Biodiesel Production from Waste Coconut Oil in Coconut Milk Manufacturing

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Abstract

The purpose of this research was to develop a 3 step biodiesel production from waste coconut oil taken from a wastewater pond in a coconut milk manufacturing plant. Special attention was paid to optimizing the first step, acid catalyzed hydrolysis, to convert the waste coconut oil into high free fatty acid oil, 83.32 wt%. The first step was the acid hydrolysis, in order to produce high free fatty acid oil. The optimum condition in acid hydrolysis was 5 % by mass of hydrochloric acid, in order to produce high free fatty acid oil that could be used as raw material for biodiesel production. The second step was the acid esterification, in order to reduce the FFA and convert FFA to methyl ester. The reduction of the FFA from 83.32 % in high free fatty acid oil to less than 2 % required 3 % by mass of hydrochloric acid, a molar ratio of methanol to oil of 10: 1, and a reaction time of 60 min. The alkaline transesterification in the third step was used triglyceride at 1.0wt% of KOH for catalysis, a molar ratio of methanol to oil of 6:1, and a reaction time of 60 min. The waste coconut oil biodiesel was further evaluated by determining its fuel quality, and most of the properties were well within ASTM and EN standards.

Keywords: Waste coconut oil, biodiesel, hydrolysis, esterification, transesterification

Introduction

Coconut milk processing manufacture has been growing in Thailand; about 2,000 - 3,000 kg coconut milk per day is lost from the process into wastewater ponds. The waste coconut oil accumulates in the wastewater pond becomes solid fat, which floats over the wastewater. This fat waste must be removed from the pond to prevent wastewater fermentation becoming biogas [1]. The waste coconut oil could be an environmental problem, emitting an odor to nearby communities.

Utilization of waste coconut oil for renewable energy as biodiesel adds value to products from coconut milk manufacturing. 12.8 % high free fatty acid (FFA) can be generated from waste coconut oil by acid hydrolysis. High FFA coconut oil can be changed to biodiesel with a 2 step reaction of acid esterification and alkali transeterification [2-5].

This research aims to develop a 3-step biodiesel synthesis process that comprises of acid catalyzed hydrolysis, acid catalyzed esterification, and alkaline transesterification. The effects of important operating parameters on acid hydrolysis, acid esterification and alkaline transesterification reaction are extensively determined. The purity of the ester content and the fuel properties of biodiesel are analyzed following biodiesel standards.

Materials and methods

Materials

Waste coconut oil was obtained from the wastewater pond of the coconut milk processing plant of Ampol Food Processing Ltd. in Thailand. The waste coconut oil was filtered to remove water; after that, it was kept at room temperature for the next experiment. A picture of the waste coconut oil is shown in **Figure 1**. Reference standards of fatty acid methyl ester with > 99 % purity were purchased from Sigma Chemical Co. Ltd (St. Louis, MO, USA). Methanol, Hydrochloric acid, Potassium hydroxide, and all other chemicals were of analytical grade.

Apparatus and reaction procedures

In the first step of acid catalyzed hydrolysis, 100 g of waste coconut oil and hydrochloric acid (HCl) were added in established amounts for each experiment in a glass reactor (400 ml.) The mixture was heated from room temperature to 100 °C with 500 rpm of stirring rate for 30 min of reaction time. When the reaction was finished, the mixture product was filtered on filter paper to separate the solid residue from high free fatty acid oil. The oil was further placed in a separation funnel and allowed to stand for 15 min; after that, the oil phase (top phase) was removed from the water phase (bottom phase). The oil was heated at 100 °C for 30 min to remove water. A picture of high free fatty acid is shown in **Figure 1b**.

In the second step of acid catalyzed esterification, the reactions were conducted in a 3 necked flask, heated, and stirred with a magnetic stirrer with an agitator heater. For the esterification experiment, the flask was charged with 20 g of acid oil and heated to the setting temperature with agitation. A certain quantity of hydrochloric acid catalyst was dissolved in the required amount of methanol. After achieving the setting temperature of the reactant and catalyst, methanol catalyst was added to the flask. The reaction was timed immediately after the addition of the catalyst and methanol. After the established reaction time, the mixture was placed in the separation funnel and allowed to stand for 3 h. Two phases could be identified; the upper phase consisted of methanol, catalyst, and water, and the bottom phase mainly consisted of oil and the esterified fatty acids. The phases were separated and the esterified product was further transesterifield by alkaline catalysis, using the same system as the esterification step.

For the third step, of alkaline catalyzed transesterification, oil with free fatty acid content of less than 2 wt% and esterified product were weighed, and a suitable amount of methanol and catalyst (KOH) were added. After reaction time, the mixture was placed in the separation funnel to separate the biodiesel and glycerol layers. The biodiesel layer was washed with warm water until it was neutral. After washing, the biodiesel was subjected to heating at 100 °C to remove excess water. The biodiesel was further characterized for its properties following ASTM and EN standards.

(a)   (b)

Figure 1 Waste coconut fat from wastewater pond (a) and high free fatty acid oil (b).

Free fatty acid content (wt%) analysis

Free fatty acid content (FFA) was determined via AOCS official method Ca Sa-40. 7 g of the oil sample was introduced into a 200 ml flask; after that, 75 ml of ethanol solution and 2 ml of 1 % phenolphthalein solution (1 g of phenolphthaline in 100 ml of ethanol) were added into the flask and titrated with 0.1 N sodium hydroxide solution. FFA content was calculated in accordance with the equation as follows:

$$\% \, FFA = \frac{(A\text{-}B) \times N \times 28.2}{W} \qquad (1)$$

where A is a milliliter of sodium hydroxide solution titrated with the sample, B is a milliliter of sodium hydroxide solution titrated with blank, N is the concentration of sodium hydroxide in the normality unit, and W is the weight of the sample in grams.

Fatty acid methyl ester content (wt%) analysis

The fatty acid methyl ester content was measured with standard EN 14103. The analyses were conducted on a gas chromatography (Agilent Technologies GC-6890) using a fused silica capillary column (DB-WAX, Agilent Technologies, USA) and a flame-ionization detector, with an injection temperature of 270 °C and a detector temperature of 270 °C. The spit ratio was 30:1. The fatty acid methyl ester content was calculated via the following equation:

$$\% \, Methyl \, ester = \frac{\sum A\text{-}Ais}{Ais} \times \frac{Cis \times Vis \times 100}{W} \qquad (2)$$

in which methyl ester content is wt%, $\sum A$ is the total peak area of methyl ester, Ais is the peak of methyl heptadecanoate which is used as an internal standard, Cis is the concentration of methyl heptadecanoate solution (mg/ml), Vis is the volume of methyl heptadecanoate solution (ml), and W is the weight of the sample in grams.

Biodiesel properties

The coconut milk fat methyl ester, or biodiesel, was characterized by determining its viscosity, density, flash point, acid value and % methyl ester. The following test methods were used: density 15 °C (ASTM D1293), viscosity 40 °C (ASTM D445), flash point (ASTM D93), acid value (ASTM D604), and % methyl ester content (EN 14103).

Results and discussion

Acid catalyzed hydrolysis reaction

The waste coconut oil from the wastewater pond included water contamination, solid particles and fat. Hence, the water portion was removed by filtering through a screen basket. A mixture of fat and solid particles was further hydrolyzed by 37 % (v/v) hydrochloric acid (HCl) at different concentrations, from room temperature to 100 °C, for 30 min and 500 rpm. The product from acid hydrolysis was filtered to separate the solid particles part, and the liquid part was further put into the separation funnel for separation into two layers. The upper layer was oil and the lower layer was water. The water layer was drawn off to leave only the oil layer. The oil layer was then heated at 100 °C for 30 min to remove water; after that, it was weighed for oil content (% wt) determination, based on waste coconut oil raw material. The high free fatty acid oil is shown in **Figure 1**, and the effect of hydrochloric acid to acid oil content is presented in **Figure 2**.

Figure 2 shows that by increasing acid concentration from 1 to 5 % (wt/wt), the percentage of oil content increased. The percentage of oil content was constant at acid concentration from 5 to 0 % (v/wt). So, this result indicates that the concentration of hydrochloric acid at 5 % (wt/wt) was the optimum concentration for the acid hydrolysis reaction. This condition gave 27.62 % (wt/wt) of oil content, 61.22 % (wt/wt) of water content, and 11.16 % (wt/wt) of solid particle content, based on the 8 of coconut milk fat raw material. The result indicates that the acid catalyzed hydrolysis reaction is necessary in preparing intermediate oil fraction product for biodiesel production. We could not prepare biodiesel directly from waste coconut fat, because it contain solid particles and high amounts of water content, so it is necessary to separate these impurities first before biodiesel production.
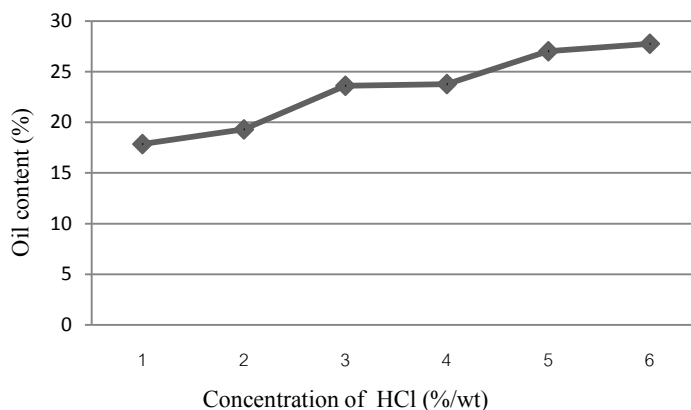

Figure 2 Effect of hydrochloric acid on acid oil content.

Table 1 Composition of fatty acid in oil prepared from coconut milk fat.

Fatty acid	Formula	Molecular weight (g/mole)	Result (%wt)	A
Octanoic acid (c_8)	$C_8H_{16}O_2$	144	3.66	7.80
Decanoic acid (c_{10})	$C_{10}H_{20}O_2$	172	4.17	6.70
Lauric acid (c_{12})	$C_{12}H_{24}O_2$	200	40.55	47.50
Myristic acid (c_{14})	$C_{14}H_{28}O_2$	228	17.43	18.10
Palmitic acid (c_{16})	$C_{16}H_{32}O_2$	256	15.14	8.80
Stearic acid (c_{18})	$C_{18}H_{36}O_2$	284	3.52	2.60
Oleic acid ($c_{18:\,1}$)	$C_{18}H_{34}O_2$	282	11.73	6.20
Linoleic acid ($c_{18:\,2}$)	$C_{18}H_{32}O_2$	280	2.90	1.70
Erucic acid ($c_{22:\,1}$)	$C_{22}H_{42}O_2$	338	0.89	0.10

A: from Ooi *et al*.

The oil portion was further analyzed for free fatty acid (FFA) content and its fatty acid composition by gas chromatograph (GC). The result showed that oil had 83.32 % of FFA content. The fatty acid composition is shown in **Table 1**.

The major fatty acids of oil are lauric acid (40.55 %), myristic acid (17.43 %), palmitic acid (15.14 %), and oleic acid (11.73 %). The minor fatty acids are decanoic acid (4.17 %), octanoic acid (3.66 %), straric acid (3.52 %), linoleic acid (2.90 %), and erucic acid (0.89 %). This composition is close to the same fatty acid composition in coconut oil, analyzed by [6].

Acid catalyzed esterification reaction

About 500 ml of the oil portion from the acid catalyzed hydrolysis reaction, called high free fatty acid oil, was further prepared for acid catalyzed esterification and alkaline catalyzed transesterification reactions. On completion of the acid esterification reaction, the product was poured into a separating funnel. The products of this process were separated into 2 layers. The upper layer was the product of this process [7]. The lower layer was a solution which contained water (from esterification of FFA), hydrochloric acid, and excess methanol. The lower layer was then drawn off. The upper layer was the emulsion between triglycerides and methyl ester, or biodiesel. It became a low FFA product which was suitable to use in the alkaline transesterification.

The effectiveness of the acid esterification was evaluated by measuring the FFA of this intermediate product. From FFA measurement, at each 30 min intervals between 0 - 150 min, the FFA content in the product became lower, but it had not changed much after 60 min of the experiment. From **Figure 3**, it is found that the optimal molar ratio, which can reduce the FFA from 84.48 to 1.58 %, is 10:1. With further increase in molar ratio, the effectiveness remained constant, and some excess methanol moved over the product layer, which also found by [8]. In this study the reason that excess methanol was required was because there was not a sufficient amount of hydrochloric acid and high water content that occurred from the reaction. This yield is the lower esterification reaction efficiency.

Figure 4 shows the relationship between the concentrations of high free fatty acid oil used in the FFA reduction.

It was revealed that the amount of the hydrochloric acid should be moved up 2 % by weight of the high free fatty acid oil, to reduce FFA to less than 2 %. In addition, the optimal reaction time was around 60 min or more, as shown in **Figure 5**.

Alkaline catalyzed transesterification reaction

The esterified product was transesterified by the alkaline transesterification process, and then the transesterified product was separated into 2 layers in the separation funnel. The lower layer was glycerol, and the upper layer was methyl ester, or biodiesel. The glycerol layer was drawn off to leave only the methyl ester layer. The methyl ester was then washed with warm water to remove the leftover impurities and glycerol. The washing was carried out until the pH of methyl ester was neutral. After that, the methyl ester was heated at 100 °C for 15 min to remove water. The final product of methyl ester was used to determine the methyl ester purity of each condition by gas chromatography (GC). The results of this step indicated that the 1 % wt KOH concentration and the methanol to oil molar ratio of 6:1 provided the highest purity of methyl ester, at around 90.45 % .These results are plotted in **Figures 6** and **7**.

The fuel properties of this optimum final product were tested and compared with the biodiesel standard of Europe (EN14214) and the USA (ASTM D6751), as detailed in **Table 2**; most of the biodiesel fuel properties met the required standards, except for the methyl ester purity being lower.
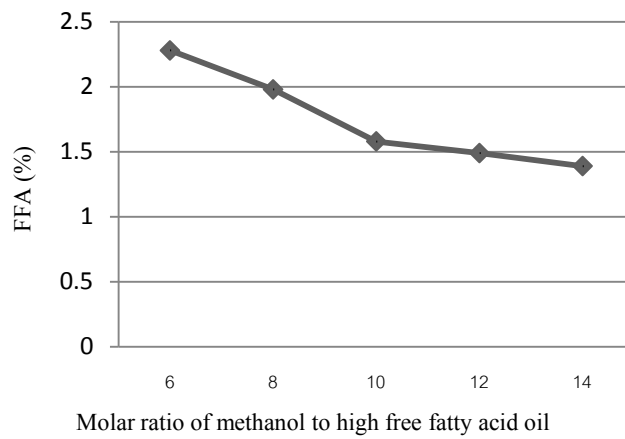
Figure 3 Effect of molar ratio of methanol on high free fatty acid oil to FFA reduction.
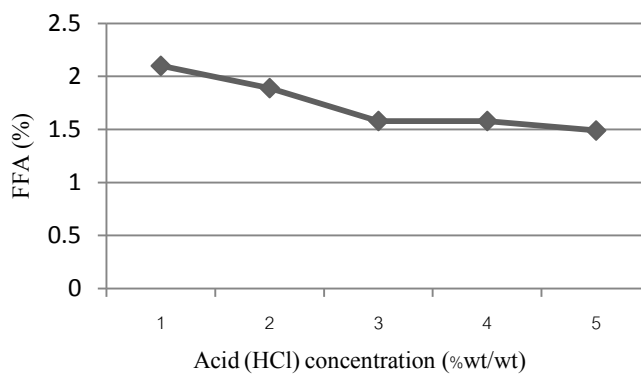

Figure 4 Effect of hydrochloric acid on high free fatty acid oil to FFA reduction.
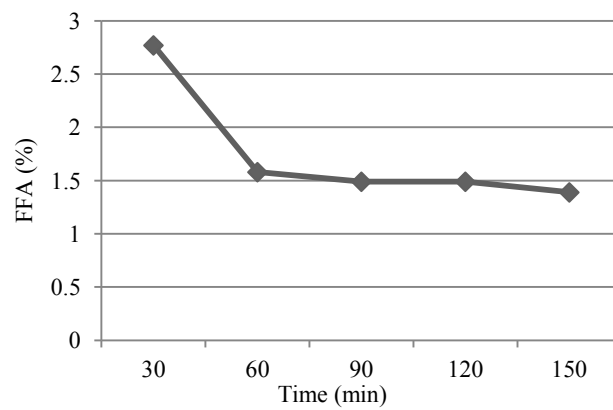

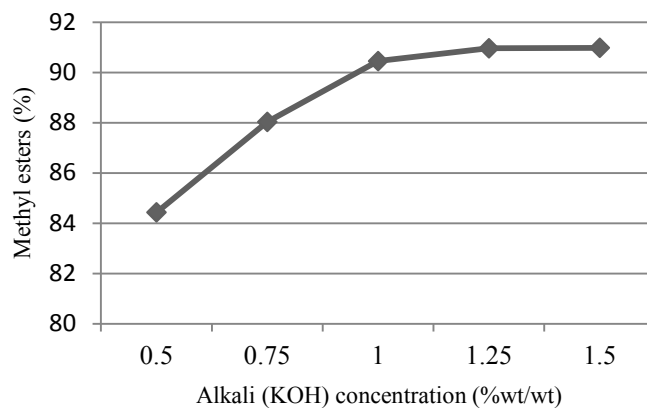**Figure 5** Effect of reaction time on FFA reduction.

Figure 6 Effect of alkaline (KOH) concentration on methyl ester purity.
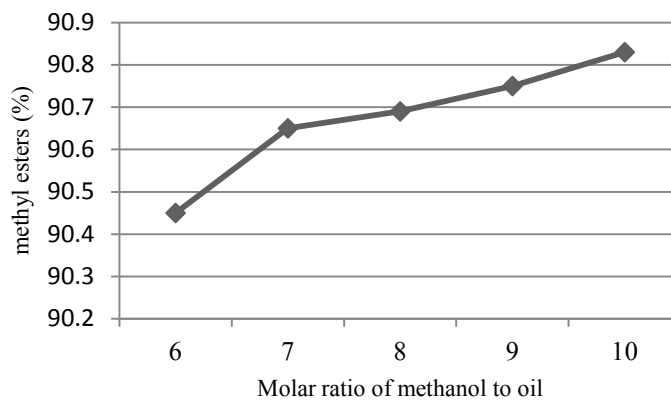

Figure 7 Effect of molar ratio of methanol on oil to methyl ester purity.

Table 2 Fuel properties of coconut milk fat biodiesel.

Fuel properties	Testing method	This work	Methyl ester standard	
			EN 14214	**ASTM D6751**
Viscosity (cst) at 40 °C	ASTM D445	3.76	3.5 - 5.0	1.96 - 6.0
Flash point (°C)	ASTM D93	184	120 min	130 min
Acid value (mgKOH/g)	ASTMD664	0.70	0.5 max	0.80 max
Methyl ester purity (%wt)	EN 14103	90.45	96.5 min	NA

NA: not available

Conclusions

The waste coconut oil biodiesel was studied in acid hydrolysis, acid esterification, and alkaline transesterification reactions. The optimum conditions in acid hydrolysis in order to produce high free fatty acid oil that could be used as raw material for biodiesel production was 5% by mass of hydrochloric acid. The second step was the acid esterification, in order to reduce the FFA and to convert the FFA to methyl ester. The condition for reducing the FFA in the oil from 83.32 % to less than 2 % were 3 % by mass of hydrochloric acid, with a molar ratio of methanol to oil of 10:1, and a reaction time of 60 min. The alkaline transesterification used triglyceride of 1.0 wt% of KOH for catalysis, a molar ratio of methanol to oil of 6:1, and a reaction time of 60 min. The fuel properties of the waste coconut oil biodiesel were close to the standard.

Acknowledgments

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