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Biodiesel Production from Solid Coconut Waste

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ABSTRACT

Biodiesel is an alternative diesel fuel produced using transesterification method where edible or non edible oil and alcohol reacts in the presence of catalyst. Biodiesel is expensive than fossil fuels because of higher raw material and production costs. Solid coconut waste is an alternative raw material from waste and suitable for biodiesel production to lower the production cost. Solid coconut waste was produced after coconut milk extraction and may still contain up to 24 wt% extractable oil content. This study introduces in situ transesterification of solid coconut waste for biodiesel production with the addition of co-solvents, n-hexane and petroleum ether to improve and reduce the cost of biodiesel production. Effect of co-solvents, temperature (55-65°C), mixing intensity (500-800 rpm), amount of n-hexane based on methanol volume (5 %, 7.5 %, 10 % and 15 %) and methanol to waste ratio (7.5:1-10:1) were studied to optimize the in situ transesterification. The highest yield was achieved at 97 % with 2.0 % of catalyst, 15 % of n-hexane, mixing of 700 rpm, 10:1 methanol to waste ratio and reaction temperature of 55°C for 3-hour.

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INTRODUCTION

Biodiesel is an alternative diesel fuel produced from biological sources such as vegetable oils. The first alkyl ester from palm oil ethyl esters was used in diesel engine in 1937, as reported in a Belgian patent. However, low-priced petroleum interrupted the use of vegetable oil [1]. For many years, petroleum fuels discontinued the research on the renewable energy. In 1970, the energy crisis brought back vegetable oil as a good substitute to petroleum based oil. In the 1980's, biodiesel was used as a renewable energy sources to reduce greenhouse gas emissions [2]. However biodiesel unable to compete with petroleum derived fuel because of its relatively high production cost. Currently, the price of biodiesel is at USD 1, 220 per tonne [3].

An effective way to reduce production cost is by introducing cheap and non edible oil; such as waste oil, jatropha and animal fat. A sustainable and economical supply of raw material was the key factor for biodiesel to be competitive commercially [4,5,6,7]. Solid coconut waste presents a promising choice as an alternative feedstock for biodiesel production and to reduce the production cost [8]. Currently, solid coconut waste is used as fertilizer or to feed cows or left to decay in the field. This waste material is light brown and there is no information on biodiesel production from solid coconut waste. Extraction process shows that there is 24 wt% of oil still left in solid coconut waste and can be utilized for biodiesel production.

In 2010, about 2 billion MT of coconut oil is produced in Asia and from this amount, Malaysia contributes 297 thousand MT [9]. It is estimated that 178 thousand tonne of oil can be produced from solid coconut waste. Up to 173 thousand tonne of biodiesel can be produced per year from coconut waste which can account for up to 35 % of the biodiesel demand in Malaysia. Currently, Malaysia produces 500 thousand tonne of biodiesel [10]. Therefore, coconut waste biodiesel can decrease the dependence on vegetable oil and reduces the production costs. This paper focuses on the conventional in situ biodiesel production to produce high yield of biodiesel and discusses the effects of co-solvents, temperature, catalyst, n-hexane, reaction time, mixing and methanol to mass of waste using solid coconut waste as the raw material.

Material and Methodology:

Solid coconut waste was collected from a shop which produces coconut milk at Petaling Jaya, Malaysia. This waste was produced after the coconut milk extraction process. Petroleum ether (Analytical grade), n-

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hexane (Analytical grade), methanol (Analytical grade) and n-hexane (GC analysis) was purchased from MERCK (Malaysia) and potassium hydroxide was purchased from Sigma Aldrich Sdn Bhd. Reference standard, supelco 10 and 30 (mix of 20% of methyl stearate, methyl palmitate, metyl linoleate, methyl linoleic, methyl oleate, methyl capric, methyl caprilic, methyl myristate and Methyl Laurate) was purchased from Sigma Aldrich Sdn Bhd for GC analysis.

Before the in situ transesterification was conducted, coconut waste was dried overnight at 90^{o}C. This temperature was found to be optimum to produce high quality oil at least drying time and above this temperature, the quality decreases [11]. The coconut waste was kept in dry cabinet during the experimental period. In situ reactions were performed in 250ml jacketed batch reactor. The reaction was conducted at 55-65^{o}C. The temperature of reaction was maintained from 55^{o}C to 65^{o}C because above 65^{o}C (vaporizes) there will be limitation of mass transfer and bubble formation of methanol [12]. Methanol to mass of coconut waste ratio was set at 10:1 and 7.5:1 (until the solvent covers the coconut waste) [13]. The catalyst was dissolved in the 100 ml of solvent in the reactor. 10 g of waste coconut poured into the mixture in the reactor and stirred for 1 to 7 hr. n-Hexane was added as co-solvent and varied from 5 to 15 %, based on the methanol volume [14]. Petroleum ether was also used to as co-solvent to extract the oil and to distinguish the effectiveness of co-solvent. Catalyst was varied in percentage quantity, 0.8-2.0 % (w/w) based on the oil. After seven hour, the solvent was recovered using a distillation setup. The mixture was filtered using Buchi filter setup attached to vacuum pump to separate the coconut waste and solution which contains oil. n-Hexane was used to wash the meal for few times to get all the oil. The solvent was recovered using a distillation setup. The mixture was poured into a separating funnel and was allowed to stand for phase separation; the methyl ester mixture formed the upper later and glycerin formed the lower layer [15]. The top layers was separated and measured.

The biodiesel composition was analyzed using GC 7890 A (Agilent). 0.1 mL of sample was diluted with 3.9 mL of n-hexane and 1 µL of sample was injected into GC. The column was a 60 m x 0.248 mm x 0.15 um DB 23 column (J& W Scientific, USA). The standard mixture of fatty acid was bought from Sigma Aldrich. Oven temperature was set to 50^{o}C for 1 min before increasing it to 175^{o}C at a rate of 4^{o}C. Then the temperature increased to 235^{o}C at a rate of 4^{o}C min and held for 5 min.The yield of biodiesel was estimated based on the fatty acid methyl esters (FAME):

$$\text{FAME Yield} = \frac{\text{Total FAME (g)}}{\text{Amount of oil used}} \times 100\% \qquad \textbf{Eqn. 1}$$

RESULTS AND DISCUSSION

Characterization of coconut waste oil:

n-Hexane and petroleum ether were used as co-solvent throughout the oil extraction process. n-Hexane and petroleum ether improves the mass transfer and diffusivity of oil with the seed if compared with other solvent such as methanol. Coconut waste oil was mainly composed of saturated short length fatty acid chains, 2.3 % of C8:0, 30.7 % of C12:0, 17.91 % of C14:0, 17.69 % of C16:0, 22.29 % of C18:0 and unsaturated fatty acids, 6.10 % and 3.01 % of C18:1 and C18:2 respectively. The highest composition of methyl ester in the coconut waste oil is lauric acid and the acid value and density are 2.3226 mg/g KOH and 0.925 g/cm^{3} respectively. The oil yield of coconut waste oil was 17 to 24 wt% and could be utilized for biodiesel production. This may result in low production costs compared to other oil seeds such as cottonseeds which have oil content of 14 %. Furthermore, solid coconut waste oil was not suitable to be used directly in diesel engine due to the difficulty in atomizing the fuel and mixing it. To improve its performance in the engine, the coconut waste oil should be converted to biodiesel.

In situ transesterification:

Effect of co-solvents:

n-Hexane and petroleum ether were used as co-solvents to improve the oil extraction. The in situ reaction was conducted at 65°C and 2.0 wt % catalysts loading. 15 % of co solvent was added in each experiment. Figure 1 shows the relationship between the n-hexane, petroleum ether and without addition of co-solvent. The yield of biodiesel using n-hexane was slightly higher and more stable throughout the experiment while for the setup with petroleum ether and without addition of the co-solvent, the yield decreases. n-Hexane proves to be a better solvent than petroleum ether. The yield of biodiesel was at the highest at 97 wt% using n-hexane as co-solvent. The graph shows that petroleum ether was not a superior co-solvent for the in situ process because the yield was close to the in situ methanolysis without adding co-solvent. This is because the boiling point of petroleum ether at 40 to 60°C causes the lower yield of biodiesel. Further, methanol is also a poor solvent for oil extraction because of its immiscibility [14]. n-Hexane is the most common solvent used for extraction Fernández et al. [16] also reported that n-hexane was the most suitable, with highest extraction yield for grape seed extraction if compared to the other solvent [16]. Adding 15 % of n-hexane in this setup improves the mass transfer of oil into

methanol and seed and intensifies the transesterification of oil and aliphatic alcohols. This was in accordance to literature where adding co solvent would increase the biodiesel yield [14].

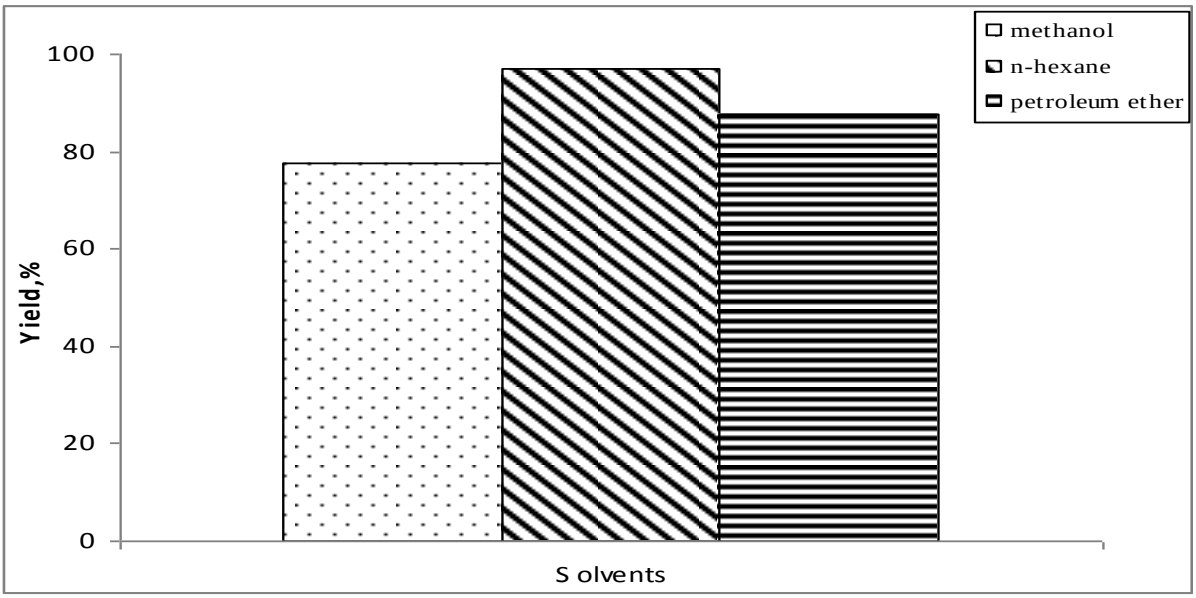

Fig. 1: Effect of n-hexane, methanol and petroleum ether on the yield.

Effect of temperature and reaction time:

To study on the effect of temperature, the experiments were conducted at 55, 60 and 65°C. The reaction was carried out using 15 % of n-hexane and 2.0 % of catalyst. The transesterification was conducted near the boiling point of the alcohol because above the boiling point, presence of alkaline catalyst causes the glycerides to saponificate fast before the process completes [17]. Figure 2 shows the effect of temperature on the reaction time on the biodiesel yield. After one hour of reaction, the yields of biodiesel were 56 %, 63 % and 75 % at 55, 60 and 65°C respectively. This shows the influence of reaction time on the biodiesel yield. After 3-hour, the yield reached the maximum and the curve has an asymptotic bent with time. The yields were found to be 78 %, 89 % and 97 % at 55, 60 and 65°C respectively. Encinar et al. [18]and Keera et al. [19] also found the similar trend during the optimization process of transesterification for production of biodiesel using Cynara cardunculus oil and rapeseed oil respectively [18,19].

Figure 2 also shows the effect of reaction time on the yield. The transesterification occurs fast and almost 50 % conversion of triglycerides into fatty acid methyl ester was achieved in the first hour. The yield increases up to 3-hour and beyond that, no noticeable change in the yield was detected, where the yield only changes slightly. This was in accordance with the results of [20] who reported that increasing the reaction time from 2 to 4 hr, no significant effect on the glyceride conversion was observed. This suggests the reaction was in the equilibrium at a slow rate. Meng et al.[21] also reported that in alkaline methanolysis, the reaction time used was from 1 to 4-hour and temperature at either 60 or 65°C [21].

Effect of Catalyst:

The effect of KOH amount on the in situ transesterification of the coconut waste was investigated with the KOH amount varied from 0.8 to 2.0 % based on the weight of oil. The reaction time was set at 7-hour and temperature of 65°C. Figure 3 shows the effect of catalyst amount on the reaction time and yield when 15 % of n-hexane was used. The maximum yield at 97 % was achieved at 2.0 % of catalyst amount and reached maximum at 3-hour. Beyond this point, observation shows there was no further increase in the coconut waste biodiesel yield. Other researchers also reported that after the reaction reaches the maximum yield, further increase in the catalyst decreases the yield [22,23]. Below 0.8 % of catalyst amount, the process almost did not occur as KOH was not enough to catalyze the reaction for completion. Observation shows that at higher catalyst amount (above 2.0 %) soap formation occurred. Soap formation in the presence of high catalyst amount increases the viscosity of the reactants and decreases the yield [18]. Chapagain et al., 2009 [24]reported that the biodiesel yield of 91.87 wt% was obtained with 2.0 wt % of KOH. Surya et al. [20] reported that 2 wt% of of KOH or NaOH was not suffieicent to obtain 95 wt% of biodiesel yield because the free fatty acid of jatropha was high, 1.39 mg/g KOH [20]. In this study, the catalyst amount was increased up to 2 % to compensate for the high free fatty acid content in the coconut waste oil [18].

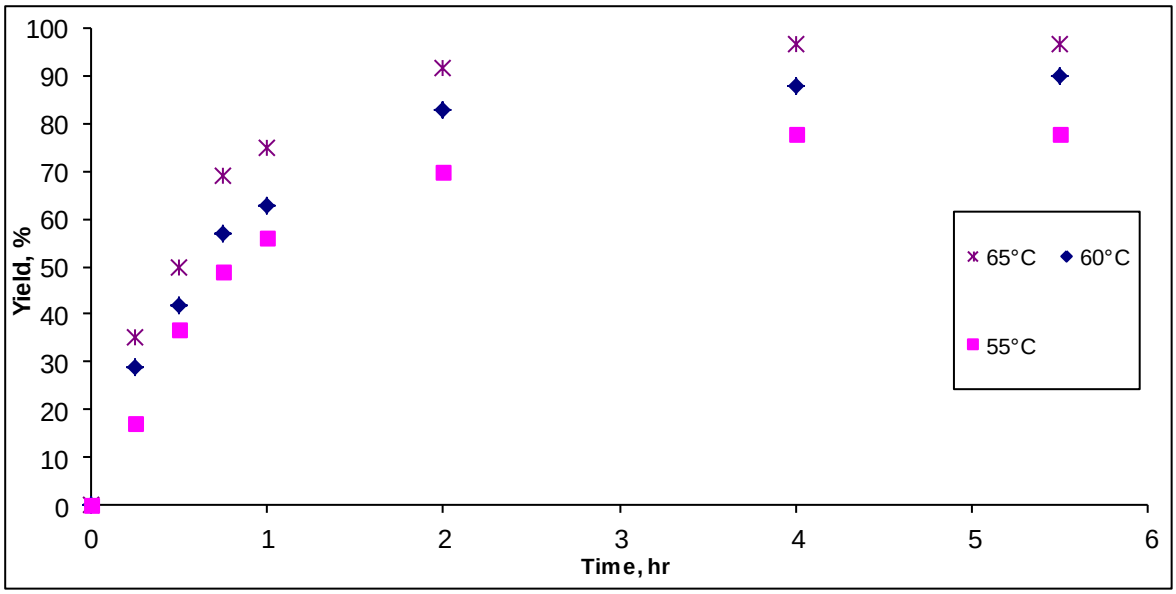

Fig. 2: Effect of temperature on in situ batch reactor.

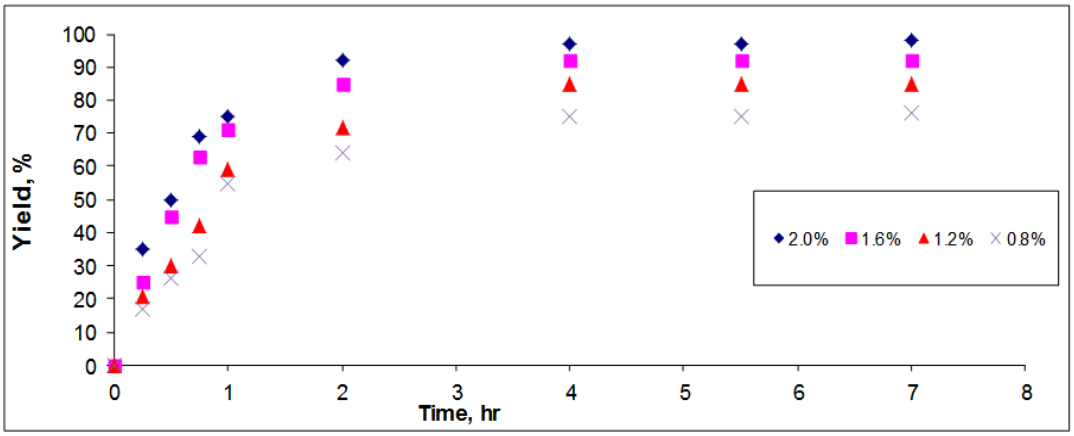

Fig. 3: Effect of catalyst - 15 % of n-hexane.

Properties of the biodiesel:

Table 1 shows the summary of the properties of the biodiesel of coconut waste oil, virgin coconut oil and palm oil. The properties of coconut waste biodiesel were within the mentioned biodiesel standards, ASTM D6751-07 and EN 14214. The result of density, acid value, viscosity and cloud point shows that coconut waste biodiesel was comparable to biodiesel produced from other raw materials, for examples palm oil and virgin coconut biodiesel.

Table 1: Properties of coconut waste oil biodiesel, virgin coconut biodiesel and palm oil biodiesel.

Properties	Unit	Coconut waste biodiesel	Virgin coconut oil biodiesel [25]	Palm oil biodiesel [26]	ASTM D6751-07	EN 14214
Density @ 15°C	kg/m^3	877.0	807.3	876.0	Not specified	860-900
Acid Value	mg/g KOH	0.34	0.29	0.08	<0.50	<0.80
Viscosity 40°C	mm^2/s	3.55	2.937	4.42	1.9-6.0	3.5-5.0
Cloud point	°C	-3	0	15	Not specified	Not specified
Pour point	°C	-7	-12	15	Not specified	Not specified
Free Glycerol	wt%	0.0045	-	-	0.020 max	0.020 max
Total glycerol	wt%	0.12	-	-	0.24 max	0.25 max

Conclusion:

This study shows that biodiesel could be produced successfully from coconut waste by alkaline in situ transesterification. It is estimated that up to 173 tonne of coconut waste biodiesel can be produced per year from coconut waste. Two co-solvents were utilized to achieve the highest yield namely petroleum ether and n-hexane. Alkaline catalyst, potassium hydroxide was used, rather than acid catalyst to associate with high FFA content, 2.3226 mg/g KOH of coconut waste oil. The highest yield, 97.0 wt% was achieved at 2.0 % of catalyst, 15 % of n-hexane, 10:1 methanol to waste ratio and reaction temperature of 55^{o}C for 3-hour. The properties of the biodiesel produced were within the specification of the ASTM D 6751-07 and EN 14214.

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