

FEASIBILITY STUDY OF BIODIESEL PRODUCTION FROM RESIDUAL OIL OF PALM OIL MILL EFFLUENT

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* Corresponding Author, Received:15 June 2016, Revised: 08 August 2016, Accepted: 30 Nov. 2016

ABSTRACT: Pollution from residual oil contaminating wastewater is a serious environmental problem. The rapid development and growth of palm oil industries in Thailand have generated large volumes of palm oil mill effluent (POME) which contains residual oil. Instead of becoming a pollutant in the environment, residual oil from POME can be used as raw material for producing biodiesel. Biodiesel has recently become more attractive as an alternative energy source due to its environmental friendly properties generated from renewable resources. This study investigated the characteristics of residual oil and found: a free fatty acid content of 22.03 % wt, fatty acid methyl ester (FAME) of 3.767 %wt, acid value of 49.29 mg KOH/g, water content of 1.01 % mg/Kg, and total glycerines as monoglycerides, diglycerides, and triglyceride at 1.15 % m/m, 11.88 % m/m, and 87.54 % m/m respectively. Optimal conditions to separate water from oil contents are also determined. Separation of residual oil from POME is carried out using the solvent extraction process.

Keywords: Residual oil, Palm oil mill effluent (POME), Biodiesel, Fatty acid methyl ester (FAME)

1. INTRODUCTION

The palm oil industry is one of the most important industries in Thailand. Increasing palm oil industry capacity also increases its effluent output [1]. The number of registered palm oil mill extraction operations nationwide numbered approximately 80 plants having a capacity of around 2,801 tons of fresh fruit bunch per hour with the volume of crude palm oil extracted at approximately 1,832,151tons / year [2]. There are a lot of factories and palm oil production which results in high energy consumption and effluent resulting during palm oil production.

The disposal of effluent is therefore a serious problem that must be solved. Although no chemicals are used during oil extraction, the effluent still must satisfy threshold values set by the Department of Industrial Works [3]. This palm oil or residual palm oil floats on the surface of wastewater in wastewater treatment ponds and covers the surface of wastewater [4].

Biofuel is inherently renewable as it is derived from biomass or waste matter. There are different types of biofuel such as biodiesel biogas and

bioalcohol [5]. Biodiesel or fatty acid methyl ester (FAME) is a renewable, economically viable alternative to petroleum-derived diesel and has received much attention as the world seeks to prevent the future oil crisis and the unpredictable consequences of climate change [6]. It is generally produced from the oils of palm, soybeans, canola, and jatropha [7].

The reaction for synthesis of biodiesel is transesterification. Transesterification is the most widely used process to reduce the viscosity of oil. Transesterification occurs due to the reaction between fat or oil and alcohol to form methyl esters or biodiesel as a product and glycerol as a by-product [8].

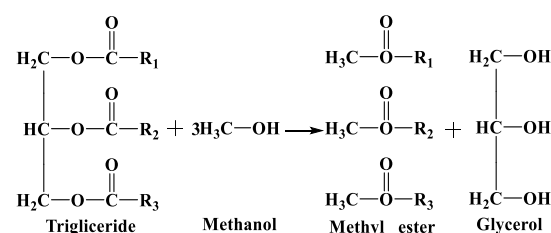


Fig. 1 Transesterification reaction

2. MATERIALS AND METHODS

2.1 Materials

Samples of residual oil from POME were collected from a palm oil mill plant in Eastern part of Thailand. The chemicals for this research are analytical grade hexane and methanol.

2.2 Oil-Water Separation

Experiments were conducted to evaluate the performance of the organic solvent n-hexane in extracting residual oil from POME. POME was transferred into a conical flask and mixed with n-hexane as the solvent for the extraction process [1]. The ratios of solvent to POME were 6:1, 9:1 and 12:1 by volume at 60 °C with a 15 min mixing rate of 200 rpm. Then the mixture product was filtrated on filter paper under vacuum filtration immediately to separate the solid particles from the mixture product. The n-hexane solution in filtrate was evaporated by using a rotary evaporator.

2.3 Transesterification Reaction

The reactions were carried out in the system shown in Fig 2. It is a cylindrical reactor of 250 mL located in a vessel of stainless steel and equipped with magnetic stirring, heating system, sampling outlet, pressure gauge and temperature controller. The pressure and temperature were monitored in real time up to a maximum value of 300 bars and 430 °C, respectively. Then, the reactor was heat with an external electrical furnace to the desired temperature while the liquid solution was stirred at a constant speed of 500 rpm. The operational temperature (210-230 °C) of the reactor was measured with a thermocouple and automatically controlled at ± 5 °C for a set time with pressure at 30-35 bars. After the transesterification was complete, the sample was recovered by simple decantation. The reaction mixture was evaporated with a rotary evaporator at 60 °C for 60 min to remove methanol.

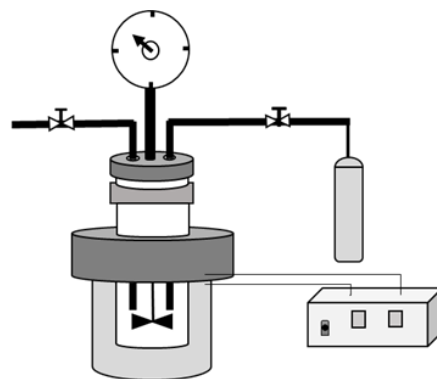


Fig. 2 Parr reactor model 4848 for transesterification.

2.4 Methods of Analysis

Biodiesel samples were analyzed by gas chromatography (GC Agilent 6890, FID). The GC was equipped with a DB-5HP capillary column with dimensions of 30.0 m x 0.1 μ m x 250 μ m. Gas chromatography was used to analyze the composition and to determine the amount of FAMES, mono-, di-, triglycerides, free glycerol and methanol in the samples. A split injector was used with a split ratio of 20 and temperature of 370 °C. Total run time of this method was 52 min. The calibration curve of peak area and the quantity of biodiesel was linear.

FAME content in crude biodiesel (%)

$$= \frac{(\sum A) - A_s}{A_s} \times \frac{\sum V_s \times C_s}{m} \times 100$$

Where: $\sum A$ is the total peak area of FAMES

A_s is the peak area of internal standard

C_s is the concentration of internal standard

(mg/L)

V_s is the volume of internal standard (mL)

m is the weight of crude biodiesel (g)

The analytical method used to determine the characteristics of the biodiesel according to the European Standard EN 14214 [9].

3. RESULTS AND DISCUSSION

The operational variables employed were molar ratios methanol to oil, temperature, and retention time that were fixed as common parameters in all experiments. Table 1 shows the composition of the fatty acid of the residual oil used as raw material in this study.

Table 1 Characterization of residual palm oil biodiesel

Fatty acid composition (% by weight)	
Palmitic acid (C16:0)	45.45
Oleic acid (C18:1)	50.85
Linoleic acid (C18:2)	11.36
Linoleic acid (C18:3)	0.41
Molecular weight ($\text{g}\cdot\text{mol}^{-1}$)	849.52
Water content	1.01
Free fatty acid (%wt.)	22.03

3.1 Effect of Solvent Ratio on Percent of Water Content

Experiments were conducted at solvent ratios of 6:1, 9:1 and 12:1. The extraction time and mixing rate were 15 minutes and 200 rpm. The optimum solvent extraction was found using organic solvents at a ratio of solvent to POME of 9:1, mixing rate of 200 rpm for 15 min. Fig. 3 shows the optimal ratio of solvent (n-hexane) to oil at 9:1 which can reduce the water content in the sample of POME down to 0.02 %. Its relatively low molecular weight and saturation made n-hexane completely miscible with oil [10].

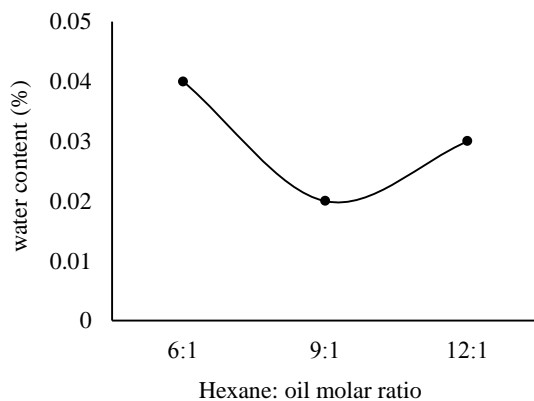


Fig. 3 Separation of residual oil from POME with different solvent ratios.

3.2 Effect of Methanol: Oil Molar Ratio

Effects of the most important variables in the transesterification of residual palm oil under subcritical methanol conditions were studied. These variables were molar ratio of methanol to oil, reaction temperature and reaction time. The condition of the runs carried out are shown in Table 2.

Table 2 Reaction condition of different methods for biodiesel

Condition	Molar ratio		T (°C)	t (hr.)	P (bar)
	oil	MeOH			
1	1	24	220	1	30
	1	24	220	3	30
	1	24	220	4	30
	1	24	220	5	30
	1	24	210	4	30
2	1	24	220	4	30
	1	24	230	4	30
	1	24	220	4	30
3	1	36	220	4	30
	1	42	220	4	30

Experimental results are shown in Fig. 4. Reactions were carried out at a fixed temperature of 220 °C with a fixed reaction time of 4 hours under different molar ratios of methanol: oil as 24:1 36:1 and 42:1. When the molar ratio of methanol to oil increased from 24:1 to 36:1 and 42:1, the methyl ester was 61.51 to 61.19 and 68.23%, respectively. Furthermore, increasing alcohol in the optimal ratio increases the yield, the surplus methanol increased contact between methanol and oil, enhance in more efficient to reaction [11]. But also increases cost for alcohol recovery [12]. The results of methanol to oil molar ratio to triglyceride and FFA are was the %wt of FFA decreased when methanol to oil molar ratio increased. Especially when above the molar ratio 42:1, the free fatty acid (FFA) volume almost achieved its lowest value. The methanol to oil molar ratio for reaction show good activity for free fatty acid (FFA) but not for triglycerides.

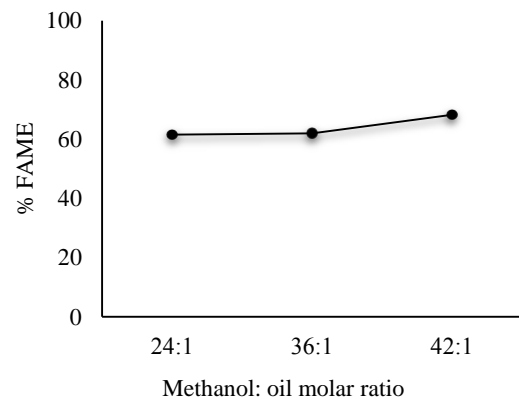


Fig. 4 Effect of methanol to oil molar ratio on biodiesel production (conditions of 220 °C reaction temperature, 4 hour reaction time).

3.3 Effect of Reaction Temperature

The non-catalytic transesterification reactions with subcritical methanol were carried out at a fixed

molar ratio of methanol to oil of 24:1 and fixed reaction time of 4 hours under different temperatures, 210-230 °C. The critical temperature of methanol is 240 °C. Fig. 6 presents the variations of the methyl ester yield with different reaction temperatures. Experimental results show that the temperature used affect reaction rate slightly due to short term temperature increases. The methyl ester yields were 59.61, 61.51, and 66.65 % as temperature rose, 210 to 220 and 230 °C. This indicates that at high temperatures, the conversion rate of FAME increases. One of the most important factors of biodiesel production is temperature. Optimizing temperature is required for the reaction and optimal temperature can slow the reaction and reduce the yield of biodiesel.

Effect of reaction temperature to triglyceride and FFA were carried out at a fixed molar ratio of methanol to oil of 24:1 and fixed reaction time of 4 hours. The percent of FAME yield from 59.56 to 66.55 at temperature of 210 to 230 °C. Thus, increasing temperature would favor improved transesterification reaction from triglyceride to diglycerides, diglycerides to monoglycerides and monoglycerides to methyl ester (biodiesel). It is transesterification reaction between triglycerides and methanol is a reversible at the time high activation energy reaction [13].

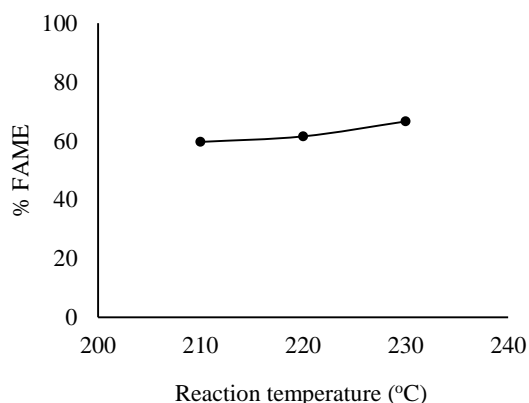


Fig. 6 Effect of reaction temperature on biodiesel production (conditions 24:1 molar ratio of MeOH: oil, 4 hour reaction time).

3.4 Effect of Reaction Time

Figure 8 shows the effect of reaction time on the biodiesel production conversion at various times: 1, 3, 4, and 5 hours, respectively. Reactions were carried out at a fixed temperatures of 220 °C and a fixed molar ratio of methanol to oil of 24:1. At 1 hour, the methyl ester conversions was 42.19 %. When the reaction time increased from 1, 3, 4 and then 5 hours, FAME increased from 42.19, 60.67,

61.51 and 77.64 %, respectively. At 4 hours, methyl ester only slightly increased compared with that at 3 hours. However, it is possible to obtain a high conversion with a molar ratio of methanol: oil at 24:1 by increasing the reaction time to 7 hours but increased cost for reaction.

Effect of reaction time to triglyceride and free fatty acid (FFA). Triglycerides volume is highest at reaction time 1 hour whilst FAME volume is lowest and conversely at reaction time 5 hours the triglyceride volume decrease the lowest whilst FAME volume is highest.

In addition, the varied of reaction time 1, 3, 4, and 5 hours is not significant for free fatty acid (FFA)

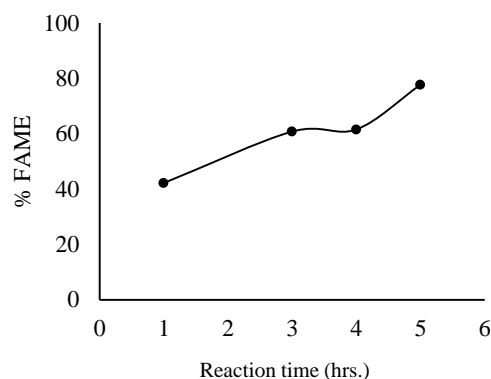


Fig. 8 Effect of reaction time on biodiesel production (conditions 24:1 molar ratio of MeOH: oil, 220 °C reaction temperature).

4. CONCLUSION

In this work, the transesterification of residual oil under subcritical conditions was carried out. Results of solvent extraction using of organic solvents at a ratio of solvent to POME of 9:1 are produced. The effect of the main variables were evaluated under different conditions molar ratio of methanol: oil (24:1, 36:1, and 42:1), reaction temperatures (210, 220 and 230 °C) and reaction times (1, 3, 4 and 5 hours). The highest methyl ester yield of 77.64 % was at a reaction temperature of 230 °C, reaction time of 5 hours and a molar ratio of methanol to oil at 42:1. However, even higher temperatures can enhance the biodiesel content, although small improvements would require high energy expenses.

5. ACKNOWLEDGEMENTS

The authors sincerely thank the Faculty of Public Health, Mahidol University, Thailand. This study received support of facilities at the laboratories of the Energy Technology Department, Thailand Institute of Scientific and Technological Research.

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