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PHYSICO-CHEMICAL PROPERTIES OF BIODIESEL PRODUCED FROM *Jatropha curcas* OIL AND PALM OIL

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ABSTRACT

Due to the increase in the petroleum fuel and edible oil prices and the continuous debate on fuel vs. *the food issue, effort has been taken to look into the possibility of using a cheaper non-edible feedstock for biodiesel production.* Jatropha curcas *oil is one of the non-edible feedstock which has been considered in recent years. In the present study,* J. curcas *oil was transesterified to jatropha oil methyl ester (JOME) and subjected to a full range biodiesel characteristics analysis. It was found that the fatty acid compositions of JOME are very different compared with palm biodiesel (methyl ester of refined, bleached and deodorised palm oil, RBDPOME). JOME consists of 43% methyl oleate and 34% methyl linoleate with total unsaturation of 79%, whereas RBDPOME consists of 39% methyl oleate and 10% methyl linoleate with total unsaturation of approximately 50%. Due to the higher degree of unsaturation especially the methyl linoleate, JOME has lower cold flow properties, namely the cloud point (4.6°C), pour point (3°C) and cold filter plugging point (0°C). JOME is more prone to oxidation and polymerisation, and possesses a lower cetane number when compared to RBDPOME.*

Keywords: biodiesel; *Jatropha curcas* oil; transesterification; refined, bleached and deodorised palm oil; palm biodiesel.

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INTRODUCTION

The fast depletion of world petroleum reserves; the increasingly uncertainty in the petroleum supply due to political and economical reasons; growing environmental awareness and increasing energy consumption worldwide have all stimulated the search for alternative sources of fossil fuels, especially petroleum diesel (Clark *et al.*, 1984; Choo *et al.*, 1997; Connemann and Fischer, 1998; Patel *et al.*, 1999; Knothe and Dunn, 2001). Biodiesel, chemically known as fatty acid methyl ester, has been identified as an important alternative fuel. The common process adopted by most of the biodiesel producers in the world is the transesterification process, in which the vegetable oils react with methanol in the presence of an alkaline catalyst to form methyl ester, the main product, and glycerol, the by-product.

Biodiesel can be produced from various oils and fats depending on the geographical location and availability. For example, rapeseed oil in European countries (Connemann and Fischer, 1998; Mittelbach and Enzelsberger, 1999; Cvengros, 1999), soyabean oil in the USA (Clark *et al.*, 1984; Ali *et al.*, 1995; Chang *et al.*, 1996) and palm oil in South-east Asia, especially in Malaysia and Indonesia (Choo *et al.*, 1995; 1997; 2005). However, the above-mentioned vegetable oils are also heavily used as food products and by converting these oils into biodiesel, it will create a shortage of edible oils in the supply chain. In this context therefore, *Jatropha curcas* oil, a non-

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edible oil has gained much attention in the past few years (Foidl *et al*., 1996; Shah *et al*., 2004; Sarin *et al*., 2007).

J. curcas originated from Central America (Henning, 2002; Schmidt, 2003; Tomomatsu *et al*., 2007). It is a small tree and can grow up to 5-7 m high (*Figure 1*). It has smooth leaves, four to six lobed and 10-15 cm in length and width (Achten *et al*., 2008). It grows well in areas of more than 600 mm of rainfall per year, and it withstands long periods of drought (Kheira and Atta, 2009). It is presently cultivated in tropical and sub-tropical countries of South America, Africa, India and South-east Asia, *i.e.* Indonesia and the Philippines. *J. curcas* is considered to be one of the alternative feedstocks for biodiesel production mainly because of its adaptability to marginal land. It has been reported that the oil yield per hectare of *Jatropha* planted land is about 1000 litres (Schmidt, 2003). If *J. curcas* is to be cultivated on fertile soil with an average rainfall of 900-1200 mm, 5 t oilseed per hectare can be harvested per annum. It is envisaged that an oil yield of 4 t ha^{-1} yr^{-1} is achievable, if good cultivation is coupled with efficient extraction mechanisms where the use of the mechanical screw press system is practiced (Achten *et al*., 2008). The pictures of *Jatropha* fruits and seeds are shown in *Figures 2* and *3*.

In the present study, the physico-chemical properties of refined, bleached and deodorised palm oil methyl ester (RBDPOME) and *Jatropha* oil methyl ester (JOME) are discussed. This article aims to provide a better understanding of JOME with the use of RBDPOME as a reference.

Figure 1. Jatropha curcas *tree.*

Figure 2. Unripe Jatropha *fruits.*

Figure 3. Ripe Jatropha *fruit and seeds.*

MATERIALS AND METHODS

Materials

Refined, bleached and deodorised (RBD) palm oil was obtained from a local palm oil refinery, while *J. curcas* oil was obtained from a local non-commercial source. A reagent grade of methanol and an ISO grade of sodium hydroxide were purchased from Merck.

Transesterification Methods

The acidity of the oil used was determined. Transesterification reaction was conducted in a 5-litre conical flask equipped with a reflux condenser and a magnetic stirrer. Oil (2000 g) was mixed with methanol in the molar ratio of methanol to oil of 10:1 in the presence of sodium hydroxide as catalyst at 0.5% concentration based on the weight of the oil used. The reaction mixture was stirred, heated to 60°C and remained at reflux temperature for 2 hr. The reaction was monitored using thin layer chromatography. After the reaction was completed, the ester layer was separated from the glycerol layer, and the ester layer was washed with distilled water until the washing was neutral. The neutralised esters were dried under vacuum.

Analyses

Fatty acid compositions (FAC) of RBDPOME and JOME were analysed by GC equipped with a flame ionisation detector (FID) in accordance to EN 14103 and the GC conditions are listed in *Table 1*. Identification of each peak was done by comparison with standard reference mixture of fatty acid methyl esters. The identified peaks areas were normalised after correction with linear detector response factors for quantification of weight percentages of each component, and omitting the internal standard methyl heptadecanoate.

The methyl esters (biodiesel) synthesised were analysed in accordance to the ASTM or EN standard methods as shown in *Table 4.*

The vitamin E content was determined using HPLC. The following conditions were used: Lichrosorb analytical silica column (25 × 0.46 cm ID, 5 μm), solvent system was n-hexane:THF:2-propanol (1000:50:3 v/v/v) with flow rate at 1.0 ml min^{-1} and a Waters 470 Fluorescence detector at 295 nm excitation and 325 nm emission.

TABLE 1. GAS CHROMATOGRAPHY CONDITIONS

Gas chromatograph	Agilent 7890
Inlet temperature	250°C
Split ratio	80:1
Injection volume	1 µl
Column flow (He)	1.5 ml min^{-1}
FID temperature	300°C
H_2 flow	40 ml min^{-1}
Air flow	400 ml min^{-1}
Make up (He)	40 ml min^{-1}
Oven program	210°C, hold 9 min; 210°C to 230°C at 20°C/min, hold 10 min
Column	J&W DB-WAX, 30 m x 0.25 mm x 0.25 µm

TABLE 2. PERCENTAGE OF FREE FATTY ACID (FFA) IN REFINED, BLEACHED AND DEODORISED (RBD) PALM OIL AND *Jatropha curcas* OIL

Oil	FFA %
RBD palm oil	0.1*
J. curcas oil	1.63**

Note: *As palmitic acid.
**As oleic acid.

RESULTS AND DISCUSSION

As shown in *Table 2*, the percentage of free fatty acids (FFA) in *J. curcas* oil (1.63%) is higher than in RBD palm oil (0.1%). This is mainly because the *J. curcas* oil is a crude oil extracted from *Jatropha* seeds without any neutralisation and/or refining process. Hence, additional 4.6 g of sodium hydroxide was added to neutralise the FFA in the *Jatropha* oil during the transesterification process.

The FAC of RBDPOME and JOME are distinctively different as shown in *Table 3*. The main carbon chains of RBDPOME are C16:0 and C18:1 whereas JOME mainly consists of C18:1 and C18:2. The RBDPOME consists of 50% saturation and 50% unsaturation but JOME is about 21% saturation and 79% unsaturation. The differences in the FAC contribute to the significant differences in some

TABLE 3. TYPICAL FATTY ACID COMPOSITION OF METHYL ESTERS OF REFINED, BLEACHED AND DEODORISED PALM OIL (RBDPOME) AND *Jatropha curcas* OIL (JOME)

Fatty acid composition (%)	RBDPOME	JOME
C10:0	ND	0.10
C12:0	0.27	ND
C14:0	0.81	0.10
C16:0	44.33	14.10
C16:1	0.19	0.65
C18:0	4.97	6.85
C18:1	39.12	43.69
C18:2	10.11	34.21
C18:3	0.20	0.15
C20:0	ND	0.15
Total unsaturated fatty acids	50.38	78.70
Total saturated fatty acids	49.62	21.30

Note: ND: non-detectable.

TABLE 4. PHYSICO-CHEMICAL PROPERTIES OF METHYL ESTERS OF REFINED, BLEACHED AND DEODORISED PALM OIL (RBDPOME) AND *Jatropha curcas* OIL (JOME)

Property	Unit	RBDPOME	JOME	EN 14214:2003	ASTM D6751:07b
Ester content	% mass	98.5	98.8	96.5 (min.)	-
Density at 15°C	kg litre^{-1}	0.8783	0.8794	0.860 - 0.900	-
Viscosity at 40°C	mm^2 s^{-1}	4.415	4.352	3.50 - 5.00	1.9 - 6.0
Flash point	°C	182.0	177.0	120 (min.)	130 (min.)
Sulphur content	mg kg^{-1}	1.2	1.6	10 (max.)	15 (min.) (Grade S15) 500 (min.) (Grade S500)
Carbon residue	% mass	0.02[a]	0.14[a]	0.30 (max.)[a]	0.05 (max.)[b]
Cetane number[c]	-	74.1	63.7	51 (min.)	47 (min.)
Sulphated ash content	% mass	<0.01	<0.01	0.02 (max.)	0.02 (max.)
Water content	% mass	0.014	0.018	0.05 (max.)	0.05 (max.)
Copper strip corrosion (3 hr at 50°C)	rating	1a	1a	Class 1	3 (max.)
Oxidative stability, 110°C	hr	16.0	4.2	6 (min.)	3 (min.)
Acid value	mg KOH g^{-1}	0.25	0.17	0.5 (max.)	0.5 (max.)
Iodine value	-	52.0	92.8	120 (max.)	-
Linolenic acid methyl ester	% mass	0.20	0.15	12 (max.)	-
Polyunsaturated methyl esters (≥ 4 double bonds)	% mass	<0.01	<0.01	1 (max.)	-
Methanol content	% mass	<0.01	<0.01	0.20 (max.)	0.2 (max.)
Monoglyceride content	% mass	0.37	0.60	0.80 (max.)	-
Diglyceride content	% mass	0.12	0.04	0.20 (max.)	-
Triglyceride content	% mass	0.02	<0.01	0.20 (max.)	-
Free glycerol	% mass	<0.01	<0.01	0.02 (max.)	0.02 (max.)
Total glycerol	% mass	0.113	0.160	0.25 (max.)	0.240 (max.)
Distillation, T90 AET[d]	°C	343.5	341.4	-	360 (max.)
Gross calorific value	MJ kg^{-1}	39.8	39.6	-	-
Cloud point	°C	15.2	4.6	-	Report
Pour point	°C	15	3	-	-
Cold filter plugging point	°C	15	0	-	-

Note: EN14214:2003 Automotive fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods.
ASTM D 6751:07b Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels.
[a] Carbon residue on 10% distillation residue.
[b] Carbon residue on 100% sample.
[c] Derived cetane number measured in accordance with ASTM D6890-08 Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber.
[d] Distillation temperature, atmospheric equivalent temperature, 90% recovered.

physico-chemical and fuel properties (*Table 4*) for example the cold flow properties, oxidative stability, iodine value and the ignition quality (cetane number).

The cetane number of JOME is slightly lower than that of RBDPOME. The higher the level of unsaturation in the methyl esters, the lower is the cetane number (Knothe *et al.*, 2003; Knothe, 2005a). A cetane number which is too high or too low can cause operational problems to the diesel engines such as incomplete combustion (Mittelbach and Remschmidt, 2004; Knothe, 2005b). In terms of oxidative stability, RBDPOME is much more stable than JOME. Rancimat induction period (IP) of RBDPOME is 16 hr, similar to the IP previously reported (Frohlich and Schober, 2007; Xin *et al.*, 2008), and is much higher than the IP of JOME (4.2 hr). The difference in the IP is due to the fact that JOME consists of a higher percentages of unsaturated methyl oleate (C18:1) and methyl

TABLE 5. VITAMIN E COMPOSITION IN METHYL ESTERS OF REFINED, BLEACHED AND DEODORISED PALM OIL (RBDPOME) AND *Jatropha curcas* OIL (JOME)

Vitamin E	α-tocopherol (mg kg^{-1})	α-tocotrienol (mg kg^{-1})	γ-tocotrienol (mg kg^{-1})	δ-tocotrienol (mg kg^{-1})
RBDPOME	50	91	350	53
JOME	ND	ND	ND	ND

Note: ND: non-detectable.

linoleate (C18:2), which are more susceptible to oxidation compared to saturated methyl esters (Knothe and Dunn, 2003; Sarin *et al*., 2007; NREL, 2009). In fact, the effect of methyl linoleate in lipid autoxidation is much greater than methyl oleate (Cosgrove *et al*., 1987). Furthermore, the presence of natural antioxidants in particular the vitamin E, *i.e*. α-tocopherol, α-tocotrienol, γ-tocotrienol and δ-tocotrienol, which are originally present in the RBD palm oil, remain intact in the RBDPOME under the mild transesterification reaction conditions, hence have significantly contributed to the high IP over JOME. In comparison, no vitamin E were detected for JOME (Table 5). The IP of JOME (4.2 hr) was reduced to 2.58 hr and 0.04 hr after storing it in a closed transparent bottle (exposed to light) for one month and four months, respectively. This further explains the instability of fatty acid methyl esters with a higher level of polyunsaturation and the importance of antioxidants.

The cold flow properties, *i.e.* cloud point, pour point and cold filter plugging point (CFPP) of JOME are much lower than that of RBDPOME (*Table 4*), mainly due to the presence of higher percentages of polyunsaturated methyl esters, *i.e*. methyl linoleate and the lower percentage of the saturated methyl palmitate.

CONCLUSION

Judging from their physico-chemical properties, it is clear that both RBDPOME and JOME are biodiesel fuels that can be used as a diesel substitute. Both RBDPOME and JOME exhibit comparable properties, with JOME having better cold flow properties, while RBDPOME possesses better stability. Thus, JOME is suitably used as a fuel in temperate countries but cannot withstand oxidation and *vice versa* for RBDPOME. The RBDPOME can be easily produced from palm oil which is commercially and abundantly available but its production has been criticised due to food *vs*. fuel issue. On the other hand, *J. curcas* oil is non-edible and its use for fuel will not compete with the food market. It is not yet commercially available and therefore its supply for JOME remains an issue. Many other issues, for example, the competing use of arable land for *Jatropha* farming, the presence of toxic substances in *Jatropha* oil and the highly labour intensive harvesting mechanism of *Jatropha* fruits remain unsolved. It needs an intensified and holistic R&D programme to realise the use of this oil as a potential source of biofuel.

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