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An Ultrasound Assisted Transesterification to Optimize Biodiesel Production from Rice Bran Oil

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Abstract. The ultrasound method is used to improve mass transfer between incompressible reactants which increases their chemical reaction and reduces reaction time as well as energy consumption. In this research, transesterification process variables of rice bran oil were optimized using response surface methodology (RSM). Three process parameters were investigated, namely methanol to oil molar ratio, catalyst concentration, and time. The optimum conditions of the transesterification process based on RSM were: (1) methanol to oil molar ratio: 1:6; (2) catalyst concentration: 0.5% wt.; and (3) time: 48 min, with methyl ester yield of 94.12 %. The optimum rice bran methyl ester yield predicted by RSM was validated by replicating three independent parameters with showed average rice bran methyl ester yield of 93.98%. The properties of the rice bran biodiesel properties were measured and the values met the requirements of the ASTM D6751 and EN 14214 standards.

Keywords: Biodiesel; Response surface methodology; Rice bran; Ultrasound

1. Introduction

Rapid depletion of fossil fuels coupled with increasing awareness of environmental issues, concerns over rising greenhouse gas emissions and escalating petroleum prices have prompted scientists and researchers to explore renewable and environmental friendly alternative energy sources (Salaheldeen et al., 2015; Said et al., 2018). Biodiesel is a type of renewable fuel, biodegradable, non-toxic and a potential alternative for fossil fuel (Tse et al., 2015; Leong, et., 2016). Rice (*Oryza sativa Linn*) bran is a thin layer between the rice and its husk which is removed to polish the rice. It consists of pericarp, tegmen (endosperm covering layer), aleurone and sub -aleurone. (Ju and Vali, 2005) and makes up 8% of the harvested rice. The oil content of rice bran is about 16-32% based on its weight (Anwar et al., 2005). The oil composition of jatropha and rubber seed are higher accounting for 55% and 45% of their respective total weight (Ramadhas et al., 2005).

Ultrasound is an energy that absorbs mass and heat transfer which is an alternative reaction system that can increase the synthesis of biodiesel process (Maghami et al., 2015). In recent years, researches have applied ultrasound probes, ultrasound baths or horns sonochemical reactors in biodiesel synthesis (Koutsouki et al., 2016). Compared with the

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conventional method, the ultrasound-assisted methods have the advantages of shorter reaction time, less catalyst time, higher methyl ester yields, and less energy in biodiesel production. (Prakash Maran and Priya, 2015). Response surface methodology (RSM) is an effective statistical technique used to establish the relationship between a set of experimental parameters and results. The RSM defines the effect of the independent variables, and also generates mathematical models. Therefore, many researchers have studied biodiesel production using RSM in order to produce high methyl ester and improve the quality of biodiesel (Dharma et al., 2016; Sebayang et al., 2017; Milano et al., 2018).

The present study is aimed at optimising the transesterification of rice bran oil using an ultrasound technique. The properties of the rice bran methyl ester were investigated using EN 14214 and ASTM D6751 standards. Results showed producing biodiesel using ultrasound can save cost, time and energy.

2. Methods

2.1. Raw Materials and Chemical Reagents

Crude rice bran oil was collected from Koperasi Lestari, Cilacap, Indonesia. Analytical grade methanol 99 % AR and KOH with a purity of 99% were purchased from Merck. Methyl nonadecanoate as GC standard (C19 with 99.5%, Supelco-Sigma-Aldrich) and C8-C24 (100 mg, Supelco-Sigma-Aldrich) were ordered from, ITTech Research (M) Sdn Bhd while phenolphthalein solution (1% in ethanol) Whatman filter papers with a diameter of 15 cm were purchased from Fluka Analytical.

2.2. Properties of Rice Bran and Methyl Ester

Rice bran methyl ester properties were determined using American standards (ASTM D6751) and European Union (EN 14214).

Fatty acid methyl ester (FAME) yield content in percent (%) was calculated using Equation 1:

$$FAME = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \qquad (1)$$

where $\sum A$ is the sum of the areas under the peaks of all the individual fatty acid methyl ester, represents the methyl heptadecanoate solution in mg/ml, represents the methyl heptadecanoate in the internal standard represents the volume of methyl heptadecanoate solution (ml).

The yield (%) was determined based on Equation 2:

$$Methyl\ ester\ yield = \frac{FAME \times B_{cp}}{O_{cp}} \times 100 \qquad (2)$$

Here, $FAME$ represents ester content (%), B_{cp} represents mass of the rice bran ester (g) and O_{so} represents mass of the rice bran oil (g).

2.3. Ultrasound-assisted in Situ Alkaline Transesterification

Ultrasound-assisted transesterification process was used to produce rice bran methyl ester for biodiesel (Figure 1). The Ultrasound Elmasonic P60 was used the transesterification process which the different value set up to 180W and variation temperature control (30–80^{o}C). The temperature was set to 55^{o}C and the temperature increase triggered by the ultrasound was used cooling coil in order to keep the temperature at the set value. Transesterification periods were: 30, 45 and 60 min; catalyst: 0.5, 0.75 and 1 wt%; and methanol to molar ratio 3:1, 6:1 and 9:1. The reaction mixture was kept in the without stirring system inside the equipment was used. Results showed that methyl ester was separated from the mixture and glycerol were removed with warm distilled water at 50^{o}C. When pH of the wash water reached the level of the distilled water, 50 g of Na_2SO_4

was added to the methyl ester to remove water, and was filtered through filter paper. The methyl ester was evaporated using a rotary evaporator.

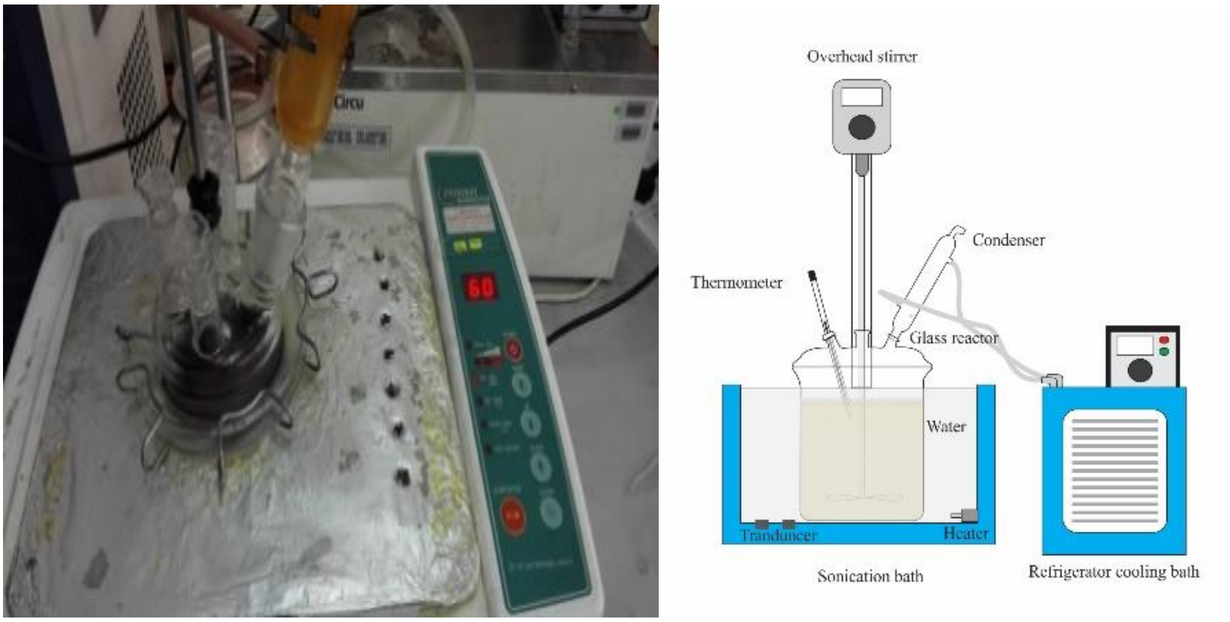

Figure 1 Biodiesel production using Ultrasound equipment system

2.4. Optimisation of Ultrasound-assisted Alkaline-catalysed Transesterification

Data obtained from the experiment was analysed using analysis of variance (ANOVA) and response surface methodology (RSM) based on Design-Expert software version 9.0.4.1 (Stat-Ease Inc., Minneapolis, USA). In this study, Box–Behnken was used to design the parameter of the transesterification rice bran oil. The following operating parameters, i.e. reaction time (x_1), amount of catalyst (x_2) and methanol to oil ratio (x_3), were varied in order to optimize the yield of RBME (Y). The coded and uncoded levels of the Box–Behnken independent variables are shown in Table 1. Data was analysed using mathematical model shown in Equation 3:

$$Y = b_o + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i>j}^{k} . \sum_{j}^{k} b_{ij} X_i X_j + e \quad (3)$$

In Equation 3, *Y* is methyl ester yield (MJ/kg), b_o, b_i, b_{ii} are regression coefficients, X_i and X_j are the design parameters, *k* is the number of factors studied and optimized in the experiment, and *e* is the experimental error attributed to *Y*.

Table 1 Factors and actual and coded levels used in the Box-Behnken design for transesterification using ultrasound method

Factor	Unit	Level		
		-1	0	1
(X_1) Time	min	30	45	60
(X_2) Catalyst	wt.%	0.5	0.75	1.0
(X_3) Methanol to oil ratio	-	3	6	9

3. Results and Discussion

3.1. Response Surface Methodology Modelling

In this experimental study, methanol to oil molar, time, and catalyst were chosen as the parameters. The Box–Behnken design matrix of the experiment runs is shown in Table 2.

Table 2 Experimental conditions for methyl ester conversion using Box Behnken design

Run	Time	Catalyst	Methanol	Methyl ester yield experiment	RSM prediction
1	45	0.75	6	95.42	95.73
2	45	0.5	3	90.88	90.52
3	60	0.75	3	86.81	87.38
4	60	1.00	6	93.77	93.02
5	30	0.5	6	92.45	93.19
6	30	1.00	6	90.82	91.03
7	60	0.5	6	95.75	95.53
8	45	0.75	6	96.12	95.73
9	30	0.75	9	88.21	87.63
10	60	0.75	9	89.63	90.01
11	45	0.75	6	95.53	95.73
12	45	0.75	6	95.42	95.73
13	45	1.00	3	87.36	87.53
14	45	0.75	6	96.18	95.73
15	30	0.75	3	85.82	85.43
16	45	0.5	9	92.45	92.28
17	45	1.00	9	90.24	90.6

The methyl ester conversion predicted model which was adjusted based on the actual values by an empirical quadratic model is shown in the following equation:

$$Methyl\ ester\ conversion\ (\%) = 50.405 + 1.10563X_1 - 7.182X_2 + 7.3552X_3 - 0.0233X_1X_2 + 0.002389X_1X_3 + 0.4367X_2X_3 - 0.011448X_1^2 + 0.628X_2^2 - 0.6156X_3^2 \quad (4)$$

The analyses of variance (ANOVA) are shown in Table 3. Table 2 shows the p-value is < 0.0001 indicating the quadratic model is highly significant (Pandit and Fulekar, 2017). The value of determination coefficient (R^2= 0.9847) showed excellent agreement between predicted and experimental rice bran methyl ester yield and only 1.53% variations were not explained by the developed model (Salamatinia et al., 2010). The value of adjusted determination coefficient was close to one, indicating the developed model has a high significance through experimental data (Dwivedi and Sharma, 2015; Prakash Maran and Priya, 2015). In addition, the value of the coefficient of variation (CV = 0.72%) is very low, indicating the developed model has a very high degree of precision and a good deal of reliability (Anwar et al., 2005; Ramadhas et al., 2005).

3.2. Interaction Effects of Molar Ratio on Conversion Methyl Ester

The three-dimension surface plots and contours for interaction effects of catalyst versus molar ratio are shown in Figure. 2. Methanol to oil ratio is varied between 3:1, 6:1, and 9:1 in order to study their effects on other parameters. The Crude Rice Brand oil is mostly composed of Saturated fatty acids (with single bonds in the fatty acid chains), this oil easily drive by methanol to oil molar ratio to increase contact between the triglycerides and alcohol molecules (Balat and Balat, 2008; Moser, 2009).

Table 3 Analysis of variance (ANOVA) for the regression model

Source	Sum of Squares	Deg. freedom	Mean Square	F Value	p-value Prob > F	
Model	197.14	9	21.9	50.05	< 0.0001	Significant
X_1-Time	9.37	1	9.37	21.42	0.0024	
X_2-Catalyst	10.9	1	10.9	24.91	0.0016	
X_3-Methanol	11.66	1	11.66	26.65	0.0013	
$X_1 X_2$	0.031	1	0.031	0.07	0.799	
$X_1 X_3$	0.046	1	0.046	0.11	0.7547	
$X_2 X_3$	0.43	1	0.43	0.98	0.3551	
X_1^2	27.93	1	27.93	63.82	< 0.0001	
X_2^2	0.006	1	0.006	0.015	0.9065	
X_3^2	129.26	1	129.26	295.32	< 0.0001	
Residual	3.06	7	0.44			
Lack of Fit	2.48	3	0.83	5.63	0.0642	not significant
Pure Error	0.59	4	0.15			
Cor Total	200.21	16				
R-squared	0.9847					
Adj R-squared	0.965					
Coef. variance	0.72					

However, it shall be noted that increasing the methanol to oil molar ratio beyond the optimal value will not increase the methyl ester yield — rather, it will increase the cost for alcohol recovery (Leung et al., 2010). The yield increases corresponding with catalyst and methanol to oil ratio. It drops after achieving a peak value, but it is favourable at lowest operating catalyst and lowest methanol to oil ratio. The results suggest methanol to oil ratio that provides the highest methyl ester yield is 6:1.

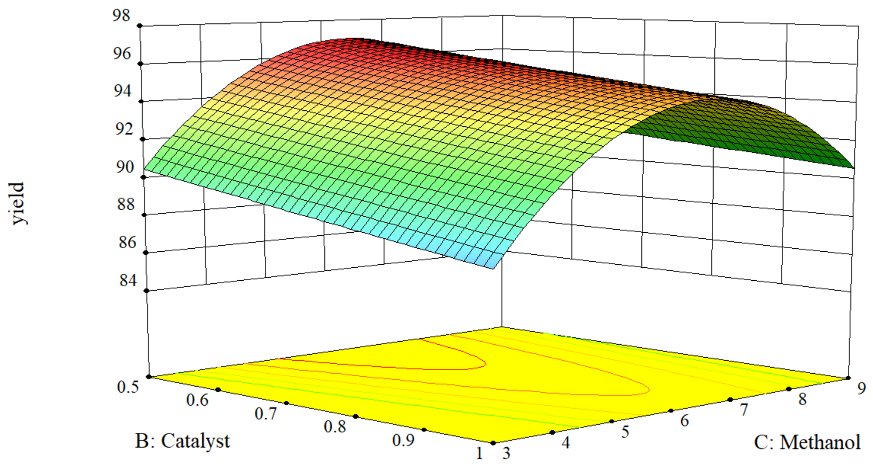

Figure 2 Interaction effects of catalyst vs molar ratio on conversion methyl ester

3.3. Interaction Effects of Catalyst Concentration on Conversion Methyl Ester

The effect of catalyst concentration reaction versus reaction time is shown in Figure 3. The conversion to methyl ester increased significantly when methanol to oil ratio changed from 3:1 to 6:1 but it reduced after it reached 94.12% yield. It can be observed that the Rice Brand Methyl Ester yield initially increases with an increase in catalyst concentration up to

0.5 wt.% and it is expected that lower KOH catalyst concentrations may result in incomplete equilibrium during the chemical reactions, resulting in lower Rice Brand Methyl Ester yields also result in lower Rice Brand Methyl Ester yields due to excess soap formation. It was reported that excessive amounts of alkaline catalyst lead to lower methyl ester yields due to the formation of emulsion and higher kinematic viscosity of the methyl ester, which leads to gelation (Ejikeme et al., 2010; Satyanarayana and Muraleedharan, 2011). The optimal yield was achieved with catalyst 0.5% wt; however, increasing the amount of catalyst led to gel formation and reduced conversion efficiency. The emulsion blocks the reaction.

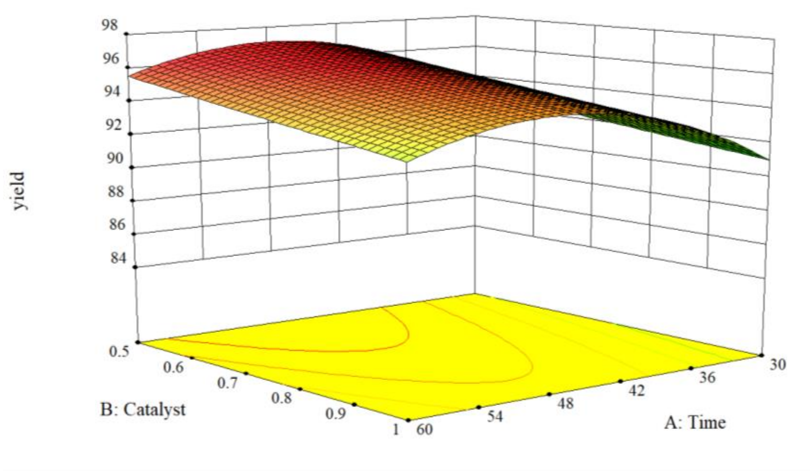

Figure 3 Interaction effects of catalyst concentration vs time on conversion of methyl ester

3.4. Interaction Effects of Reaction Time on Conversion Methyl Ester

Figure 4 below shows conversion efficiency increased significantly with reaction time 0 to 49 min and then decreased significantly. The longer period of reaction time does not lead to an increase in methyl ester yield. It is assumed prolonging the reaction time for an equilibrium condition will cause a reversible process in transesterification and as a consequence, the level of glycerides in the methyl ester will increase. Moreover, the higher methyl ester yield achieved using the ultrasound technique may be due to high speed mixing and mass transfer between the methanol and triolein as well as the formation of micro-emulsion resulting from ultrasound cavitation (Prakash Maran and Priya, 2015). The best method is the one that achieves the highest conversion in the shortest period of time.

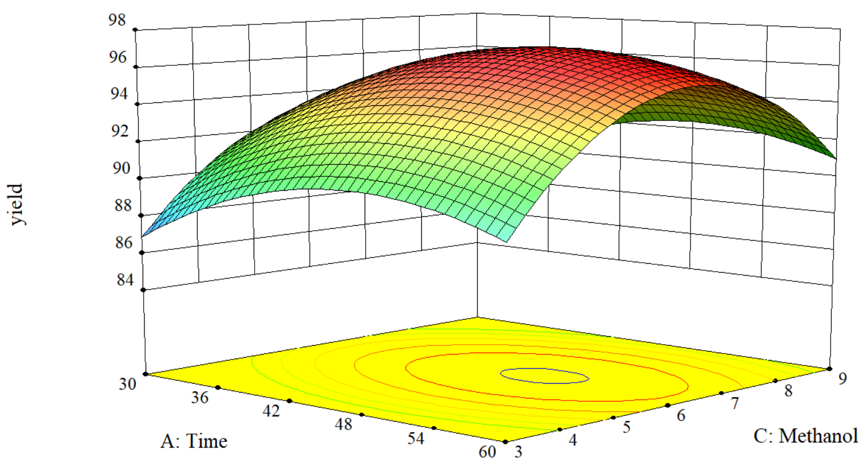

Figure 4 Interaction effects of reaction time on conversion of methyl ester

3.5. Interaction Effects of Reaction Time on Conversion Methyl Ester

Figure 5 below shows conversion efficiency increased significantly with reaction time 0 to 49 min and then decreased significantly. The longer period of reaction time does not lead to an increase in methyl ester yield. It is assumed prolonging the reaction time for an equilibrium condition will cause a reversible process in transesterification and as a consequence, the level of glycerides in the methyl ester will increase. Moreover, the higher methyl ester yield achieved using the ultrasound technique may be due to high speed mixing and mass transfer between the methanol and triolein as well as the formation of micro-emulsion resulting from ultrasound cavitation (Prakash Maran and Priya, 2015). The best method is the one that achieves the highest conversion in the shortest period of time.

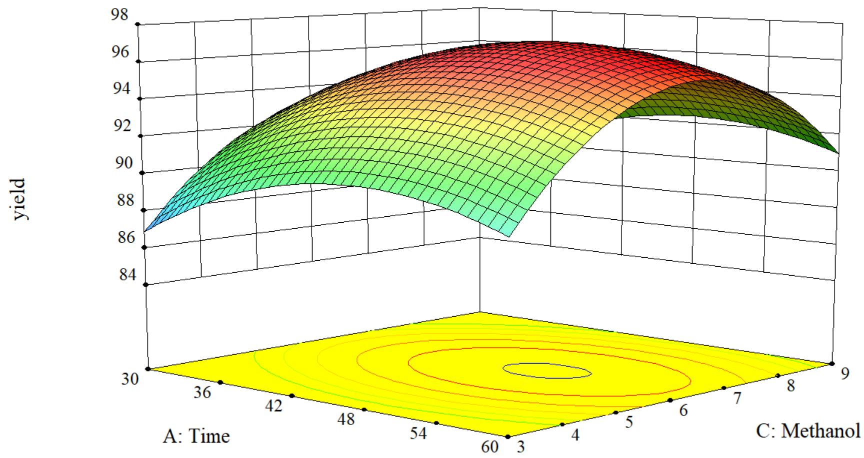

Figure 5 Interaction effects of reaction time on conversion of methyl ester

3.6. Optimization and Validation

The predicted optimum yield for rice bran oil based on the developed model are reaction time 48 (min), KOH catalyst concentration 0.5 (w/w)%, and methanol to oil ratio 6:1 with 94.21% yield. Three independent experiments were replicated using selected parameters in order to validate the model (see Table 4). The average of methyl ester yield from all three experiments was 93.98%. It is clear the difference between the predicted and experimental validation on the rice bran methyl ester yield is very low (0.14%) with a standard error of 0.07. Therefore, the regression model is reliable and showed quicker results (60 min) and lower catalyst concentration (1.0 to 1.75 (w/w)%) than achieved by Pereira et al. (2015).

Table 4 Three independent experiments to validate the predicted optimum rice bran methyl ester yield

Run	Time	Catalyst	Methanol	Yield
1	48	0.5	6:1	93.82%
2	48	0.5	6:1	93.91%
3	48	0.5	6:1	94.22%
Average				93.98%
Predicted optimum				94.12%
STD				0.07

3.7. Properties of Rice Bran Oil and Methyl Ester

Properties of crude rice bran oil and methyl ester are shown in Table 5. Kinematic viscosity of crude rice bran oil is 21.11mm^2/s and its flash point 210.5°C which is high. Therefore, properties of rice bran methyl ester produced using ultrasound method met the ASTDM D6751 standards. This method is therefore feasible for biodiesel production as the resultant rice bran methyl ester has desirable physicochemical properties.

Table 5 Properties of rice bran methyl ester compared with diesel fuel

Properties	Unit	Standard test method	ASTM D6751	Diesel	Crude rice bran oil	Rice bran methyl ester
Viscosity at 40 °C	mm^2/s	D 445	1.9-6.0	2.86	21.11	4.8
Density at 15 °C	kg/m^3	D 1298	860-880	833	886.8	879.2
Acid number	mg KOH/g	D 664	Max. 0.5	0.06	1.68	0.17
Flash point	°C	D 93	Min. 130	70.5	210.5	175
Calorific value	MJ/kg	D 975	Min. 35	45.82	35.27	40.44
Oxidation stability at 110 ^{o}C	h	EN 14112	Max. 3	15.2	4.26	8.89

4. Conclusions

In this study, ultrasound-assisted biodiesel production from crude rice bran oil was evaluated through RSM modelling. The optimisation process was conducted based on three main parameters: methanol to oil ratio, reaction time and catalyse concentration. The optimal parameters are methanol to oil ratio 6:1, reaction time: 48 min and catalyst used: 0.51 wt.%. The methyl ester yield predicted under these process conditions is 94.12%. The limitation of this experiment was the capacity the equipment. Therefore, using a more powerful ultrasound can be explored in future studies to find out if that increases yields. Results showed the RSM model is reliable in predicting the values of dependent variables on the conversion of rice bran methyl ester using ultrasound.

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