): It is widely known that for any kind of biodiesel, the boiling point will be the effective average of the types and quantities of esters of fatty acids present. The TGA analysis is quick and inexpensive technique and can be used to esters boiling point determination and to monitoring transesterification reaction, when one compares the parent oil TGA curve and esters TGA curve. Figure 3 shows the temperatures properties and loss mass that were found to sample JOMEs.

TGA curves of biodiesel/JOMEs showed 3 steps, where the first weight loss started to decrease at approximately 160°C, and this steps was attributed to a boiling point of biodiesel, the second one started to decrease at 200°C and it was attributed to boiling point of the esters with unsatured bondings, and the third step started to decrease at 218°C, and it may be due to some Jatropha oil that was not transesterified. TGA curve of JOMEs were attributed to boiling points of biodiesels/methyl esters with unsatured bondings, and did not show any step in 589°C, confirmed that the transesterification reaction was complete.
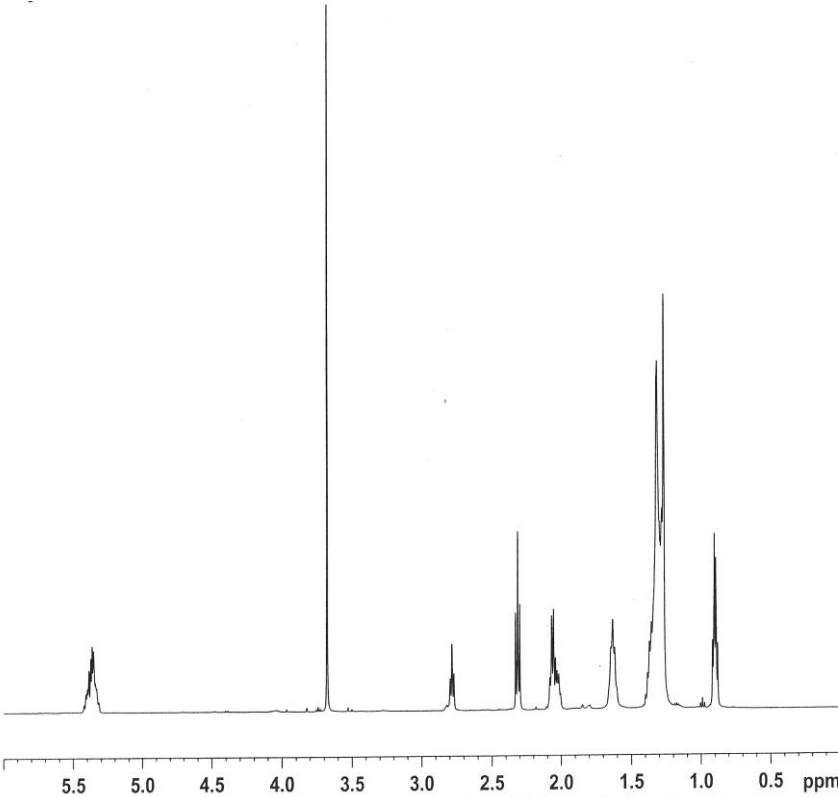
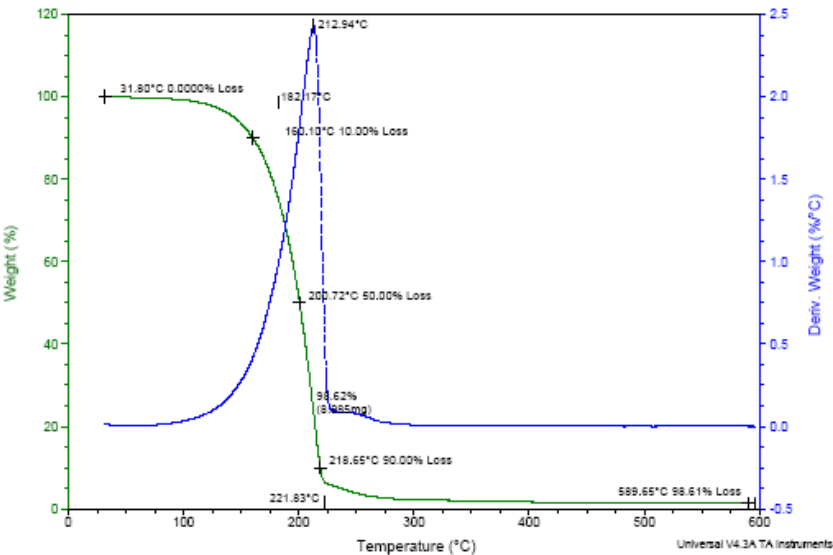Fig. 2. ¹H-NMR spectrum of Jatropha oil methyl esters (JOMEs).

Fig. 3. TGA spectrum of Jatropha oil methyl esters (JOMEs).

Table 2. Fuel properties of Jatropha oil methyl esters (JOMEs) / biodiesel.

Property	JOMEs	ASTM D6751	EN 14214
Kinematic viscosity (mm^2/s; 40 °C)	4.80 ± 0.17	1.9-6.0	3.5-5.0
Lubricity (HFRR; μm)	137 ± 1.3	_a)	_a)
Cloud point (°C)	10.0 ± 0.1	Report	_b)
Pour point (°C)	6.0 ± 0.2	_c)	_b)
Flash point (°C)	188 ± 3.0	93 min	120 min
Sulfur content (%)	0.011 ± 0.001	0.05 max	-
Ash content (%)	0.016 ± 0.001	0.02 max	0.02 max
Acid value (mg KOH/g)	0.40 ± 0.03	0.50 max	0.50 max
Copper strip corrosion (50 °C, 3 h)	1a	No. 3 max	No. 1 min
Density (15°C), kg.m^{-3}	880 ± 14.2	-	860-900
Ester contents (%)	96.80 ± 2.53	-	96.5% min

Values are mean ± SD of triplicate determinations

a) Not specified. Maximum wear scar value of 460 and 520 μm are prescribed in petro diesel standards EN 580 and ASTM D975

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

c) Not specified

Fuel properties of Jatropha oil methyl esters (JOMEs): The properties of JOMEs are summarized in Table 2 alongwith specifications from the biodiesel standards ASTM D6751 and EN 14214.

Kinematic viscosity: Kinematic viscosity limits are present both in ASTM D6751 (1.9-6.0 mm^2/s @ 40°C) and EN 14214 (3.5-5.0 mm^2/s @ 40°C), respectively for biodiesel fuels. Viscosity is a key fuel property because it persuades the atomization of a fuel upon injection into the diesel engine ignition chamber and ultimately, the formation of engine deposits (Knothe & Steidley, 2005). The viscosity of transesterified oil i.e., biodiesel, in the present study is lower than that of the parent oil. In the current study, JOMEs had kinematic viscosity (4.8 mm^2/s) that fell was within the scope of both the American and EU biodiesel specification ranges.

Lubricity: Lubricity determination was performed at 60°C according to the standard method ASTM D6079, with a HFRR lubricity tester obtained from PCS Instruments (London, England). Biodiesel standards do not currently contain lubricity specifications. Fuel with poor lubricity can cause failure of diesel engine parts that rely on lubrication by the fuel (Knothe *et al*., 2005). As such, lubricity has been included in the European petrodiesel standard EN 590 (CEN, 2004) and the American petro-diesel standard ASTM D975. The maximum wear scars are 460 μm in the EN 590 standard and 520 μm in the ASTM D975 standard. Three tests of JOMEs using the HFRR lubricity tester gave ball wear scars of 137 μm. These values are below the maximum values prescribed in the petro-diesel standards ASTM D 975 and EN 590, indicating that material would be acceptable with regard to lubricity. JOMEs also shows good lubricity, which is in accordance with the results on lubricity for biodiesel derived from other oils (Knothe & Steidley, 2005).

Low-temperature properties: Biodiesel is less appropriate for use at low temperature than petro-diesel. These are static tests that indicate first wax and non-flow temperatures for the fuel. The cloud point (CP) and pour point (PP) observed for JOMEs (CP 10°C, PP

6°C; Table 2), but, are not as high as observed for methyl tallowate (CP 17°C, PP 15°C) (Foglia *et al.*, 1997) but almost comparable to yellow grease methyl esters (CP 8°C, PP 6°C) (Wang *et al.*, 2005). Rapeseed methyl esters have better cold flow properties (CP -3°C, PP -9°C) (Rashid & Anwar, 2008), when compared to JOMEs.

Flash point: Flash point (FP) is an important factor to consider in the handling, storage, and safety of fuels and flammable materials. In the current work, the flash point determined for JOMEs (FP 188°C; Table 2), is within the prescribed limits in American and European biodiesel standards but it is also higher than that of No.2 diesel fuel.

Sulfur and ash contents: The sulfur contents of the JOMEs were analyzed using wavelength-dispersive X-ray fluorescence spectrometery by ASTM D 4294. The value was 0.011%, as depicted in Table 2. The presence of sulfur contents in biodiesel may be from vegetable oils, for example, from phospholipids present in all vegetable oils or glucosinolates present in Jatropha based biodiesel (Knothe, 2006). Ash content reflects the contents of inorganic contaminants, such as abrasive solids and catalyst residues, and the concentration of soluble metal soaps contained in a fuel sample. In the present study, the JOMEs had 0.016% of ash contents which were within the limits of ASTM standard.

Acid and copper strip corrosion values: The acid value was determined by using the ASTM D 974. The acid value of the biodiesel synthesized was 0.40 mg KOH/g (Table 1). The ASTM biodiesel standard D 6751 and European standard approved a maximum acid value for biodiesel of 0.5 mg KOH/g which was accomplished by the produced JOMEs. The copper strip corrosion test of the JOMEs was measured using a standard test specified by ASTM D 130. The degree of tarnish on the corroded strip correlates to the overall corrosiveness of the fuel sample. As depicted in Table 2, the value was No. 1 for the JOMEs. The copper strip corrosion property of the investigated methyl esters was found to be within the specifications of ASTM and EU methods.

Conclusion

The quality characteristics of biodiesel obtained in this work were in good agreement with ASTM D 6751 and EN 1424 specifications. Therefore, we can conclude that JOMEs is an acceptable and suitable substitute for diesel fuel. As the Jatropha crop has very good potential to be grown in Pakistan therefore it is recommended that it should be cultivated on large scale production to produce non-conventional oil that can be transmethylated into an acceptable biodiesel.

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