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The Optimization Process of Biodiesel Production Using Multiple Feedstock (CPO And Jatropha) with Assistance of Ultrasound at 40 Khz

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INTRODUCTION

The issue of fuel becomes a hot topic in recent years. Based on the United States Energy Information Administration (eia), total world energy consumption is 406 quadrillion British thermal units (Btu) in 2000 and is projected to increase to 769.8 quadrillion Btu in 2035 [5]. This is an increase of approximately 47.25%, and oil is the largest source of world energy consumption, exceeding coal, natural gas, nuclear and renewable energy [2].

Dwindling sources of fuel has lead to the increasing number of research and development of alternative energy sources as a substitute for fossil fuels, in particular from renewable energy sources. Based on these conditions, the development of an alternative renewable energy to substitute for petroleum fuel becomes indispensable, one of which is biodiesel. Biodiesel is an alternative fuel derived from vegetable oils that are environmentally friendly. Biodiesel can be made from palm oil which is made an edible vegetable oil. As such, while CPO is quite abundant in Indonesia and Malaysia, biodiesel production from CPO competes with food needs. To reduce this competition, it is necessary to mix the CPO with Jatropha oil which is a non-edible vegetable oil [1].

Biodiesel from palm oil has weaknesses that can interfere with the performance of diesel engines. The biodiesel from palm oil at low temperature will form some wax crystals that will interfere the fluidity and can cause clogging of the fuel filter. The fog point and pour point are two indicators used to measure performance of biodiesel at low temperatures. The fog point is the temperature at which the wax crystals will be formed and cause an increase in viscosity. The pour point of biodiesel is the temperature at which it becomes semi solid and loses its flow characteristics. In a high pour point of oil is generally associated with the degree of saturation and the length of the carbon chain. The biodiesel from CPO has a higher the pour point temperature than the biodiesel from Jatropha. Therefore, a mixture of Jatropha and CPO to produce biodiesel will improve its pour point temperature [5].

The main reactions in the formation of biodiesel are esterification and transesterification, in which triglyceride reacts with alcohol (methanol) to produce methyl ester and glycerol as a byproduct. When producing biodiesel in conventional process, a considerable time is required at 4-8 hours and it also requires a lot of catalyst and alcohol. The conventional process also often has a reaction that is not perfect, so that the yield is low. Therefore, this study uses ultrasonic waves that can reduce the reaction time to 30-60 minutes and result in a yield that is higher than conventional processes.

The ultrasonic method is an effective method for increasing the mass transfer in heterogeneous liquid phase to accelerate the transesterification reaction and in this way will get a higher yield, less energy consumption, and increased efficiency in the use of methanol and a catalyst.

This study was performed on a laboratory scale where the parameter varied is a volume of the ratio of CPO and Jatropha oil, a mole ratio between methanol and a mixture of CPO oil with Jatropha oil and the time to get optimal results. The purpose of this study was to determine the optimum transesterification process, wherein the certain ratio of jatropha, palm oil and methanol produces the highest yield at 40 kHz.

EXPERIMENTAL METHOD

² The vegetable oil used in this study was CPO and Jatropha oil. Potassium hydroxide was used as catalyst. The transesterification was carried out in an ultrasonic generator.



FIGURE 1. The ultrasonic Generator



FIGURE 2. Transesterification CPO, Jatropha oil and Methanol on ultrasonic generator

The ultrasonic generator was used to perform the transesterification reaction as can be seen in Figure 1 and Figure 2. The frequency was set at 40 kHz. Potassium hydroxide was dissolved into the methanol in the methanol tank. Jatropha oil was blended with CPO in the ratios of 1: 1, 3: 1 and 4: 1. Then, the oil mixture was mixed with methanol at ratios of 5: 1, 6: 1 and 7: 1. The mixtures of oil and methanol were then poured into 200ml Erlenmeyer flasks. Afterwards, the mixture was placed on the ultrasonic generator as can be seen in Figure 2 with transesterification times of 50,60 and 70 minutes.

The biodiesel (FAME) yields of transesterification were calculated from the weight of FAME in the FAME phase and the theoretical material balance of the transesterification reaction, as shown in the following equation:

$$FAME \text{ yield } (\%) = \frac{W_{FAME} / M_{FAME}}{3W_{oil} / M_{oil}} \quad (1)$$

where W_{FAME} and W_{oil} were the weight of FAME in the FAME phase and the weight of oil used respectively. M_{FAME} and M_{oil} were the mean of molecular weight of the FAME and the oil respectively. The factor of 3 in the equation indicates that one mole of tryglyceride yields three moles of FAME.

The yield of biodiesel during transesterification were measured and analyzed. The yield of biodiesel, the frequency of ultrasonic bath and the ratio of oil and methanol mixture were recorded. Biodiesel as a final product was analyzed based on SNI-04-7182-2006 which is the National Indonesian Standard of Biodiesel Quality.

RESPONSE SURFACE METHODOLOGY

Response surface methodology is a collection of techniques and mathematical statistics useful for analyzing the problem of several independent variables that affect the dependent variables or responses and for optimizing the response [4].

The conversion will be processed by RSM to determine the effect on the response variable and the observations of the influencing variables. The responses were observed evaluating the relationship between oil ratio, the amount of catalyst and the ratio of the oil with methanol to the catalyst [3].

The study design will be processed by Central Composite Design (CCD) where the conversion will be the output (y) and variables defined in the beginning as the dependent variable (x). The following correlations based on Response Surface Methodology (RSM): $y = f(x)$.

Optimization based RSM will be used to determine the optimal process conditions of transesterification with ultrasonic waves. Using STATISTICA 6.0 software, the results for the 3 variables for 16 experimental runs was evaluated. The midpoints of each variable were repeated 2 times and has a critical value for each variable. The study design Central Composite Design with 3 variables using STATISTICA 6.0 software can be seen in Table 1.

Table 1. Experimental Design Central Composite Design 3 Variables

Run	Block	X ₁	X ₂	X ₃	Y
1	1	-1	-1	-1	Y ₁
2	1	-1	-1	1	Y ₂
3	1	-1	1	-1	Y ₃
4	1	-1	1	1	Y ₄
5	1	1	-1	-1	Y ₅
6	1	1	-1	1	Y ₆
7	1	1	1	-1	Y ₇
8	1	1	1	1	Y ₈
9	1	0	0	0	Y ₉
10	2	-1.76	0	0	Y ₁₀
11	2	1.76	0	0	Y ₁₁
12	2	0	-1.76	0	Y ₁₂
13	2	0	1.76	0	Y ₁₃
14	2	0	0	-1.76	Y ₁₄
15	2	0	0	1.76	Y ₁₅
16	2	0	0	0	Y ₁₆

Description:

X₁ = encoding to oil ratio variables

X₂ = encoding for the variable ratio of oil and methanol
X₃ = encoding for a variable time comparison

Y = conversion reaction

Response experiment results are a conversion (Y) for each experiment. Results of data processing are presented in Table 2.

TABLE 2. The experiment design with Central Composite Design

RUN	Block	X ₁	X ₂	X ₃	Y (%)
1	1	-1	-1	-1	87.79
2	1	-1	-1	1	91.23
3	1	-1	1	-1	95.77
4	1	-1	1	1	96.14
5	1	1	-1	-1	89.27
6	1	1	-1	1	92.33
7	1	1	1	-1	95.85
8	1	1	1	1	97.81
9	1	0	0	0	100.30
10	2	-1,76	0	0	88.27
11	2	1,76	0	0	90.77
12	2	0	-1,76	0	84.90
13	2	0	1,76	0	91.15
14	2	0	0	-1,76	91.22
15	2	0	0	1,76	92.09
16	2	0	0	0	97.42

Furthermore, to determine the most influential variables, performed data processing to obtain a mathematical model equation. In the experiment the number of independent variables were 3, so that polynomial equation becomes:

$$Y_u = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (2)$$

So the equation becomes:

$$Y_u = 99.06473 + 1.2297X_1 - 4.95096X_2 + 5.0582X_3 - 5.91503X_2^2 + 1.4576X_3 - 3.57818X_3^2 - 0.21X_1X_2 + 0.30058X_1X_3 - 1.04414X_2X_3 \quad (3)$$

From the equation, it can be seen that the coefficients X1, X2, X3, X1 and X3 are positive, it will have a great impact to increase the yield of biodiesel. Methanol is the most influential variable to the yield.

ANOVA was used to determine the suitability of significant and quadratic models wherein if $R^2 > 0.7$ then the quadratic model is suitable and acceptable. ANOVA also specify the variables that affect and influence to get yield by comparing the value of the F (ratio of mean square) and the value P (probability). A F value greater than the value of P means the variable effect. A value P less than 0.05, then the variable is very influential in getting the yield. Analysis of variance obtained from STATISTICA 6.0 software can be seen in Table 3.

TABLE 3. Analysis of Variance (ANOVA)

Effect	SS	DF	MS	F	P
X_1	5.376	1	5.37641	0.6384	0.4547
X_1^2	63.96	1	63.9649	7.5952	0.0330
X_2	90.97	1	90.9701	10.801	0.0166
X_2^2	91.30	1	91.3014	10.841	0.0165
X_3	7.554	1	7.55409	0.8969	0.3801
X_3^2	33.41	1	33.41082	3.9672	0.0934
X_1X_2	0.088	1	0.08821	0.0104	0.9218
X_1X_3	0.180	1	0.18070	0.0214	0.8883
X_2X_3	2.180	1	2.18044	0.2589	0.6290
Error	50.53	6	8.42169		
Total SS	264.6	15			
R^2	0.809				

From Table 3, it can be seen that the p-value less than 0.05 in the variable X_1^2 , X_2^2 and X_2^2 have the meaning that these variables have a significant effect on yield.

PROFILE CONTOUR AND SURFACE PLOT ANALYSIS

Figure 3 a) and b) show a 3D plot and contour plot of the interaction between oil mixture (X_1) and the ratio of oil methanol (X_2) to yield biodiesel. At this interaction reaction time (X_3) set at 60 minutes.

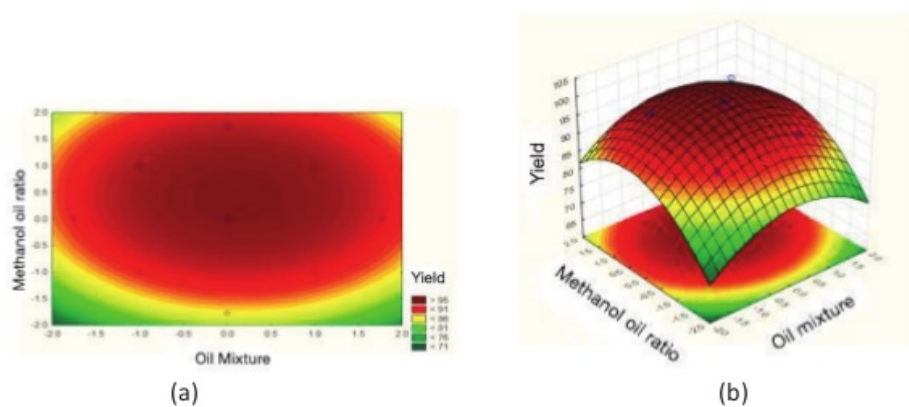


FIGURE 3. Interaction oil mixture (X_1) and methanol-oil ratio (X_2), reaction time (X_3) = 60 minutes, (a) Contour Plot (b) Plot 3D

Figure 3 shows the optimum conditions in the oil mixing ratio between 130: 70 and 160: 40 and the ratio of oil and methanol between the 6: 1 to 7: 1, which gives a yield above 95%. From Figure 3, it can be seen also that methanol is highly significant to the yield. The oil volume ratio does not really give a significant effect on yield, but the use of palm oil is yields little more than Jatropha oil.

Figure 4 a. and b. show a 3D plot and contour plot of the interaction between oil mixture (X_1) and reaction time (X_3) to yield biodiesel. At this interaction methanol-oil ratio (X_2) is set at 6: 1.

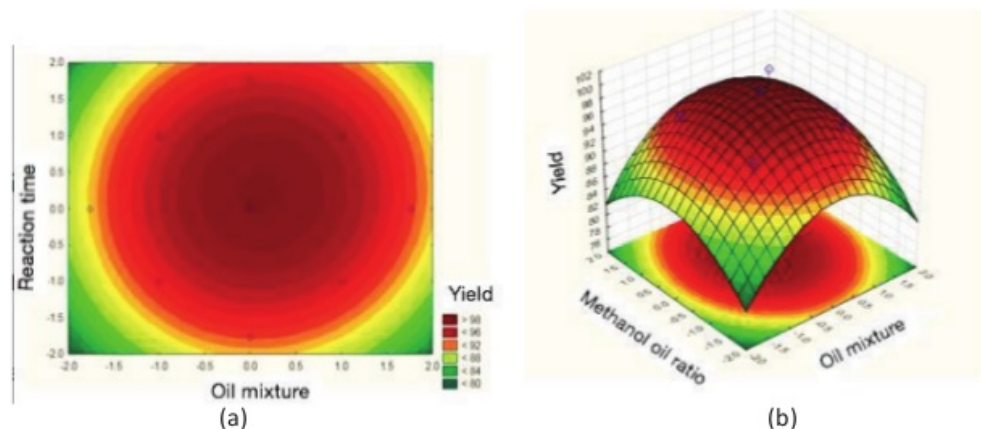


FIGURE 4. Interaction oil mixture (X_1) and reaction time (X_3), methanol-oil ratio (X_2) = 6: 1 (a) Contour Plot (b) Plot 3D

In Figure 4 the optimum condition was obtained with an oil mixture at 100: 100 and 60 minutes that the yield is to achieve greater than 96%. Volume ratio jatropha oil and palm oil does not have a significant effect on yield where the use of raw materials, palm oil or jatropha oil will give results that are not much different to the yield. But CPO yielding slightly more than Jatropha. Reaction time also seems less significant to the yield in the period in which 50- 70 are generally already obtained a yield above 90%. This means that the transesterification reaction is already in a state of equilibrium, so that the added time is not significant to the yield.

Figure 5 a. and b. show a 3D plot and contour plot of the interaction between methanol-oil ratio (X_2) and reaction time (X_3) to yield biodiesel. At these interactions oil mixtures (X_1) is set at 3: 1.

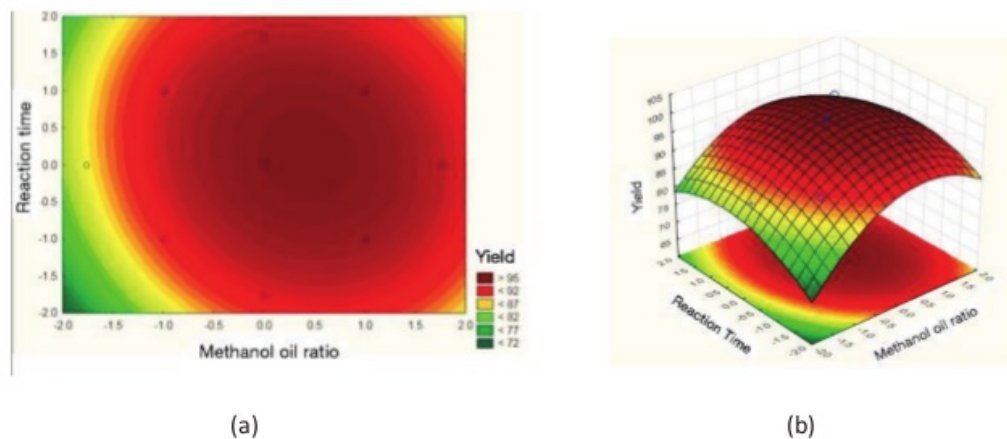


FIGURE 5. Interaction methanol ratio (X_2) and reaction time (X_3), a mixture of oil (X_1) = 1: 1, (a) Contour Plot (b) Plot 3D

In Figure 5, it can be seen that the effect of methanol is more significant while the time is not too significant. At low reaction times, methanol ratios significantly affects the increase in yield (87 to 96%). But on a low methanol ratio, increased reaction time does not have a significant effect on the yield, because the transesterification reaction reaches equilibrium conditions at the time of 40 minutes so that additional time does not have a significant impact on yield.

CONCLUSIONS

The application of experimental design techniques in this research causes improved process yields, reduced variability and closer conformance to nominal or target requirements, reduced development time, reduce overall cost. The conclusions are that the optimum conditions obtained from this study using response surface method at 40 KHz for biodiesel yield is 2.8: 1 mixture of CPO-Jatropha, 6.4: 1 molar ratio of methanol-oil and 61.5 minutes of reaction time.

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