

BLENDING STUDY OF PALM OIL METHYL ESTERS WITH JATROPHA OIL METHYL ESTERS TO IMPROVE FUEL PROPERTIES

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Abstract

Palm oil methyl esters (POMEs) showed high induction period (IP) of 21.15 h whereas Jatropha oil methyl esters (JOMEs) exhibited significantly lower value of 4.6 h. The IP of JOMEs was improved during the blending with POMEs. Gas Chromatography (GC) analysis of blended biodiesel indicated the reduction in saturated fatty acids and increase in unsaturated fatty acids as compared to pure POMEs. Due to reduction in saturated fatty acids of blended biodiesel, a significant improvement was observed in the cold flow properties. Moreover, important fuel properties i.e. kinematic viscosity, water content, density and acid values of POMEs and JOMEs and their blends were determined. All the tested fuel properties were within the specified permissible limits of biodiesel standards (ASTM D6751 and EN 14214).

Keywords: Palm oil; Jatropha oil; Gas chromatography; Induction period; Cold flow properties.

1. Introduction

Rapid human population and industrial developments are leading towards the depletion of limited fossil fuel resources (gasoline, petro-diesel and natural gas) of the world. In view of the anticipated shortage of fossil fuels, much effort is currently devoted towards exploration of alternative renewable fuels [1]. Several types of liquid fuels derived from biomass such as bio-ethanol, bio-methanol, and methyl esters from vegetable oil/animal fat have been searched as an alternative to fossil fuels [2,3].

Biodiesel is an alternative diesel fuel consisting of alkyl esters of fatty acids derived from vegetable oils or animal fats [4]. The production of biodiesel involves conversion of vegetable oils/fats to fatty acid methyl esters (FAMEs), using methanol and a catalyst through a process termed as "transesterification". In this reaction, an alcohol, preferably methanol is allowed to react with triglycerides in the presence of a strong acid or base catalyst, producing fatty acid alkyl esters and glycerol [2, 5-7].

Malaysia is the largest producer of palm oil in the world. Almost all of the currently processed oils in the biodiesel industry come from edible vegetable oil sources. Using edible oil sources has contributed in the rising prices of food sources worldwide and adds more burdens on the population. In this context, research on non-edible vegetable oils as sources for biodiesel synthesis has been carried out [4,8]. Nowadays, there is growing interest in the use of Jatropha curcas as a raw material for biodiesel production. It had been found that Jatropha seeds yield good amount of oil between 30-40 weight percent [9]. With high amount of oil that can

extracted from the seeds and possibility of synthesizing biodiesel from the oil, Jatropha seed oil can be regarded as a good non-edible source for biofuel production in Malaysia.

Vegetable oils consist of natural antioxidants that tend to increase the oxidation stability of fuel but as the vegetable oils are subjected to higher temperature conditions, the natural antioxidants present in the oil start deteriorating at a faster rate, thereby, decreasing its stability [8]. As the biodiesel comes in contact with engine, it gets heated leading to the decrease in fuel stability. Xin et al. [9] studied the oxidation stability of biodiesel prepared from supercritical methanol method.

The blending of FAMEs prepared from different feedstocks to improve fuel property has been reported previously. Moser [10] studied the blending FAMEs from canola, palm, soybean and sunflower oils along with palm, rapeseed and soybean blends. In another study, Park et al. [11] also discussed the castor, cotton seed and soybean blends as well as canola, castor, cotton seed and soybean. Alternatively, Yusup and Khan [12] evaluated the pre-blended palm oil and rubber seed oil biodiesel for fuel properties. In this paper, blending of palm oil methyl esters (POMEs) with Jatropha oil methyl esters (JOMEs) was done to improve the fuel properties of blended biodiesel especially the induction period and cold flow properties. Efforts were also done to determine the effect of fatty acid composition in the blended biodiesel on oxidation stability and cold flow properties as well.

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2. Experimental

2.1. Materials

The crude *Jatropha* oil was procured from Bionas Sdn. Bhd. Malaysia and crude palm oil was supplied from Felcra Bhd. Perak, Malaysia. The standards of fatty acid methyl esters were attained from Sigma Chemical Company (St. Louis, MO, USA). The chemicals and reagents used were analytical purity grade and acquired from Merck Chemical Company (Darmstadt, Germany).

2.2. Pretreatment

Before base catalyst transesterification, pretreatment of the Palm and *Jatropha* oils were done with methanol using H_2SO_4 as a catalyst due to the high acid values of crude palm (1.12 mg KOH/g) and *Jatropha* (8.77 mg KOH/g) oils using previously reported method [13].

2.3. Transesterification

Transesterification was carried out in the round bottom flask with thermocouple, sampling port and reflux condenser. The reactants were heated in water bath on hot plate and stirred by magnetic stirrer [1]. Methanolysis of palm and *Jatropha* oils were done with sodium methoxide catalyst (1.0 % with respect to oil), 6:1 molar ratio of methanol to oil, 65 °C reaction temperature and 60 min reaction time. After the completion of reaction, the reacted material was shifted into separating funnel and kept in a state of equilibrium for the complete separation of two divergent phases. From the two clearly separated phases, the upper layer consisted of methyl esters, whereas the lower phase contained glycerol and other contaminants (un-used methanol, un-reacted catalysts, soaps derived during the reaction, some suspended esters and partial glycerides). The purified methyl esters layer was collected by distilling off residual methanol. The un-reacted catalyst and glycerol were eliminated through successive distilled water washings. Then residual contents of water were dried with sodium sulfate followed by filtration [1]. The biodiesel yield (%) was determined using the following formula;

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

2.4. Analytical Procedure

The prepared fatty acid methyl esters (FAMES) of palm- and *Jatropha* oils were analysed according to the method established by Rashid

and Anwar [1] using GC 2010 SHIMADZU, Japan equipped with FID detector and BP1 (Supelco, Bellefonte, PA) column (30 m × 0.25 mm i.d.; film thickness 0.20 µm). Nitrogen was used as a carrier gas at a flow rate of 1.0 mL min⁻¹. Column temperature was programmed from 100 to 240 °C at the rate of 10 °C/min. Initial and final temperatures were held for 1 and 10 min, respectively. Injector and detector were set at 250 °C and 260 °C, respectively. The fatty acid composition was reported as a relative percentage of the total peak area. The FAMES were identified by comparison to the retention time of reference standards.

2.5. Blending Of Samples

In the present study, following post-blends were prepared; 20, 30, 40, 50, 60, 70, 80 vol%. The measured amount of POMEs and JOMEs were put in a beaker with continuous stirring to ensure the uniform mixing. Blends were analyzed for oxidative stability, cloud point, pour point, kinematic viscosity, water content and acid value.

2.6. Fuel Properties

The following properties of the biodiesel produced were determined: kinematic viscosity (ASTM D 445), cloud point (ASTM D 2500), pour point (ASTM D 97), water content (ASTM D 95) and acid value (ASTM D 664). The oxidative stability of blended biodiesel samples were also determined with the Model 873 Rancimat (Metrohm AG, Herisau, Switzerland) following standard EN14112. The samples of 3 g, held in heating block at 110 °C, were analyzed under constant airflow of 10 L/h. All determinations of induction period (IP) were performed in triplicate and reported as IP.

3. Results And Discussion

3.1. Parent Oil Characteristics

Crude *Jatropha* oil had following properties; kinematic viscosity at 40 °C, 38.9 mm² s⁻¹; acid value (AV), 8.77 mg KOH g⁻¹ and water content 0.022 %. Whereas, crude palm oil showed that kinematic viscosity at 40 °C was 34.8 mm² s⁻¹; acid value (AV) was 1.22 mg KOH g⁻¹ and water content 0.035 %.

3.2. Quality Of POMEs, JOMEs And Their Blend

The quality of produced POMEs, JOMEs and their blend in terms of fatty acid profile was evaluated using gas chromatography (GC) as shown in Table 1. The major fatty acids (FAs) in Palm oil are palmitic (42.77 %) and oleic (41.72 %) with negligible amounts of palmitoleic

and linolenic. Jatropha oil has 40.82 % oleic acid and 34.99 % linoleic acid as major FAs. The major difference between Jatropha and palm oil is the higher amount of palmitic acid in the latter (42.77 %). The detected fatty acids are grouped into three major categories: saturated FA (SFA) containing palmitic (C16:0) and stearic (C18:0), unsaturated FA (USFA) containing palmitoleic (C16:1), oleic (C18:1), linoleic (C18:2) and linolenic (C18:3) acids. The percent composition of these categories SFA, and USFA of POMEs, JOMEs and its equivolume blend is shown in Table 1. POMEs (47.69 %) has the highest amount of saturated fatty acids (SFA) followed by equivolume blend (50:50) of POMEs and JOMEs (35.69 %) and the least amount in JOMEs (23.08 %). USFA are highest in JOMEs (76.66 %) followed by blended biodiesel (63.74 %), and least in POMEs (51.81 %).

Table 1 : Fatty acid profiles (area %) of POMEs, JOMEs and their equivolume (vol %) blend

Fatty acids	POMEs	JOMEs	Blend
Palmitic acid	42.77	15.28	30.61
Palmitoleic acid	0.16	0.66	0.27
Stearic acid	4.92	7.8	5.08
Oleic acid	41.72	40.82	39.50
Linoleic acid	9.68	34.99	23.77
Linolenic acid	0.25	0.19	0.20
Σ Saturated	47.69	23.08	35.69
Σ Unsaturated	51.81	76.66	63.74

POMEs=Palm oil methyl esters; JOMEs=Jatropha oil methyl esters

3.3. Blending Of POMEs With JOMEs

Figure 1 depicts the oxidative stability of POMEs, JOMEs and their different blends. POMEs (21.15 h) have the highest induction period (IP) and the smallest IP observed for JOMEs (4.6 h). As depicted in Figure 1, when the POMEs were blended with JOMEs, the induction period of the blended biodiesel increased with the volume percentage of POMEs. Our trends of results are in line with the reports of Park et al. [11] and Knothe [14]. The reason for higher induction period in case of POMEs is the presence of low amount of polyunsaturated fatty acids in palm oil as compared to Jatropha oil because polyunsaturated fatty acid content was an important factor for determining the oxidation stability [11]. In another study, Knothe [14] reported that saturated fatty acid compounds had considerably higher melting points than unsaturated fatty acids. In the present study, POMEs have higher amount of saturated fatty

acids (47.69 %) than JOMEs (23.08 %). When POMEs are blended with JOMEs up to 50 %, the oxidation stability or IP of the blended biodiesel satisfied the limit of 6 h for ASTM D6751 standard.

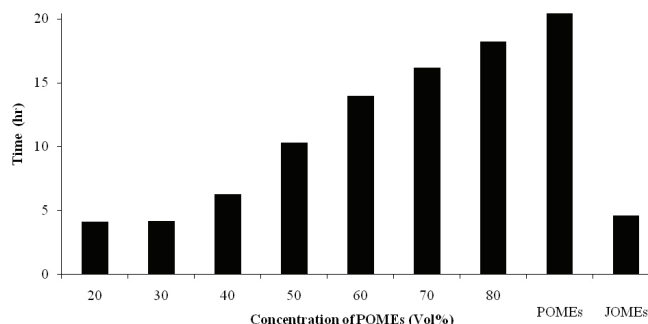


Figure 1 : Oxidation stability chart for the blends of POME and JOME

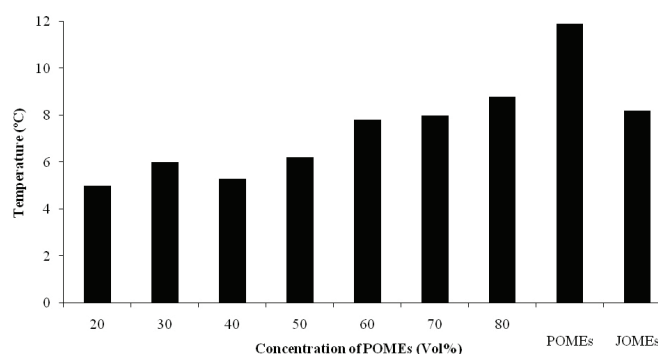


Figure 2 : Cloud point chart for the blends of POME and JOME

The key flow properties for biodiesel fuel specification are cloud point (CP) and pour points (PP) which are expressed in Figures 2 and 3. These properties have also an important indicator of the commercial applicability of the fuel. These are static tests that indicate first wax and non-flow temperatures for the fuel [1]. In the present study, the CP and PP of POMEs was observed as 11.9 °C and 10.2 °C, respectively. Whereas, JOMEs shows CP (8.2 °C) and PP (4.8 °C). The higher CP and PP in the POMEs is due to the presence of a larger amount of SFA (47.69 %) in palm oil. When POMEs were blended with JOMEs with different ratios, slight improvement was observed in the low temperature flow properties. The most improvement of CP (5 °C) and PP (4.5 °C) was observed at 20 vol % of POMEs blend with JOMEs. Furthermore, when POMEs became more than 20 vol %, the cold flow properties of blended biodiesel showed no improvement. Our results are comparable with the previous study which indicated that cold flow properties could be improved through the blending with rapeseed methyl ester (RME) and soybean methyl esters (SME) [11].

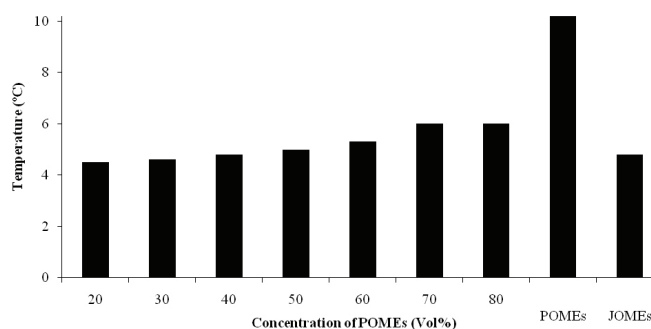


Figure 3 : Pour point chart for the blends of POME and JOME

Table 2 depicts some typical fuel properties of POMEs, JOMEs and their blends. The kinematic viscosity (KV) values of the obtained biodiesel at 40 °C, are presented in Table 2. The ASTM standard D6751 prescribed an acceptable viscosity at 40 °C range for biodiesel of 1.9-6.0 mm²/s which was satisfied by biodiesel produced and their blends.

Table 2 : Fuel properties of JOMEs blended with POMEs along with pure palm and Jatropha biodiesels as well as comparison to biodiesel standards

POMEs (vol.%)	KV (mm ² s ⁻¹)	Water content (%)	AV (mg KOH g ⁻¹)
20	3.90	0.029	0.45
30	3.93	0.028	0.40
40	3.95	0.028	0.38
50	3.96	0.026	0.39
60	3.97	0.024	0.41
70	3.98	0.024	0.46
80	4.10	0.022	0.45
POMEs	3.8	0.035	0.35
JOMEs	4.15	0.022	0.48
ASTM 6751 Specifications	1.9-6.0	0.05 max	0.50 mg KOH g ⁻¹ max
EN 14214 Specifications	3.5-5.0	0.05 max	0.50 mg KOH g ⁻¹ max

POMEs=Palm oil methyl esters; JOMEs=Jatropha oil methyl esters;
KV=kinematic viscosity; AV= acid value

All the blends KV were ranged between 3.90-4.10 mm²s⁻¹. The high KV was observed for JOMEs whereas 20 vol % blends shows the lowest value among the produced biodiesel. ASTM D974 was used to determine the acid values (AV) of produced POMEs, JOMEs and their different blends. Blending did not affect the AV of the produced biodiesel. The AV of all the methyl esters was within ASTM D6751 specifications (Table 2). The water content of the produced biodiesel was measured using a method specified by ASTM D95 method. In the present work, the quality of methyl esters and their blend were investigated for their water content using described method. The water contents were between 0.022-0.035 wt%. The blended biodiesel and pure methyl esters were within the limits prescribed in ASTM D6751. Water in the sample can promote microbial growth, lead to tank corrosion, participate in the formation of emulsions, as well as cause hydrolysis or hydrolytic oxidation [1].

4. Conclusions

The present study illustrated the blending effect of POMEs with JOMEs on important fuel properties. The POMEs depicted the highest IP (21.15 h) where JOMEs showed the smallest value of IP. When JOMEs are blended with POMEs having higher IP, the IP of the blended biodiesel was improved. The high flow properties of POMEs were also lowered to some extent by blending with JOMEs. The IP and cold flow properties of the blended biodiesel had close relationship with the fatty acid composition. The IP of the produced biodiesel decreased as the amount of polysaturated fatty acid increased. Whereas the cold flow properties decreased as the unsaturated fatty acids amount increased in the blend. The other fuel properties such as KV, AV and water content for blended biodiesel products were also within the prescribed range of standards. To solve the critical problem of poor fuel properties, blending of biodiesels produced from non-edible oil and edible oil can be employed. The relationship between fatty acids composition and biodiesel properties, blending of more saturated methyl esters with less saturated fatty acid can be done to improve the IP and also cold flow properties.

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