Production of biodiesel from *Jatropha curcas* mixed with waste cooking oil assisted by ultrasound

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**Abstract.** *Jatropha curcas* oil has a high amount of free fatty acid, while waste cooking oil has a low amount of free fatty acid content. The purpose of this study was to investigate the production of biodiesel from a mixture of *Jatropha curcas* and waste cooking. The highest biodiesel yields from the mixture of *Jatropha curcas* and waste cooking was obtained at 99.3%. The result shows that the physicochemical properties of mixed *Jatropha curcas* and waste cooking oil methyl ester met the standard requirements laid in ASTM D6751 and EN 14214.

1. Introduction

In the recent years, the growing emission of greenhouse gases and diminishing of fossil fuel led the concern of researchers to find the alternative fuels. Among the various types of alternative fuels, biodiesel is widely perceived as an environmentally-friendly option since it is clean, non-toxic, and can be used in most diesel engines without major modifications [1-3]. Biodiesels is produced by methanolysis of vegetable oils and animal fats. Due to the concern on food versus fuel issue, researchers began to vigorously explore non-edible vegetable oils in biodiesel production [4-7].

*Jatropha curcas* grows in areas with a climate of low annual rainfall in the height of between 250 and 3000 mm. In general, the oil content of the *Jatropha curcas* seed is 33.16 to 56.61% [8]. Millions of litres of waste cooking oils are disposed daily, creating a critical issue in the food and beverage industry. The critical issue caused by disposal of waste oil is land pollution as many dispose the oil on the ground, water pollution, drainage being fill with oil and sludge causing blockage then lastly problems to sewage [9]. By converting the waste oil to biodiesel will help to reduce the above environmental issues [10].

Many researchers have conducted work to enhance the properties of biodiesel by mixing various raw materials. Fadhil et al. (2017) revealed that blending castor seed oil with waste fish oil resulted in low viscosity and density biodiesel [11]. Milano et al. (2018), reported that mixing waste cooking oil and *Calophyllum inophyllum* oil improves the cold flow properties and oxidation stability [12].
In addition, biodiesel production can be further assisted by various technologies. By using ultrasound, higher biodiesel yield can be obtained while consuming less energy compared to conventional method due to the ultrasound’s cavitation effect. The ultrasonic cavitation effect will create the field that collapsed the cavitation bubbles which will generate the physical and chemical effect [13-15].

The high level of free fatty acid (FFA) in raw material of biodiesel production could reduce the mass production and the formation of soap is favoured. [16]. Since *Jatropha curcas* oil contains a high level of free fatty acid (FFA), this study aims to improve the acid value properties of *Jatropha curcas* oils (JCO) by mixing it with waste cooking oils (WCO). In this study, JCO and WCO were blended using different volume ratios and reaction parameters (potassium hydroxide KOH, methanol to oil ratio, and reaction time) in the ultrasound assisted transesterification process was investigated. The properties of the biodiesel obtained from the process were then evaluated based on standards set in ASTM D6751 and EN 14214.

2. Methodology

2.1. Materials Used and Experimental Set Up

*Jatropha curcas* oil (JCO) was procured from Cilacap, Centre Java, Indonesia, while the waste cooking oil (WCO) was collected from various restaurants in Malaysia. Methanol and KOH were obtained from Chemolab, Selangor, Malaysia. The ultrasonic device (500W and 20kHz) with 1-inch-probe and 250ml glass reactor were used in this study. The amplitude of the ultrasonic device was set to be at 40%. The experiment setup used in the study is illustrated in Figure 1.

![Figure 1](image-url) Comparison of conventional transesterification, dry in situ transesterification and wet in situ transesterification of microalgae biomass

2.2. Crude Oil Mixing Process

The JCO and WCO were prepared in different weight ratios of 10:90, 20:80, 30:70, 40:60 and 50:50 w/w%. The crude oil was mixed by using a mechanical stirrer for 30 minutes at 60°C. Several properties such as density, kinematic viscosity, and acid value were evaluated using ASTM D6751 and EN 14214 standard before determining the best mixture.

2.3. Esterification Process

Acid-catalyzed esterification was opted in order to reduce the free fatty acid content. During the acid-catalyzed esterification process, 1% (v/v) of sulphuric acid (H₂SO₄) and 60% methanol to oil ratio was added into 50 g of esterified JCO50WCO50 oil mixture. The acid-catalyzed esterification process was...
carried out at various time frames such as 10, 15, 20, 25, and 30 minutes, respectively. Once completed, the esterified oil was transferred into a separating funnel and was let to settle under gravity for 8 hours in the effort to separate the excess methanol. Subsequently, in order to remove the excess methanol, the esterified JCO50WCO50 oil mixture was heated at 60°C in a rotary evaporator under vacuum conditions.

2.4. Transesterification Process
The 50 g of esterified JCO50WCO50 was loaded into a 250 ml glass reactor. KOH catalyst varying from 0.75, 1.00 and 1.25 w/t.%, was diluted using methanol ranging from 30, 45 and 60 w/w% and added into the oil. The reaction time of transesterification process was varied at 10, 15, and 20 minutes, respectively. During the whole transesterification processes, the amplitude and the pulse of the ultrasound were kept constant at 40% and 5 sec on and 2 sec off, respectively. After the reaction had ended, the mixture was then transferred into a separating funnel and was let to settle for 8 hours. The lower layer (glycerine) was separated and discarded, followed by washing with distilled water in the effort to remove the impurities. Rotary evaporator was set at 60°C in order to further remove the excess methanol and water contained in the product. Finally, Whatman filter paper was used for the final filtration process of the product.

2.5. Physicochemical Properties of JCO-WCO Methyl Ester
The physico-chemical properties of JCO, WCO and 50% *Jatropha curcas* oil mixed with 50% waste cooking oil methyl ester (JCO50WCO50ME) were tested according to the standards stated in ASTM D6751 and EN 14214. The density and viscosity of JCO50WCO50ME were determined using Anton Paar SVM3000; while the calorific value was determined by using Parr 6200 Isoperibol (USA). The JCO50WCO50ME was characterized using Fourier transform infrared (FTIR) equipped with a detector having a spectral range 11,000–350 cm⁻¹ using TENSOR 27, Bruker Optics Inc. (USA). The acid value was measured by an automatic titration rondo 20 (Mettler Toledo, Switzerland). The JCO50WCO50ME yield (%) was calculated using the formula presented in Eq. 1 [17]:

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Yield = \frac{\text{Weight of methyl ester (g)}}{\text{Weight of oil used (g)}} \times 100\%
\]  

3. Results and discussion

3.1. Physicochemical Properties of *Jatropha curcas* (JCO) and waste cooking oil (WCO).
The physicochemical properties of mixed JCO and WCO were presented in table 1. From table 1, it shown that the density and kinematic viscosity of the oil increased slightly when the concentration of WCO increases (from JCO90WCO10ME (34.843 mm²/s) to JCO50WCO50ME (40.693 mm²/s)) while the acid value of JCO decreases significantly with increasing the WCO percentage in the blended oils. It could be concluded that lower acid value is found in the mixture of JCO50WCO50 compared to other mixture of JCO-WCO oils. This result is in line with Milano et al (2017); that the blending 70% Calophyllum inophyllum oil (CIO) and 30% waste cooking oil (CSO) could reduce the acid value from 63.05 to 19.75 mg KOH/g [12].
Table 1. Properties of JCO, WCO and mixed JCO+WCO.

| Property               | Unit | JCO  | WCO  | JCO90 WCO10 (%) | JCO80 WCO20 (%) | JCO70 WCO30 (%) | JCO60 WCO40 (%) | JCO50 WCO50 (%) |
|------------------------|------|------|------|----------------|----------------|----------------|----------------|----------------|
| Kinematic viscosity    | mm²/s|      |      |                |                |                |                |                |
| at 40°C                |      | 36.13| 41.37| 36.84          | 37.75          | 39.42          | 40.69          |                |
| Density at 15°C        | kg/m³| 900.6| 919.0| 901.3          | 901.5          | 901.6          | 901.7          | 901.8          |
| Acid value             | mg KOH/g | 40.49| 1.72 | 29.74          | 27.26          | 23.62          | 20.19          | 17.21          |

3.2. Esterification

In this study, the esterification process of the JCO50WCO50 oil was triplicate for each experiment and the average value is taken then shown in Figure 2. From Figure 2, it can be seen that acid value decreases from 10 to 20 min and then increases significantly after 20 min reaction time. This could be due to the undesirable side reactions of the presence of H₂SO₄ at longer reaction times which resulted in slow equilibrium reaction [13]. It can be seen that the lowest acid value was determined at 20 min reaction time, with the value of 1.54 mg KOH/g, that corresponds to the most suitable condition for the transesterification process.

![Figure 2. Relationship between acid value and reaction time of the esterified oil](image)

3.3. Effect of reaction time

Reaction time plays a crucial role in driving the reaction into completion [18]. The effect of reaction time (10, 15 and 20 min) on biodiesel yield was evaluated at methanol to oil ratio of 50 (w/w)% using 1(w.t)% of KOH. From figure 3, it could be observed that biodiesel yield increases with reaction time of 10 to 15 min (98.67%) and then decreases to 95.45 % at 20 min reaction time. This observation could be explained that longer period of reaction time caused a reversible process in transesterification which resulted in higher glycerides [19].
3.4. Effect of KOH catalyst
The effect of KOH loading (0.75 to 1.25 wt.%) on biodiesel yield was evaluated at methanol to oil ratio of 50 (w/w)%, with 15 min reaction time. It was shown in Figure 4 that the biodiesel yield increases from 96.8 % to 98.72 % as the KOH loading increases from 0.75 to 1.0 wt.% and significantly decreased to 93.42 % afterwards. This could be explained that more triglycerides are formed in the saponification side reaction due to the excessive addition of KOH catalyst [20]. It was found that the optimum catalyst loading in this study was 1.0 wt.% with biodiesel conversion of 96%.

3.5. Effect of methanol to oil ratio
To determine the optimal amount of methanol to oil ratio, amount of 40, 50, 60 and 70 (w/w) % were evaluated. Other parameters were maintained constant at KOH loading of 1.0 wt.% with the reaction time of 15 min. By observing Figure 5, when methanol to oil ratio increased from 40 to 60 (w/w) %, biodiesel yield increased from 94.62 to 99.32%. However, further increment of methanol from 60 to 70 (w/w) % resulted in decreasing biodiesel yield from 99.32 to 98.92%. Reduction in the biodiesel yield with further increment of molar to oil ratio from 60 (w/w) % onwards might be attributed to the over dilution of methyl ester and glycerol which initiated the reverse reaction to reduce the effective yield [21].
3.6. Analysis of biodiesel

The JCO50WCO50ME was characterized using FTIR spectra (Figure 6). The JCO50WCO50ME consist of long-chain fatty acid methyl esters. From Figure 6, it shows that there are absorption peaks at 846, 881, 1016, 1118, 1170, 1196, 1244, 1361, 1436 and 1463 cm⁻¹, which is the ‘fingerprint’ region of biodiesel [12]. It can also be observed that the JCO50WCO50ME consists of absorption peaks at 1436 cm⁻¹ and 1196 cm⁻¹ that corresponds to asymmetric stretch of –CH₃ and the stretching of O–CH₃, respectively. High content of methyl ester in the JCO50WCO50ME is shown by the decrease in the intensities in the wave ranging from 1000 to 1800 cm⁻¹ of the absorption peaks.

The fuel properties of JCO50WCO50ME are tabulated in Table 2 and it is found that the properties of JCO50WCO50ME produced using ultrasound met both the criteria set by ASTDM D6751 and EN 14214 standards. Therefore, the mixture of CPO50WCO50ME is found to be a suitable substitute fuel for diesel engines.
Table 2. Properties of JCO50WCO50ME

| Property                        | Unit  | ASTM D6751 | EN 14214 | Diesel | JC50WC 50ME |
|--------------------------------|-------|------------|----------|--------|------------|
| Kinematic viscosity at 40°C     | mm²/s | 1.9-6.0    | 3.5–5.0  | 2.86   | 4.7747     |
| Density at 15°C                 | kg/m³ | 860-880    | 860–900  | 833    | 878        |
| Acid value                      | mg KOH/g | Max. 0.5 | Max 0.5  | 0.06   | 0.227      |
| Higher heating value            | MJ/kg | Min. 35    | 35       | 45.82  | 39.5712    |

4. Conclusion
The physicochemical properties of Jatropha curcas oil (JCO) and waste cooking oil (WCO) different blends (10:90–50:50 w/w%) were evaluated. The suitability of alkaline transesterification of JCO50WCO50 was then evaluated. The maximum biodiesel yield from the experiment was achieved at 98.70 wt% using 1.0 w/t.% KOH, 50 w/w% methanol to oils ratio, with 15 min reaction time. From the result, it could be concluded that the obtained methyl ester JCO50WCO50ME is a good candidate as an alternative to diesel fuel.

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