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Conventional Homogeneous Catalytic Process with Continuous-typed Microwave and Mechanical Stirrer for Biodiesel Production from Palm Stearin

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Abstract. In this study, biodiesel production from palm stearin was carried out by applying a mechanical stirrer and using continuous-typed microwave as a heating source. Transesterification of palm stearin with methanol in the presence of 0.5 wt% NaOH catalyst was performed. The aims of the study are to determine optimal radiation time and optimal methanol to oil molar ratio. Biodiesel yield and purity were obtained to compare with the previous work without the stirrer. The experiments were carried out at 60 ºC of reaction temperature, 0.15 W/g of palm stearin and 600 rpm of mixing speed at various radiation times of 40, 50, 60, 80, 120 s. The different methanol to oil molar ratios of 5:1, 6:1 and 7:1 were investigated after obtaining optimal radiation time. The results found that radiation time of 50 s and methanol to oil molar ratio of 7:1 were optimum for biodiesel production from palm stearin. Biodiesel yield and purity obtaining from these conditions were 97.5% and 98.33%, respectively. The fuel properties of stearin biodiesel were determined according to biodiesel standards (ASTM D 6751 and EN 14214).

Keywords: Biodiesel, Transesterification, Palm stearin, Microwave irradiation.

1. Introduction

Petroleum-based fuel plays an important role in the energy sector mainly as fuel for vehicles and engines in the transportation. However, it is not sustainable energy and its prices also tend to increase continuously. Thus, alternative fuels especially renewable and non-toxic energy are becoming significantly important.

The well-known alternative energy is biodiesel. It can be derived by transesterification reaction of vegetable oils or animal fats with alcohol in the presence of catalyst [1]. The major factors affecting on the biodiesel production such as reaction temperature, reaction time, catalyst, methanol to oil molar ratio and raw material have been widely studied. In conventional method, the temperature and reaction time are 55-65ºC and 30 min to 2 h., respectively. Theoretical methanol to oil molar ratio is 3:1 but the higher molar ratio in the range of 6:1-9:1 is used for completing forward reaction [2]. Transesterification reaction can be activated by catalysts such as acid, base and lipase depending %FFA in raw material. Typically, it should not exceed 1% leading to the base catalysts including NaOH and KOH are preferred over the others [3]. In addition, non-edible and low cost raw materials have been widely used. For example, palm stearin which is a by-product of the vegetable oil industry.

Several techniques for biodiesel synthesis include conventional heating, lipase catalyst method, ultrasonic method and microwave irradiation [4]. In comparison, the conventional heating method requires longer reaction times with higher energy inputs and losses to surrounding. Microwave-assisted method, on

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the other hand, is an energy-efficient and rapid method because the reactant molecules can receive the energy directly.

From the previous work, microwave assisted transesterification of palm stearin have been studied the effects of operating conditions on biodiesel yield. The results found that 0.5 wt% NaOH, 80 s of radiation time, 7:1 of methanol to oil molar ratio and 1 W/g of palm stearin were optimum for obtaining the highest yield and purity of 95.58% and 93.5%, respectively [5]. However, the results were lower than the ASTM D 6751 standard because methanol was evaporated and condensed on surface of the immiscible liquids. The interfacial areas between two phases were reduced leading to low biodiesel yield.

In this study, transesterification of palm stearin using continuous-typed microwave irradiation were performed. In addition, mechanical stirrer was applied to improve the biodiesel yield and purity. The optimal radiation time and methanol to oil molar ratio were determined. The biodiesel yield and purity were then compared with the previous work without the stirrer.

2. Methodology

2.1. Materials

Refined palm stearin oils were obtained from Patum Vegetable Oil Company Limited. Analytical reagent grade chemicals such as methanol, sodium hydroxide and n-heptane were purchased from Merck Ltd., Thailand. For biodiesel analysis, methyl heptadecanoate (C17:0) was use as internal standard which purchased from Sigma-Aldrich company.

2.2. Experimental Setup

Microwave oven (LG model MS2127 CW) controlled by computer software and the control box was used in this experiment. The glass reactor equipped with reflux condenser and mechanical stirrer system to prevent methanol evaporation and increase contacting between oil and methanol molecules. The microwave irradiation system was shown in Fig. 1.

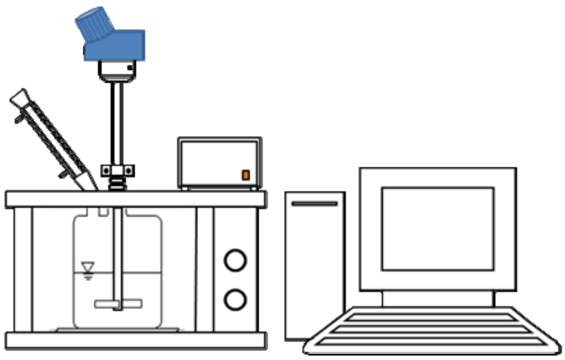

Fig. 1: Schematic diagram of modified domestic microwave oven for batch experiments.

2.3. Transesterification of Palm Stearin

Initially, palm stearin was heated to become liquid and remove moistures. Then, the reactor was charged with 400 g of palm stearin. It was placed in microwave oven and equipped a reflux condenser and mechanical stirrer. 0.5 wt% NaOH catalyst to oil can be dissolved in the required amount of methanol. The solution was then added in the reactor when the temperature of palm stearin reached 60 ºC. The microwave power is 0.15 W/g of palm stearin with mixing speed of 600 rpm. The various radiation times of 40, 50, 60, 80, 120 s were investigated. And, methanol to oil molar ratio can be varied at 5:1, 6:1 and 7:1. Once the reaction completed, the reaction mixture was poured into separatory funnel and settled overnight to completely separate glycerol from ester layer. Hot water sprayed over the ester layer many times to remove the impurities and the glycerol. Finally, washed biodiesel was dried for water evaporation. Biodiesel yield can be calculated following equation:

$$\%Yield = \frac{Biodiesel(g)}{Triglyceride(g)} \times 100\%$$

2.4. Ester content and Fuel Properties of Biodiesel

Biodiesel purity as methyl ester content can be analyzed by gas chromatography (Shimadzu GC-2010 plus equipped with FID detector) according to EN 14103 with the DB-WAX column of 30 m length, 0.25 mm inner diameter and maximum temperature of 250 ºC. The nitrogen was used as a carrier gas. Methyl heptadecanoate (C17:0) was used as internal standard for determining fatty acid methyl ester content which can be calculated using following equation:

$$C = \frac{\Sigma A - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m} \times 100\%$$

It can be expressed as the peak area of each composition at different retention times. In above equation, ΣA is the total peak area of methyl ester, A_{IS} is the peak area of internal standard, C_{IS} is the concentration of internal standard in mg/ml, V_{IS} is the volume of internal standard in ml. and m is the mass of sample in mg.

Biodiesel properties such as density and viscosity can be measured by the Anton Paar density meter DMA 4500M and viscometer, respectively.

3. Results and Discussion

3.1. Properties of Palm Stearin and Biodiesel

Fatty acid compositions of palm stearin are shown in Table 1. Free fatty acid analyzed by AOCS Ca 5a-40 method was 0.04%. Iodine value which indicates total number of double bonds in the oil was 37.3 within the maximum limit of 120. Moisture and impurities was found about 0.03%. Due to high fraction of saturated oil, it has high melting point at 50ºC and becomes solid phase at room temperature.

Table 1: Fatty acid composition of palm stearin

Fatty acid		Fatty acid composition (%)
Saturated fraction:	Myristic acid (C14:0)	0.94
	Palmitic acid (C16:0)	58.39
	Stearic acid (C18:0)	4.69
Unsaturated fraction:	Oleic acid (C18:1)	29.54
	Linoleic acid (C18:2)	5.92

Table 2: Properties of palm stearin biodiesel

Properties	ASTM D 6751	EN 14214	Palm stearin biodiesel
Kinematic viscosity(cSt) @ 40 ºC	1.9-6.0	3.5-5	4.818
Density (g/cm^3) @15°C	0.87-0.89	0.86-0.9	0.871
Specific gravity	0.87-0.89	0.86-0.9	0.872
Flash point (ºC)	130	>120	198
Iodine value (g I_2/100g)	-	<120	39.1
Acid value (mg KOH/g)	<0.5	<0.5	<0.1
Cloud point (ºC)	-	-	17
Pour point (ºC)	-	-	18
Gross heat of combustion (cal/g)	-	-	9473

The physical properties of palm stearin biodiesel can be measured such as kinematic viscosity at 40 ºC, density at 15 ºC and acid value as shown in Table 2. The results found that its properties were within the range of biodiesel standard ASTM D 6751. In addition, the chromatogram of methyl ester content that was analyzed by GC was shown in Fig. 2 and the major composition in stearin biodiesel is methyl palmitate (C16:0).

3.2. Influence of Radiation Time on Biodiesel Yield and Purity

Experiments were carried out with 0.5 wt% NaOH catalyst, 6:1 molar ratio of methanol to oil, 600 rpm of mixing speed and 0.15 W/g of palm stearin to investigate the effect of radiation times on biodiesel yield and purity as shown in Fig. 3a) and Fig. 3b), respectively. The yields were 95.98%, 97.5%, 97.09%, 96.93% and 97.08% for 40, 50, 60, 80 and 120 s, respectively. Biodiesel yield increased with increasing time until the yield was not significant increasing. And then, it continuously decreased because of irreversible reaction. Typically, the biodiesel yield should be higher than the preferable value (96%). As shown in Fig. 3a), there were insignificant difference at various radiation times ($P<0.05$, $n=3$). However, the results of purity analysis were found 95.62%, 98.33%, 96.78%, 96.76% and 98.62%. The minimum ester content according to EN14214 is greater than 96.5%. It can be found that the purity of 40 s was lower than the limit value and had a significant increasing from 40 s to 50 s ($P<0.05$, $n=3$). After that, the results were still over the limit as shown in Fig. 3b). Thus, the optimal radiation time was 50 s.

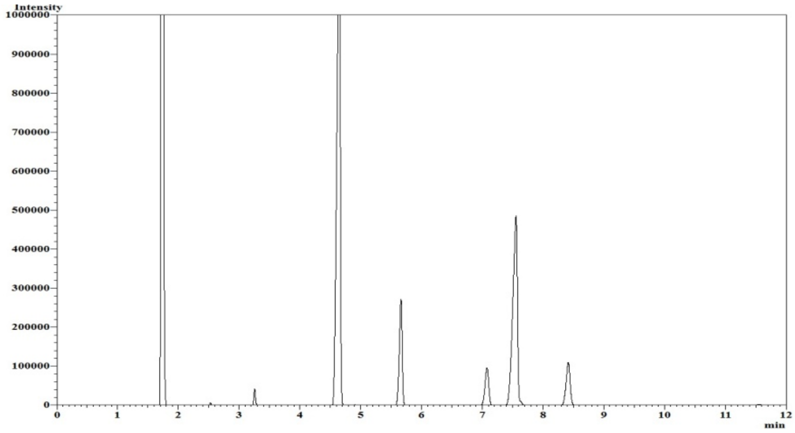

Fig. 2: GC chromatogram of palm stearin biodiesel at 50 s of irradiation time, 7:1 methanol to oil molar ratio, 60 ºC, 0.5% NaOH, 600 rpm of mixing speed and 0.15 W/g of palm stearin.

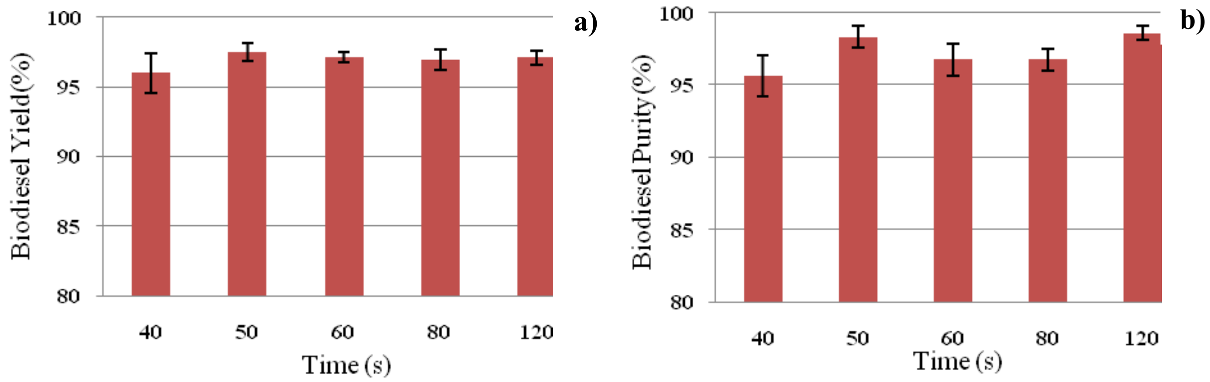

Fig. 3: Effect of radiation times on a) biodiesel yield, b) biodiesel purity at 7:1 methanol to oil molar ratio, 60 ºC, 0.5% NaOH, 600 rpm of mixing speed and 0.15 W/g of palm stearin.

3.3. Influence of Methanol to Oil Molar Ratio on Biodiesel Yield and Purity

Experiments were carried out with 50 s of radiation time, 0.5 wt% NaOH catalyst, 600 rpm of mixing speed, 0.15 W/g of palm stearin and various methanol to oil molar ratios of 5:1, 6:1 and 7:1. The result was shown in Fig. 4. The yields of 5:1, 6:1 and 7:1 were 89.76%, 97.79% and 97.5%, respectively and the ester contents were 86.1%, 95.55% and 98.33%, respectively. The lowest result occurred at molar ratio of 5:1 because unreacted stearin solids suspended in biodiesel phase. The biodiesel yield and purity increase with increasing methanol to oil molar ratio. Theoretically, the molar ratio of methanol to oil is 3:1 but methanol can evaporate and do not contact with oil during the reaction time. Therefore, the excess amounts of methanol are necessary for completing reaction. In practice, the optimal molar ratio of methanol to oil is 6:1 for olein feedstocks. In this experiment from stearin feedstocks, the purity of molar ratio of 6:1 was lower than the biodiesel standard (EN 14214). Thus, the optimal molar ratio of methanol to oil was 7:1.

4. Conclusion

The biodiesel from transesterification of palm stearin was successfully produced by continuous typed microwave irradiation and mechanical stirrer. The experimental results of the previous work without a stirrer indicated that 80 s of radiation time, 0.5 wt% NaOH catalyst, 7:1 methanol to oil molar ratio and 1 W/g of palm stearin were optimum for the reaction. Mechanical stirrer was applying in this experiment during irradiation in order to enhance homogeneity between methanol and oil. The results showed that the reaction can be done in 50 s at methanol to oil molar ratio of 7:1 and constant mixing speed of 600 rpm. The energy requirements were about 6.5 times lower than that of without stirrer. The properties of biodiesel from palm stearin were in the range of biodiesel standard except the cloud point. Due to saturated oil feedstocks, it causes high melting point and cloud point. Therefore, the uses of stearin biodiesel in engines are not suitable for low temperature operation.

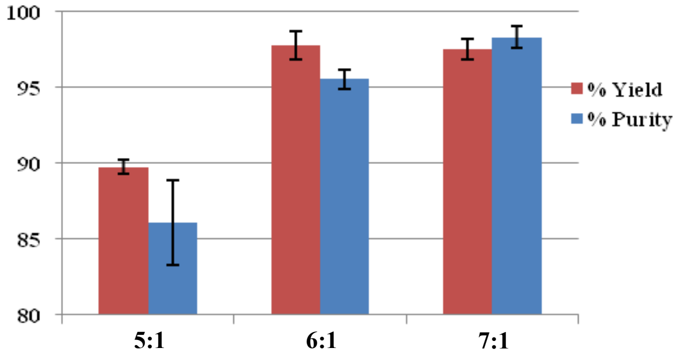

Fig. 4: Effect of methanol to oil molar ratios on biodiesel yield and purity at 50 s of radiation time, 60 ºC, 0.5% NaOH, 600 rpm of mixing speed and 0.15 W/g of palm stearin.

5. Acknowledgements

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