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Feasibility of Using Ultrasound-Assisted Biodiesel Production from Degummed-Deacidified Mixed Crude Palm Oil Using Small-Scale Circulation

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ABSTRACT

A transesterification reaction of degummed-deacidified mixed crude palm oil (DDMCPO) with methanol in the presence of alkali-catalyst NaOH was performed in a 400 W small-scale ultrasonic circulation process at a low frequency of 20 kHz with an input capacity of 4 × 100 W. The various parameters used were methanol (16, 23 and 30% by volume) and a base catalyst of 3, 5 and 7 g NaOH per liter of oil. The results of the fatty acid methyl ester (FAME) conversion with and without ultrasonic irradiation assistance were compared and showed that the maximum FAME conversion of 92.5% by weight could be achieved with 7 g NaOH per liter of oil and 23% by volume methanol with a reaction temperature of 45 ^{o}C and a total residence time of more than 6 min. Furthermore, these conditions were used to compare the effect of FAME conversion with and without the ultrasonic irradiation. The results clearly indicated that circulation of the mixture using ultrasound energy had more significant potential in the conversion of oil to FAME than the circulation of the mixture through the reactor without ultrasound energy. Consequently, the use of ultrasound irradiation can reduce the reaction time and increase the FAME conversion.

Keywords: ultrasound, circulation, biodiesel, transesterification, mixed crude palm oil

INTRODUCTION

Biodiesel is one of the important renewable energy sources used in many countries in the world. It is a renewable alternative fuel that can be produced from vegetable oils or animal fats and used without any engine modification (Stavarache *et al*., 2005; Lee *et al*., 2011). Moreover, biodiesel fuel has many advantages over petroleum diesel fuel, as it produces less smoke and airborne particles. It is nontoxic together with having lower carbon monoxide levels and low hydrocarbon emissions and being a biodegradable, renewable fuel (Ma and Hanna, 1999; Prateepchaikul *et al*., 2009; Santos *et al*., 2009). Biodiesel is defined as a fatty acid methyl ester (FAME) or fatty acid ethyl ester (FAEE). It can be produced by transesterification of triglycerides with mono-alcohol in the presence of either an alkaline or acidic catalyst. The triglyceride is converted in three steps to diglyceride (DG), monoglyceride (MG), and glycerol (GL) in the production of three moles of esters and one mole of glycerol (Darnoko and Cheryan, 2000).

The major problem in the production of biodiesel from mixed crude palm oil (MCPO)

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arises from the free fatty acid (FFA) content. The FFA content in the raw material using a transesterification reaction should not be higher than 1% by weight since it will react with alkalis to produce soap (the saponification process). As a result, ester conversion is decreased by the formation of soap (Gerpen, 2005). MCPO contains gums and high levels of free fatty acids (Prateepchaikul *et al.*, 2007). To achieve good conversion from degummed-deacidified mixed crude palm oils (DDMCPO) to an ester, the FFA of the DDMCPO should not exceed 1% by weight. One of the methods for treating the MCPO is the degumming and deacidification process. Both processes are pretreatment methods for removing the gum or phosphatides and reducing the FFA content in MCPO, respectively (Thaiyasuit *et al.*, 2012).

To produce FAME, oil with low FFA is normally mixed with a solution of alcohol and a catalyst in a tank reactor with constant stirring. This is time and energy consuming. Using ultrasound instead of a mechanical stirrer, the reaction time can be shortened. Ultrasound can generate acoustic cavitations through high intensity acoustic fields in the medium phase until they reach a cavitation phenomenon that creates a bubble collapse. Before the bubbles collapse, the inside of the bubble may have a pressure as high as 506.6 MPa that causes an instant temperature rise to at least 7,200 °C which in turn causes rapid changes in the physical and chemical reactions of the reaction mixture. In addition, the ultrasonic field can increase the interface area between the immiscible fluids, resulting in rapid mixing in the liquids (Mason and Lorimer, 2002; Ensminger and Stulen, 2008).

Hanh *et al.* (2008) tested the methanolysis reaction with triolein, using: 0.5, 1, 1.5 and 3% by weight of KOH; molar ratios of 3:1, 4:1, 5:1, 6:1 and 9:1 (methanol to triolein); and reaction times of 10–140 min using an ultrasonic cleaner (40 kHz with a maximum power of 1200 W). They found that the higher yield of methyl esters depended on the higher amount of KOH and the molar ratio of methanol to triolein. The optimum conditions for the production of methyl ester under sonication were a 6:1 molar ratio of methanol to triolein with 1% by weight of KOH and a reaction time of 30 min.

Thanh *et al.* (2010) used canola oil to produce biodiesel with an ultrasonic transducer (model UIP 2000; Hielscher Ultrasonics GmbH; Teltow, Germany) having a frequency of 20 kHz and an operating input power of 1,000 W in a 800 mL reactor. The mixture was circulated through the ultrasonic reactor at a flow rate of 8 $L.min^{-1}$. In each experiment, 54 L of canola oil were fed with molar ratios of 1:1, 2:1, 3:1, 4:1, 5:1 and 6:1 (methanol to canola oil); 0.3, 0.5, 0.7 and 1.0% by weight of KOH, with a temperature of 25 ± 2 ^{o}C. The maximum FAME yield of 99% was achieved with the methanol/oil molar ratio of 5:1, 0.7% by weight KOH and 50 min reaction time.

Stavarache *et al.* (2005) studied the effects of alcohols on the transesterification of neat vegetable oil under ultrasound and mechanical stirring with a molar ratio of 6:1 (alcohol to oil), an alkali-catalyst of 0.5, 1.0 and 1.5% by weight (NaOH and KOH), at room temperature. Frequencies of 28 kHz and 40 kHz (60% of the maximum ultrasonic power of 1200W) were employed in their experiments. The results showed that the normal-chain alcohols (methanol, ethanol, *n*-propanol and *n*-butanol) exhibited quite rapid reaction producing yields of 88–98% by weight of ester within 10–20 min reaction time using an ultrasonic frequency of 40 kHz and 0.5% by weight NaOH. Moreover, the yields of biodiesel in the ultrasonic process were higher than those from traditional stirring, and the ultrasonic system affected the reduction of soap. Furthermore, the low frequency ultrasound of 28 kHz produced a yield of 98% by weight of ester, but the reaction time was longer than for the high frequency ultrasound treatment.

Hanh *et al*. (2009) studied the production of fatty acid ethyl esters from oleic acid with alcohols (methanol, ethanol, propanol, butanol, hexanol, octanol and decanol) under ultrasonic irradiation. The various conditions imposed were: molar ratios of 1:1 to 10:1 (alcohol to oleic acid), reaction temperatures of 10–60 ºC, acid catalyst of 0.5–10% by weight H_2SO_4 and irradiation times of 1 to 10 h. The results showed that the optimum conditions for producing the maximum ester conversion in a batch esterification process were a molar ratio of alcohol to oleic acid of 3:1, 5% by weight H_2SO_4 using an ultrasonic irradiation time of 2 h and a reaction temperature of 60 ºC.

Worapun *et al*. (2012a) studied two-step biodiesel production from crude *Jatropha curcas* L. oil (CJCO) using ultrasonic irradiation assisted by low-frequency ultrasonic irradiation (40 kHz). The first-step process involved acid-catalyzed esterification to reduce the FFA from 12.5% to less than 3% with methanol (15% by weight), sulfuric acid (3.0% by weight) and an ultrasonic irradiation time of 20 min at a reaction temperature of 30 ºC. The second-step used base-catalyzed transesterification to produce the biodiesel. A biodiesel conversion rate of 98% was achieved with methanol (15% by weight), KOH (1% by weight) and an ultrasonic irradiation time of 30 min at a reaction temperature of 30 ºC. In their comparison of biodiesel conversion using either ultrasonic irradiation or conventional stirring methods, they found that ultrasonic irradiation was significantly more efficient than the conventional method, especially for the high FFA oil.

Thus, as discussed above, many researchers have studied the production of biodiesel from vegetable oils and alcohols with an alkaline or an acid catalyst using batch ultrasonic radiation. In the batch process, increasing the productivity of biodiesel can be achieved by increasing the volume of ultrasonic reactor. This causes a reduction in the acoustic energy density in the reactor because this density is defined as the ultrasonic power divided by the total volume of the mixture. When the density decreases because of the increase in the volume of the reactor, the reaction time is undesirably longer. Instead of the traditional batch process, a shorter reaction time could be achieved to obtain a comparable production volume using a small reactor via an ultrasonic circulation process of the biodiesel. In the current study, the feasibility of using low intensity and low frequency ultrasound-assisted biodiesel production was investigated. Thus, low free fatty oil as DDMCPO was selected for a preliminary study of biodiesel production via ultrasound in a circulation process. This work studied the transesterification of DDMCPO with methanol in the presence of an NaOH catalyst and the reaction was carried out in a small-scale, ultrasonic circulation process. Furthermore, the effects of the residence time of reactants in the ultrasonic reactor, the amount of methanol and the amount of alkali-catalyst were investigated.

MATERIALS AND METHODS

Materials

The raw material used in this study was degummed-deacidified mixed crude palm oil (DDMCPO) containing 0.3–0.5% by weight of free fatty acid that was purchased from a small-scale palm oil factory in southern Thailand. All chemicals, including 99% sodium hydroxide (NaOH) and 98% methanol (MeOH), were commercial grade. A thin layer chromatograph with flame ionization detection (TLC/FID) (IATROSCAN MK-65; Mishubishi Kagahu Latron Inc.; Tokyo, Japan) was used to analyze the conversion of oil and biodiesel. Analysis used the following chemical standards: tripalmitin, palmitic acid, methyl palmitate (sourced from Nacala Tesque); 1,3-distearin; DL palmitin (mono palmitin) (sourced from Sigma Aldrich); and 1,2-di-stearin 99%, (sourced from Research Plus).

Methods

Apparatus

Figure 1 depicts the equipment used in this experiment. Four 100 W, 20 kHz ultrasonic transducers were mounted to a rectangular 108 mL reactor with dimensions of 15 mm width, 36 mm height, 210 mm length and 1.5 mm thickness. A mixture of oil and sodium methoxide was circulated through the ultrasonic reactor via a peristaltic pump (model 520U; Watson Marlow Pumps Group; Falmouth, UK).

Procedures

A sample of 1,000 mL of DDMCPO was preheated to 45 ^{o}C in a beaker on a stirrer hotplate and the solution of NaOH and methanol was added. The mixture was circulated through the ultrasonic reactor and back to the beaker via the peristaltic pump with a flow rate of 56 mL.min^{-1} and a residence time in the ultrasonic reactor of 2 min. The mixture was circulated through the reactor for 20 min in each experiment. Samples were collected every 2 min from the sampling port of the ultrasonic reactor and were placed in cool water in order to stop the reaction. Then, the samples were washed three times with water to eliminate the residual acid-catalyst and methanol. The compositions of the cleaned samples were analyzed using TLC/FID. Each experiment was repeated three times. The Reynolds number (*Re*) for the rectangular duct in the ultrasonic reactor was calculated using Equation 1:

$$Re = \rho v D_H / \mu \quad (1)$$

where ρ is the density of the fluid (kg.m^{-3}), v is velocity of the fluid based on the actual cross-sectional area of the duct (m.s^{-1}), μ is the dynamic viscosity of the fluid (Pa.s), and D_H is the hydraulic diameter of the rectangular duct (m). The hydraulic diameter was calculated using Equation 2:

$$D_H = 2ab/(a + b) \quad (2)$$

where a is the height of the duct (m) and b is the width of the duct (m). Thus, the Reynolds number of the ultrasonic reactor was 15.55 with a flow rate of the reactant mixture of 56 mL.min^{-1}, a velocity of the fluid of 0.002357 m.s^{-1} and a hydraulic diameter of 0.0176 m. Table 1 shows the properties of the biodiesel produced from the DDMCPO under ultrasonic irradiation.

RESULTS AND DISCUSSION

Effect of methanol concentration

The amount of methanol is a significant variable affecting the purity of the FAME, especially when the residence time in the reactor is low. The

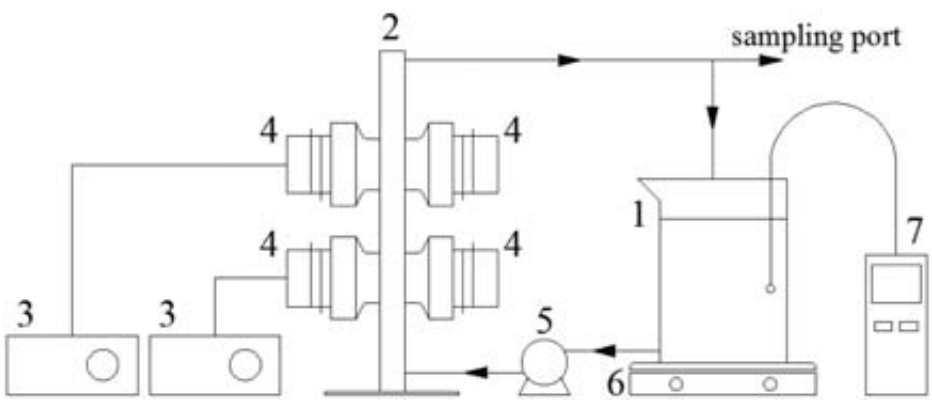

Figure 1 Schematic diagram of equipment used: 1) Beaker; 2) Ultrasonic reactor; 3) Ultrasonic generator; 4) Ultrasonic transducer; 5) Peristaltic pump; 6) Hotplate stirrer; and 7) Temperature indicator.

effect of methanol on the FAME conversion at 16, 23 and 30% by volume of methanol to oil at a temperature of 45 °C and alkali-catalyst of 5 g NaOH per liter of oil is shown in Figure 2. Apart from the 16% by volume of methanol, the results show that methyl ester could be more effectively obtained under the other two conditions when the mixture of reactants was circulated through the ultrasonic reactor for at least 12 min (6 cycles). Nevertheless, the maximum purity of methyl ester of 90.73% by weight could only be obtained when the amount of 23% by volume of methanol was used in the reaction. However, this at least pointed out that a very high concentration of methanol is not necessary. Moreover, the glycerides were converted rapidly to the FAME because the oil to methanol ratio has a substantial effect on the reaction rate in transesterification. The results from using 23% by volume of methanol showed that the FAME rapidly increased and therefore this was a more suitable concentration with regard to the reaction rate than the other conditions. However,

Table 1 Properties of biodiesel produced from degummed-deacidified mixed crude palm oils under ultrasonic irradiation.

Property	Ultrasonic irradiation
Kinematic viscosity at 40 °C (cSt)	2.66
Density at 15 °C (kg.m^{-3})	862
Acid value (mg of KOH.g^{-1})	0.35
Cloud point (°C)	12
Pour point, °C	9
Monoglycerides (% by weight)	1.4
Diglycerides (% by weight)	0.8
Triglycerides (% by weight)	5.3
Esters (% by weight)	92.5

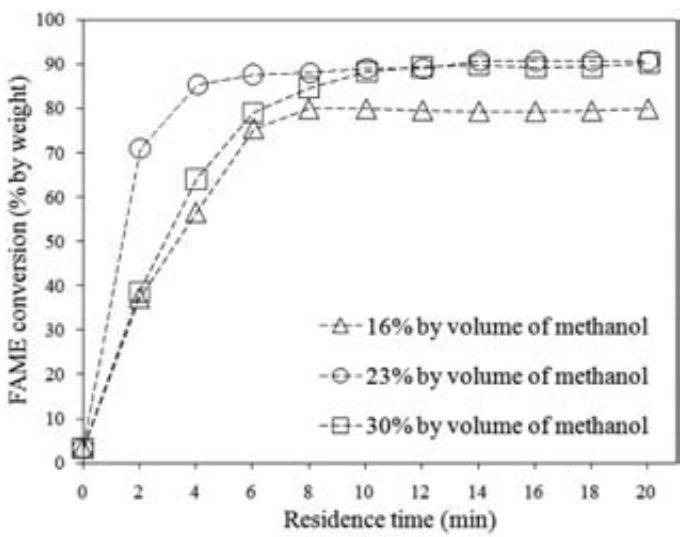

Figure 2 Effect of methanol concentration on fatty acid methyl ester (FAME) conversion with ultrasonic irradiation in the presence of 5 g NaOH per liter of oil and reaction temperature of 45 °C.

when 30% by volume of methanol was used, the FAME conversion decreased slightly as a result of the dilution of some catalyst by the excess methanol (Wang *et al.*, 2006).

Effect of alkali-catalyst

The effect of alkali-catalyst on the FAME conversion at a temperature of 45 °C and 23% by volume of methanol (Figure 3) was investigated at various amounts of 3, 5 and 7 g NaOH per liter of oil. The results indicated that the methyl ester conversion sharply increased after one cycle (2 min) of circulation of the mixture through the reactor, but with a lower increase with a lower amount of catalyst. Conversion of the FAME tended to approach equilibrium after three cycles (6 min) of circulation. A maximum purity of the methyl ester of 92% by weight was achieved when 7 g NaOH per liter of oil as alkali-catalyst was used in the reaction. A good result was also obtained with 5 g NaOH per liter of oil as alkali-catalyst, albeit to a lesser degree. Cost-effectiveness should be further studied taking into account the specific local conditions. Furthermore, adding too much base catalyst in the transesterification reaction causes the glycerides to react with the base catalyst producing soap as a result of the saponification process.

Effect of FAME conversion with and without ultrasonic irradiation

Comparison of the FAME conversion employing circulation of the mixture of reactant through the reactor with and without ultrasonic irradiation (Figure 4) was conducted using the previously established conditions of 23% by volume of methanol, 7 g NaOH per liter of oil and a reaction temperature of 45 °C. The results showed that with the ultrasonic circulation process, 90% by weight of FAME could be achieved when a residence time of at least 6 min was attained. The circulation process without ultrasonic irradiation led to only 65% by weight of FAME conversion gained after a residence time of 12 min or longer

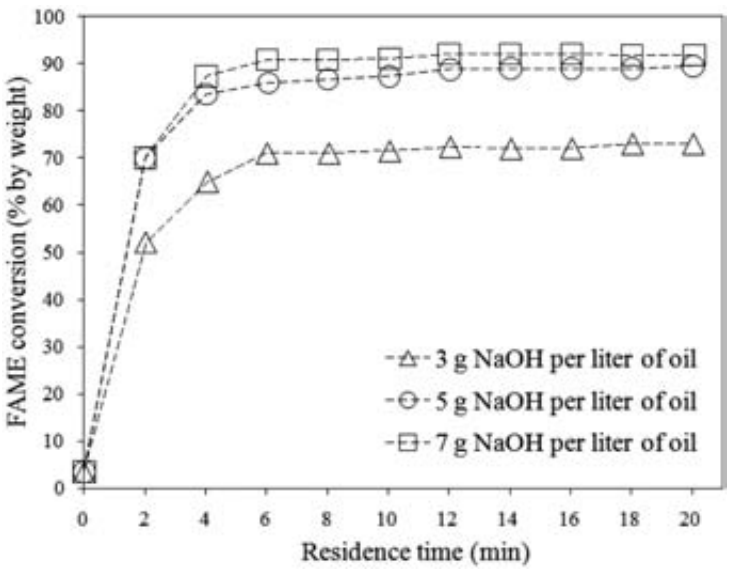

Figure 3 Effect of alkali-catalyst on fatty acid methyl ester (FAME) conversion with ultrasonic irradiation in the presence of 23% by volume of methanol and reaction temperature of 45 °C.

because, as described earlier in the literature review, ultrasonic irradiation causes cavitation and bubble collapse that affect the liquid-liquid phases which improve the mass transfer of the mixture, emulsification formation and the effect of phase transfer catalysts (Mason and Lorimer, 2002; Worapun *et al.*, 2012b). Thus, this effect was confirmed in the current experiment.

CONCLUSION

FAME from DDMCPO can be produced quite efficiently by circulation of the mixture through a 20 kHz, 400 W ultrasonic reactor. A maximum FAME conversion of 92.5% by weight was achieved with alkali-catalyst of 7 g NaOH per liter of oil and 23% by volume of methanol under a reaction temperature of 45 ^{o}C and a residence time of more than 6 min. The ultrasonic circulation process was shown to be very efficient and time saving when applied to transesterification with short-chain alcohols to produce biodiesel. Experiments on the effect of the FAME conversion with and without ultrasonic irradiation showed that ultrasonic irradiation can increase the FAME conversion compared to the circulation process without irradiation. It was confirmed that the ultrasonic field induces effective emulsification and rapid mass transfer so that the rate of ester conversion under the ultrasonic circulation process is higher than the process without ultrasonic irradiation.

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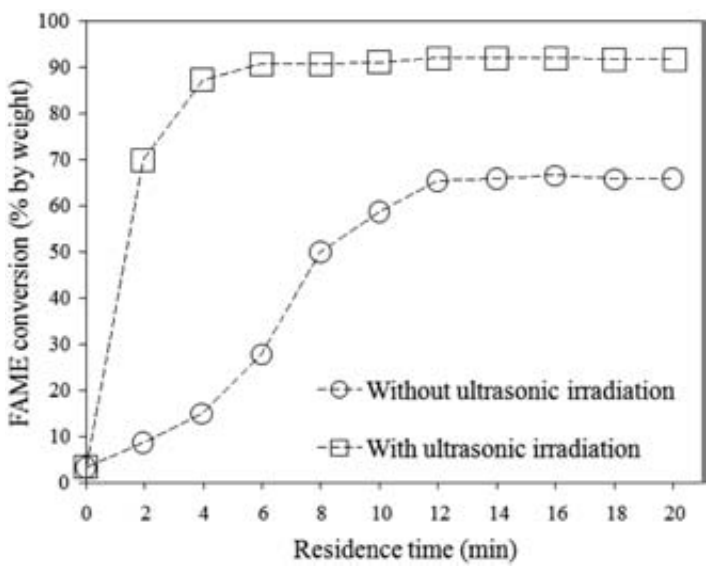

Figure 4 Effect of fatty acid methyl ester (FAME) conversion with and without ultrasonic irradiation in the presence of 7 g NaOH per liter of oil, 23% by volume of methanol and reaction temperature of 45 ^{o}C.

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