ไบโอดีเซลจากน้ำมันกรดดำโดยใช้โพแทสเซียมไฮดรอกไซด์และเฟอริกซัลเฟตเป็นตัวเร่งปฏิกิริยา

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บทคัดย่อ

ประเทศไทยใช้น้ำมันปาล์มเป็นวัตถุดิบสำหรับการผลิตไบโอดีเซล แต่เนื่องจากการผลิตน้ำมันปาล์มไม่เพียงพอต่อความต้องการ งานวิจัยนี้ศึกษาการผลิตไบโอดีเซลจากน้ำมันกรดดำโดยใช้โพแทสเซียมไฮดรอกไซด์และเฟอริกซัลเฟตเป็นตัวเร่งปฏิกิริยา เราหาสภาวะที่มีผลต่อผลได้ไบโอดีเซล ได้แก่ อัตราส่วนโดยปริมาตรของเมทานอลต่อน้ำมันกรดดำ อุณหภูมิในการทำปฏิกิริยา เวลาในการทำปฏิกิริยา และปริมาณของตัวเร่งปฏิกิริยา เราพบว่าสภาวะที่เหมาะสมสำหรับการเกิดไบโอดีเซลอยู่ที่อัตราส่วนโดยปริมาตรของเมทานอลต่อน้ำมันกรด 5 ต่อ 1 อุณหภูมิในการทำปฏิกิริยาที่ 70 องศาเซลเซียส เวลาในการทำปฏิกิริยา 120 นาที ด้วยโพแทสเซียมไฮดรอกไซด์ 1.5 เปอร์เซ็นต์โดยน้ำหนัก และเฟอริกซัลเฟต 1 เปอร์เซ็นต์โดยน้ำหนักของน้ำมันกรดดำ ผลได้ไบโอดีเซลเป็น 87.5 และ 70.0 เปอร์เซ็นต์ ตามลำดับ

คำสำคัญ : ไบโอดีเซล, น้ำมันกรดดำ, โพแทสเซียมไฮดรอกไซด์, เฟอริกซัลเฟต

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BIODIESEL FROM BLACK ACID OIL USING KOH AND $Fe_2(SO_4)_3$ CATALYSTS

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Abstract

Thailand uses palm oil as a raw material for biodiesel, but palm oil production does meet the biodiesel demand. This study examined the production of biodiesel from black acid oil, using KOH and $Fe_2(SO_4)_3$ as catalysts. We determined conditions such as the methanol to black acid oil volume ratio, reaction temperature, reaction time and catalyst loading that would optimize biodiesel yield. We found that the optimum yield of biodiesel occurred with methanol to black acid oil volume ratio 5:1; reaction at 70°C for 120 min; with 1.5 wt% of KOH and 1 wt% $Fe_2(SO_4)_3$ loading. The biodiesel yield was 87.5% using KOH and 70.0% using $Fe_2(SO_4)_3$ catalysts.

Keywords : biodiesel, black acid oil, potassium hydroxide, ferric sulphate

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Introduction

The price of petroleum is constantly increasing: this impacts the overall economy and may hinder both current and future national growth. Thailand does not produce enough crude oil to meet internal demands and it imports oil. Demand for fossil fuel is high, especially for diesel, which is mainly used for transportation. Therefore, development of alternative fuels to replace petroleum and diesel must be established as a matter of urgency and this drives research on domestic raw materials, such as vegetable oils, from which biodiesel can be produced.

Biodiesels are renewable resources, biodegradable and nontoxic, thus they affect the environment less than traditional diesels. They have similar properties to diesel and can be used as fuel for vehicles, without modifications to the engine; it also helps to maintain the condition of the engine, which lasts longer as the oxygen in biodiesel leads to more complete combustion, which, in turn, leads to fewer exhaust products, such as black smoke and carbon monoxide and a reduction in air pollution. Moreover, biodiesel reduces blockages in the exhaust system, as it contains no sulfur and the oxygen content, not only gives better combustion, but reduces pollution from sulfur dioxide, hydrocarbons, carbon monoxide and dust. Biodiesel has, therefore, become a very promising alternative to diesel from fossil fuel.

Currently, biodiesels are made from vegetable oil, used vegetable oil, animal fats, palm oil, physic nut, soybean, peanut, castor and sunflower oils. However, another type of oil increasingly used is coconut oil from the pulp of coconuts or black acid oil. The main components of coconut oil are saturated fatty acids, with medium chain length molecules, such as lauric acid. This is more easily absorbed by the body and accumulates less in fatty tissue than fatty acids with longer chains. The basic production of biodiesel from vegetable oils, has been described in detail by Cervero et al. (2008): vegetable oil fatty acids, with short to medium length carbon chains, are transesterified, using an alkaline catalyst (sodium or potassium hydroxide at ~80°C). Ethanol is obtained from the fermentation of sugars, present in the vegetable structure (McCoy, M., 1998; Wright, JD., 1988). The direct use of vegetable oils as fuels has not been satisfactory in diesel engines, because of their high viscosity, low volatility, polyunsaturated compound content, high concentration of free fatty acids, resins and rubber (formed by oxidation or spontaneous polymerization) and cinder deposits. Thus, the chemical modification of vegetable oils to obtain suitable fuels, in particular, the synthesis of fatty acid esters, yielding the so-called biodiesel, has been studied. A simple life-cycle analysis shows that the conversion of vegetable oils to biodiesel requires a substantial amount of energy, because of the high temperature needed for effective reaction (Van Gerpe, J., 2005). The enzymatic catalyzed reaction generates smaller waste streams and enzymes can efficiently convert both triglycerides and free fatty acids into biodiesel, under mild conditions. Phase stability leads to a

product with few impurities and the aqueous phase, which contains the catalyst is very stable (Vicente, G., et al., 2007).

In this study, biodiesel can also be used as a heating fuel in domestic and commercial boilers. Research is underway to determine whether such main components of coconut oil are saturated fatty acids, with medium length chains such as lauric acid. This is more easily absorbed by the body and accumulates less in fatty tissue than long chain fatty acids. Our key objectives were 1) to investigate the optimum conditions for biodiesel production from black acid oil, 2) to analyze the influence of operating conditions, such as; the volume ratio of methanol to black acid oil, reaction temperature and reaction time using KOH and $Fe_2(SO_4)_3$ as catalysts and 3) to obtain a high yield of biodiesel from black acid oil.

Research objectives

This study examined the production of biodiesel from black acid oil, using KOH and $Fe_2(SO_4)_3$ as catalysts

Methodology

1. Preparation of material

Biodiesel is derived from vegetable oils; the black acid oil was selected by various methods, among which transesterification were the most widely used. The present work explored the effects of variations in free fatty acids (FFA) of vegetable oils on the biodiesel production method as well as on the yield. Black acid oil was purchased from Saengsook Industry Co. Ltd, Samutprakan Province, Thailand and was heated at 100°C for 15 min to remove moisture. Methanol, potassium hydroxide (KOH) and ferric sulphate ($Fe_2(SO_4)_3$) were Laboratory Reagent (LR) grade.

2. To analyze the influence of operating conditions

We analyzed the influence of operating conditions, including the volume ratio of methanol to black acid oil, reaction temperature and reaction time, using KOH and $Fe_2(SO_4)_3$ as the catalyst, using typical edible plant oils, such as black acid oil, for the production of biodiesel. These raw materials are not entirely suitable, thus we investigated the influence of operating variables on the transesterification of *black acid oil* to biodiesel over KOH and $Fe_2(SO_4)_3$ catalysts. The individual and combined effects of three variables: reaction time, reaction temperature and catalyst amounts were evaluated. The conversion of black acid oil to biodiesel was achieved through the transesterification reaction over the catalysts at various methanol-to-oil volume ratios in a batch reactor. Physicochemical properties of the KOH and $Fe_2(SO_4)_3$ catalysts were obtained.

3. To synthesize the biodiesel production from black acid oil that was obtained a high yield of biodiesel

This step explored the effects of variations in free fatty acids (FFA), namely; black acid oil of vegetable oils on the biodiesel production methodology as well as on the yield. This wealth has led to an increased development of production, transformation and preservation of from Saengsook Industry Co.,Ltd, which generates large amounts of coconut oil mill waste.

4. To synthesize of the properties of black acid oil

The following properties of black acid oil were measured: pH value, acid value (AOAC, 1989), saponification value (PORIM Test Methods, 1995) and iodine value (AOAC, 1997). Production of biodiesel from black acid oil and methanol in presence of KOH and $Fe_2(SO_4)_3$ as catalyst was measured in a 200 ml round-bottom flask, equipped with magnetic stirrer and reflux condenser (Figure 1(b)). The methanol to black acid oil volume ratios varied over a 3:1-10:1 range. Reaction temperatures were 40°C, 50°C, 60°C and 70°C. for times ranging ranging from 30, 60, 90 to 120 min and catalyst loading from 0.5 1.0 1.5 to 2.0 wt%. The reaction was started by stirring at 250 rpm. After the reaction, the upper layer consisted of biodiesel, while the lower layer was glycerol. The biodiesel was washed several times with warm water and heated at 70°C for 30 min to remove the methanol. The biodiesel yield was calculated from:

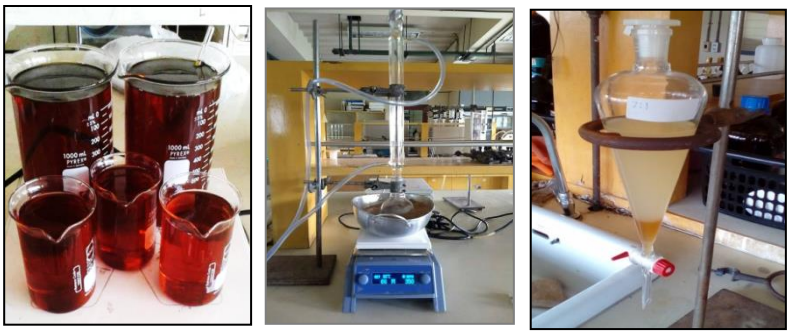
Yield (%) = (Weight of biodiesel / Weight of oil) x 100

5. To synthesize the biodiesel production from black acid oil that was obtained a high yield of biodiesel

In this work, we focused on managing the black acid oil fraction efficiently when producing biodiesel and investigated KOH and $Fe_2(SO_4)_3$ as catalyts transesterification to produce biodiesel. For the transesterification, we also synthesized KOH and $Fe_2(SO_4)_3$ composites, by the direct impregnation method, as base and acid catalysts for the transesterification of hydrolyzed littered edible oil fraction. The successful development of this process would greatly increase the prospects of using a low-quality feedstock for economical biodiesel production.

6. Catalyst formulation

The correct amount of catalyst needs to be used, because both excess as well as insufficient amount of catalyst will cause soap formation. Correct amount of catalyst can be determined by volumetric titration of the oil. Commonly used alkaline catalysts in the biodiesel industry are potassium hydroxide (KOH) and sodium hydroxide (NaOH) flakes which are inexpensive and easy to handle in transportation and storage. Here we used KOH pellets and $Fe_2(SO_4)_3$ as the catalyst, i.e. a solid chemical catalyst, whose advantages are short reaction time, usually between 1 hour to 4 hours, requiring low catalysts concentration (about 1%). This catalyst is also cheap and does not inhibit the reaction.



(a) (b) (c)

Figure 1. Experimental setup (a) Black acid oil (b) Reflux set for biodiesel production and (c) Biodiesel produced.

Result and discussion

The black acid oil was very dark brown (Figure 1a). The pH was 4.65. The acidity was 233 mg-KOH/g, the saponification value was 268 mg-KOH/g and the iodine value was 57.3 g-I_2/g (Trisupakitti, S., 2016).

1. Effect of methanol to oil volume ratio

One of the most important parameters affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Stoichiometrically 3 moles of alcohol and 1 mole of triglyceride are required for transesterification to yield 3 moles of fatty acid methyl/ethyl esters and 1 mole of glycerol. In order to shift the reaction to the right, it is necessary to either use excess alcohol or remove one of the products from the reaction mixture. The second option is usually preferred for the reaction to proceed to completion. The reaction rate washighest when 100% excess methanol was used (Shereena, K.M. & Thangaraj, T., 2009; Ghaly, A.E., Dave, D., Brooks M.S. & Budge, S., 2010). Although methanol, ethanol, propanol, butanol and amyl alcohol can be used, methanol is applied more frequently, as its cost is low and it is physically and chemically advantageous (more polar as the shortest chain alcohol). On the other hand, ethanol may be preferred over methanol, since it is derived from agricultural products and is renewable and biologically less damaging in the environment. The effect of the ratio of methanol or ethanol to oil was studied. The highest biodiesel yield was nearly 99.5% at 6:1 methanol/oil. In comparison, biodiesel yield using methanol continuously increases with the raise of methanol molar ratio (Hossain, A.B.M.S. & Boyce, A.N., 2009).

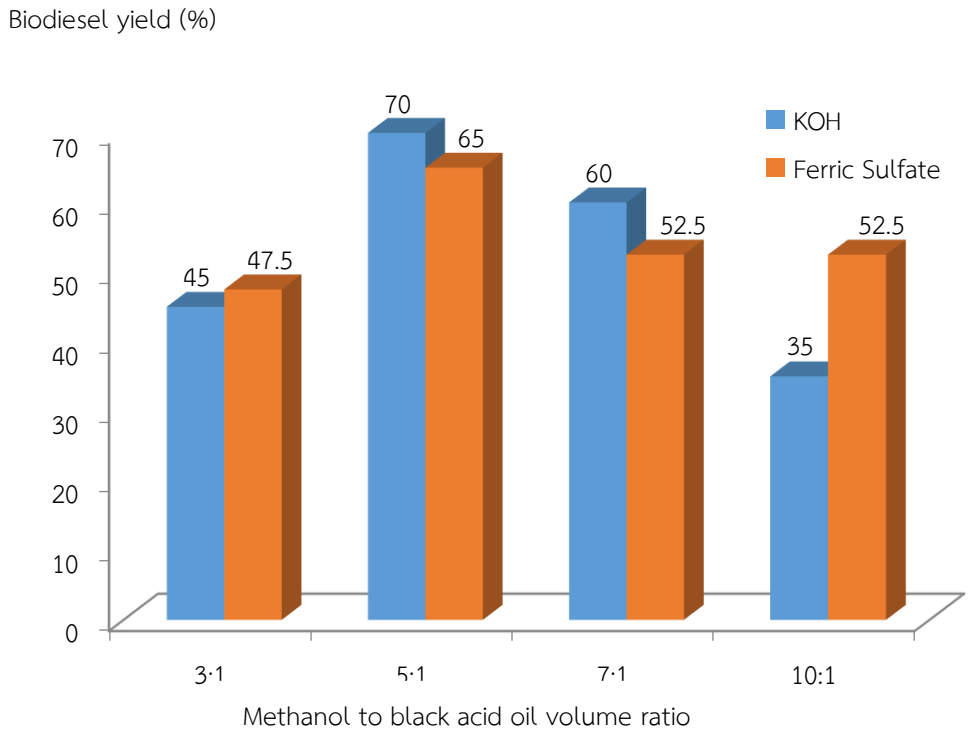


Figure 2. Biodiesel yield (%) vs methanol to black acid oil volume ratio. Reaction conditions: reaction time 120 min, catalyst 1 wt% and reaction temperature 60^{o}C.

Figure 2 shows the effect of methanol to black acid oil volume ratio on biodiesel yield. The volume ratio of methanol to black acid oil at 5:1 shows the highest yield of biodiesel at 70% was produced from transesterification using KOH as a catalyst, while $Fe_2(SO_4)_3$ catalyst shows the highest yield at 65%. However, when the proportion of methanol to black acid oil increased to over 5:1, biodiesel yield decreased. This might be because transesterification is a diverted reaction and the alcohol content must be large enough to drive the reaction in the right direction and increase the yield of biodiesel. Our results were similar to those of Phan and Phan (2008), who used vegetable cooking oil as a renewable energy option. Therefore, the 5:1 volume ratio of methanol to black acid oil was selected in our study, as this generated the best biodiesel yield. However, this value depends on the properties of black acid oil and the type of catalyst used. For example, Centikaya and Karaosmanoglu (2004) found that a methanol:oil ratio below 5:1 is insufficient for the base-catalyzed transesterification, while Zheng et al. (2006) observed that the methanol:oil ratio could be up to 250:1 in the presence of an acidic catalyst.

2. Effect of reaction temperature

Biodiesel yield was highest at 60°C. At 70°C, the temperature exceeds the boiling point of methanol (64.7°C). Methanol readily evaporated and many bubbles were observed. This led to a three-phase system (Islam et al., 2013), in which the bubbles reduced reactant contact. Although higher temperature would normally accelerate the reaction, the biodiesel yield peaked at 65°C, just below the methanol boiling point (Usta et al., 2016). Other reports similarly found that peak yields occurred just below the methanol boiling point (Khan, N.A. & Dessouky, E.H., 2009; Ma, F. & Hanna, M.A., 2009; Pramanik, K., 2003; Srivastava, A. & Prasad, R., 2000).

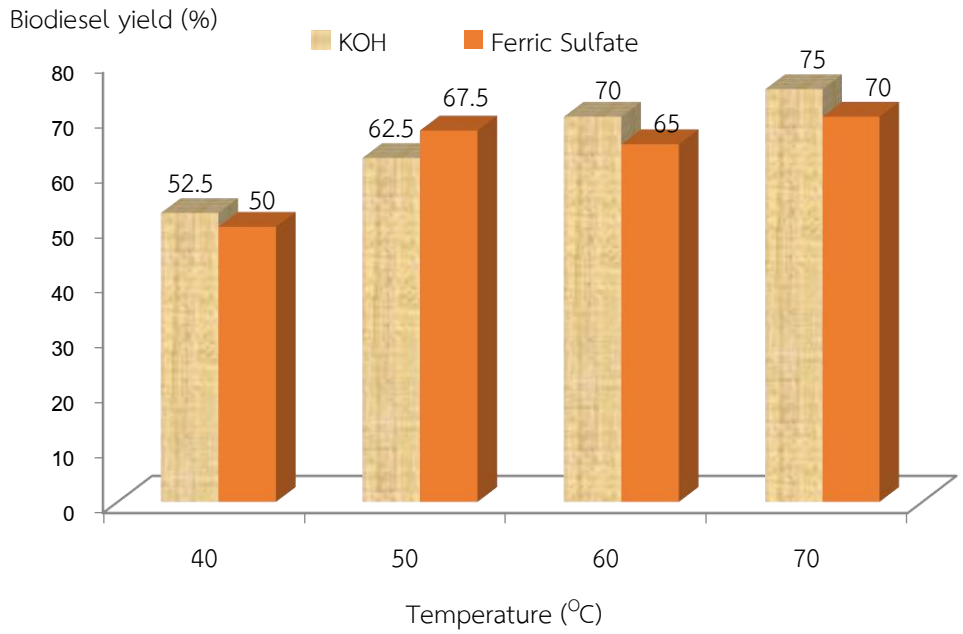


Figure 3. Yield *vs* reaction temperature: Reaction condition: methanol to black acid oil ratio 5:1, reaction time 120 min and catalyst loading 1 wt%.

Figure 3 shows the effect of reaction temperature on biodiesel yield. The optimum reaction temperature was 60-70°C. Raising the reaction temperature had a positive effect on methanolysis of black acid oil. These results are similar to those of Cvengros and Povazance (1996) for biodiesel from rapeseed. They showed a maximum yield at68 -70°C. However, as the reaction system was operated at ambient pressure, it was impossible to rise the temperature further: at 70°C. methanol kept boiling.

3. Effect of reaction time

Fatty acid ester conversion increased with reaction time. The reaction is slow at the beginning due to mixing and dispersion of alcohol and oil. After that the reaction proceeded very quickly. Further increase in reaction time did not increase the yield, i.e. biodiesel/mono alkyl ester. Besides, longer reaction time led to reduction of end product (biodiesel), due to the reversible transesterification reaction, resulting in loss of esters as well as soap formation (Mathiyazhagan, M. & Ganapathi, A., 2011; Musa, I.A., 2016). This was in accordance with the results of Meng et al. (2008), who reported that increasing the reaction time from 2 to 4 h had no significant effect on the glyceride conversion was observed. This suggests the reaction was in the equilibrium at a slow rate. Meng et al. (2008) also reported that, in alkaline methanolysis, the reaction time was from 1 to 4-hours with temperature at 60 or 65°C.

Figure 4 also illustrates the change of biodiesel yield of two catalysts as function of reaction time. Under the same reaction conditions, the yield increased with the reaction time from 30 to 120 min. However, the reaction time at 120 min shows the biodiesel yield reached 75% for KOH and 70% for $Fe_2(SO_4)_3$ as catalysts.

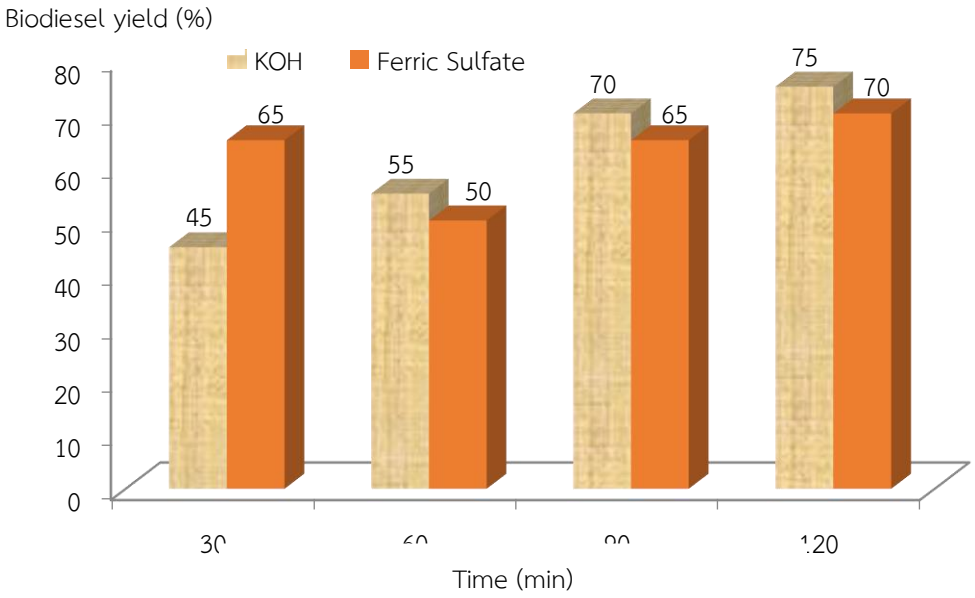


Figure 4. Yield *vs* reaction time: Reaction conditions: methanol to black acid oil ratio 5:1, reaction temperature 70°C and catalyst loading 1 wt%.

4. Effect of catalyst loading

Biodiesel formation was also affected by the concentration of catalyst. Commonly used catalysts for biodiesel production are sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Mathiyazhagan, M. & Ganapathi, A., 2011). The type and amount of catalyst required in the transesterification usually depended on the quality of the feedstock and method of the transesterification. For a purified feedstock, any type of catalyst could be used for the transesterification. However, for feedstock with high moisture and free fatty acid content, homogenous transesterification was unsuitable, due to the high possibility for saponification, to occur instead of transesterification. The yield of fatty acid alkyl esters generally increased with increasing amount of catalyst. This was due to availability of more active sites by addition of larger amounts of catalyst. However, from an economic perspective, a larger amount of catalyst may not be profitable, due to the cost of the catalyst itself. Therefore, similar to the ratio of oil to alcohol, optimization is necessary to determine the optimum amount of catalyst required for transesterification (Musa, I.A., 2016; Colombo, K., Ender, L. & Barros, A.A.C., 2017). Other researchers reported that, after the reaction reached the maximum yield, further increase in the catalyst decreased the yield (Jiang, S. T., Zhang, F. J. & Pan, L. J., 2010; Efavi, J. K., Kanbogtah, D., Apalangya, V., Nyankson, E., Tiburu, E.K., Dodoo-Arhin, D., Onwona-Agyeman, B. & Yaya, A., 2018). Below 0.8 % of catalyst, the little transesterification occured as there was not enough KOH to drive the reaction to completion. Observations showed that at higher catalyst amount (above 2.0 %), saponification occurred. Soap formation in the presence of high catalyst amount increased the viscosity of the reactants and decreased yield (Hossain, A.B.M.S., Boyce, A.N., Salleh, A. & Chandran, S., 2010). Karmakar et al. (2010) reported that a 91.8 wt% biodiesel yield was obtained with 2.0 wt % of KOH. Surya et al. (2012) 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. In this study, the catalyst amount was increased to 2 % to compensate for the high free fatty acid content in coconut waste oil (Keera, S.T., El Sabagh, S.M. & A.R. Taman, A.R., 2011).

The effect of catalyst loading on yield of biodiesel is shown in Figure 5. The biodiesel yield increased to 87.5% with KOH catalyst with increased catalyst amount, but when the catalyst loading reached 1.5 wt%, it started to decrease. This was attributed to the formation of soap, which hindered the separation of the methyl ester phase during the washing step: the saponification of free fatty acid with KOH is shown in equation (I). The decrease in yield was due to soap formation at higher KOH loading. Furthermore, Figure 5 shows the effect of $Fe_2(SO_4)_3$ loading on biodiesel yield for heterogenous catalysis. $Fe_2(SO_4)_3$ is an effective solid acid catalyst in the esterification shown in equation (II). At 1 wt% catalyst loading, a maximum yield (70%) was found. On further increasing the amount of catalyst, biodiesel yield decreased as the mixture of reactant and catalyst became viscous, leading to insufficient mixing and

therefore imcomplete reaction.

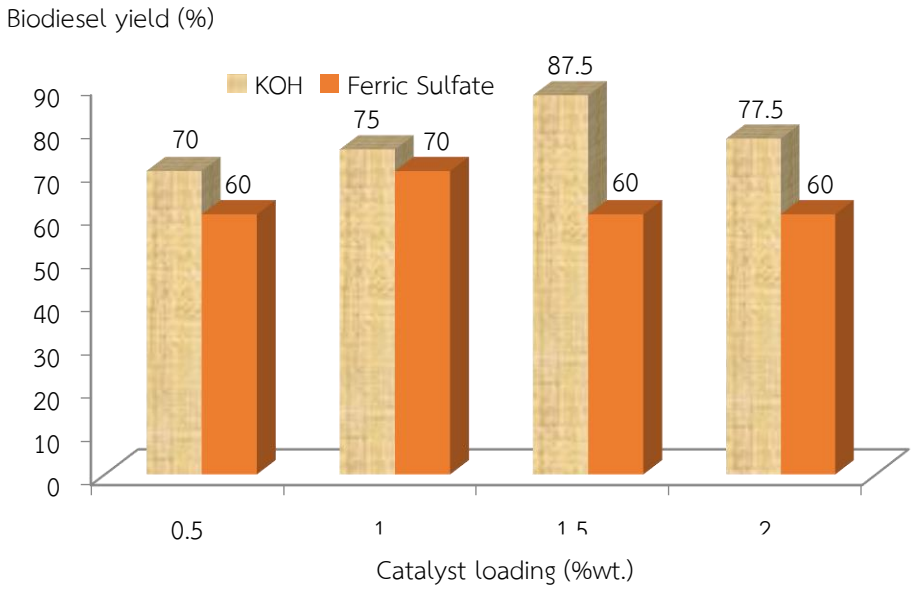


Figure 5. Effect of catalyst loading on biodiesel yield. Reaction conditions: methanol to black acid oil ratio 5:1, reaction temperature 70°C and reaction time 120 min.

$$\underset{\text{free fatty acid}}{R_1COOH} + KOH \xrightarrow{H_2O} \underset{\text{soap}}{R_1COOK^+} + H_2O \qquad \text{(I)}$$

$$\underset{\text{free fatty acid}}{RCOOH} + R'OH \xrightleftharpoons{Fe_3(SO_4)_3} \underset{\text{ester}}{RCOOR'} + H_2O \qquad \text{(II)}$$

Basically, making biodiesel from oil, methanol (or ethanol) and catalyst, is a simple chemical process. The problem lies in the chemical reaction kinetics. The conventional transesterification of the triglycerides to fatty methyl esters and glycerine is slow and not complete. During the conversion, not all fatty acid chains are turned into alkyl esters (biodiesel). This reduces biodiesel quality and yield significantly. All kinds of plant oils and waste materials, for example, cooking oil wastes have been suggested as feedstocks for biodiesel production through transesterification. Chemical transesterification, in presence of alkaline catalysts, has been the method of choice for biodiesel production and commercialized in many places. It has been shown that enzymatic transesterification can be successful with a variety of lipases with higher yields using a large variety of oils, fats and acyl acceptors. Optimization of parameters of reaction systems will reduce the cost of the production of biodiesel and will make enzymatic

transesterification for biodiesel production more promising (Ghaly, A.E., Dave, D., Brooks M.S. & Budge, S., 2010).

Conclusion

We determined the optimum conditions for producing biodiesel from black acid oil using transesterification and esterification. For transesterification using KOH catalyst, the maximum biodiesel yield was 87.5% at a 5:1 volume ratio of methanol to oil at 70°C for 1.5 wt% catalyst and 120 min reaction time . Esterification using $Fe_2(SO_4)_3$ catalyst produced maximum biodiesel at 70% with a 5:1 volume ratio of methanol to black acid oil at 70°C, catalyst loading at 1 wt% and reaction time at 120 minutes.

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