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Optimization of Biodiesel Production Process from Oil-Palm off Grade using CaO from Chicken Eggshell

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ABSTRACT

In this work, response surface methodology was used to optimize the conditions for the transesterification of oil-palm off grade with methanol, using CaO from chicken eggshell as catalyst. By experimental design a quadratic polynomial equation was obtained for biodiesel yield. Multiple regression analysis and verification experiments confirmed the validity of the predicted model. The studied variables were reaction temperature (50, 60 and 70 °C), catalyst weight base oil (2,4 and 6%) and methanol to oil-palm off grade molar ratio (7:1; 9:1 and 11:1). Results from the optimation study showed that reaction temperature and molar ratio methanol to oil-palm off grade can be optimized. Catalyst characterization was carried out by X-ray Diffraction. Biodiesel with highest methyl ester content (87.41%) was obtained at 70 °C, 1:11 methanol to oil-palm off grade molar ratio and 2% catalyst concentration. The produced biodiesel was found to fulfill the specifications of the SNI-2012 regarding viscosity, flash point and acid value.

KEY WORDS: *biodiesel, chicken eggshell, oil-palm off grade, optimization, response surface methodology*

1.0 INTRODUCTION

Due to the diminishing of fossil fuel, global warming and environmental problems, development and discovery of environmentally benign and renewable energy fuels have become an important issue. Biodiesel has become an alternative energy fuel due to its raw material being in abundance, its potential for large scale production [1], and its better physical and chemical properties as compared to the petroleum-based diesel such as better lubricating efficiency, higher flash point, lower sulfur contamination, and very few pollutants produced [2,3].

Transesterification of vegetable oils or animal fats with alcohol in the presence of catalyst is the main process for biodiesel production [4]. There are various types of catalysts utilized, e.g., base catalysts, acid catalysts, and enzyme catalysts [5-7]. Although homogeneous base catalysts, such as potassium or sodium hydroxides, carbonates or alkoxides are commonly utilized for the commercial production of biodiesel [8], these catalysts have several major problems such as hazards in handling, high corrosiveness, difficulty in catalyst separation and non-reusability of catalysts, and massive wastewater generation [9]. Therefore, heterogeneous catalysts have been extensively developed to replace the homogeneous catalysts, offering several advantages in overcoming the aforesaid problems of homogeneous catalysts; this is mainly due to the extensive separation and purification procedures are not required for heterogeneous catalysts [10, 11].

Among heterogeneous catalysts, calcium oxide (CaO) has intensively attracted as a heterogeneous base catalyst for transesterification of vegetable oils with methanol due to its high basicity and strong basic strength, non-toxicity, and lower solubility in biodiesel [12, 13]. Furthermore, the CaO catalyst can be synthesized from natural waste materials, for example, chicken eggshell [14], freshwater mussel [15], shells of crab and oysters [16], mollusk [17], Turbonillastriatula [18], shells of cockle [19] and snails [20]. The discovery of inexpensive catalysts with high catalytic activity from the abandoned waste materials makes the biodiesel production process highly capable of competing on a cost and quality basis with the diesel fuel produced from petroleum [21].

Oil-palm off gradeis a source of vegetable oil available in large quantities, which is about 7-10 tons produced from palm oil mill with a capacity of 30 tons/hour and sold at prices 30-40% cheaper than good quality CPO [22]. Besides having a great availability and low price, oil-palm off gradehas not been utilized to the maximum and potentially be used as raw material for biodiesel. The weakness of oil-palm off gradeis to have high levels of FFA. The weakness can be overcome with the use of two-stage reaction due to high FFA levels. FFA can be reduced through esterification reaction before continuing to the transesterification reaction. FFA levels allowed in the transesterification reaction is <2% [11]. In this work, response surface modelling is applied to optimize the transesterification reaction of oil-palm off gradecatalyzed by CaO from chicken eggshell at mild conditions. Hence, the main aim of this work is to describe the effects and relationships among reaction temperature, molar ratio methanol to off grade oil palm and catalyst weight, in order to obtain an optimum biodiesel quality and yield. This is expected to reduce research time and costs.

2.0 RESEARCH METHODOLOGY

2.1 Materials and Equipment

The equipment used are three-neck flask with a capacity of 500 ml as a batch reactor equipped with a heating mantle, condenser, thermometer, and magnetic stirrer. The raw material used is oil of oil-palm off gradeextracted using spindle hydraulic press. Methanol 98% is used in the esterification and transesterification reaction As reactants. For catalyst, the esterification reaction used H_2SO_4 and transesterification used CaO from chicken eggshell.

2.2 Preparation of CaO catalysts

The waste chicken eggshells were collected from local bakeries. Then, they werewashed with tap water, dried at 100 °C for2 h in an oven and then grinded using grinding mill with rotational speed 340 rpm and time 8 min. Then, they were sieved to constant sizes(<0.07 mm). Calcination was performed in a muffle furnaceat 900 °C for 2h. The calcinatedcatalysts were then stored in dark screw capped vessels toavoidreaction with humidity and CO_2 in air before usage. Structural property of catalysts was analyzed by powder X-ray diffraction technique using a SHIMADZU XRD-600 diffractometer with Cu Ka radiation (k = 0.154 nm), operated at 40 kV and 30 mA.

2.3 Transesterification Reaction

All the transesterification reactions were carried out for 2 h at atmospheric pressure in a 500 ml reactor with mechanical stirring at 400 rpm, thermostat and condensation system. The reactor was immersed in a constant-temperature bath. The accuracy of the temperature measurement was ±1°C. The investigated reaction conditions were: methanol to oil molar ratio (7:1; 9:1 and 11:1), reaction temperature (50, 60 anf 70 °C); catalyst concentration refereed to initial oil weight (2, 4 and 6%). Centrifugation was used to recover the catalyst; then the methanol was separated via rotary evaporation and finally the glycerol was recovered by settling.

2.4 Design of Experiments

Data Processing in this study used response surface Central Composite Design (CCD). The reaction parameters were reaction temperature, methanol to oil molar ratio and catalyst concentration. Table 1shows the range and levels of the three independentvariables studied. The CCD was used to investigate linear, quadratic and cross-product effects of these three independent transesterification process variables on the yield of croton biodiesel. The value of alpha (α) was fixed at 2. All variables at zero level constitute to the center points and the combination of each of the variable at either its lowest (-2.0) level or highest (+2.0) level with the other variables at zero level constitutes the axial points. Each response of the transesterification process was used to develop a mathematical model that correlates the yield of biodiesel to the transesterification process variables studied through first order, second order and interaction terms, according to the following second order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1} \sum_{j=i+1} \beta_{ij} x_i x_j + \varepsilon$$

where Y is the predicted biodiesel yield (mol/mol), xi and xj representthe parameters, b_0 is the offset term, bj is the linear effect, bij is the first order interaction effect and bjj is the squared effect.

Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used for regression analysis of the experimental data to fit the second order polynomial equation and also for evaluation of statistical significance of the equation developed.

Table 1: Levels of transesterification variables

Variable	Coding	Unit	Levels				
			-α	-1	0	+1	+α
Reaction temperature Methanol to oil molar ratio Amount of catalyst	X_1 X_2 X_3	°C mol/mol wt%	43 6 1	50 7 2	60 9 4	70 11 6	77 12 7

3.0 RESULTS AND DISCUSSIONS

3.1 Characteristics of Activated Zeolite Catalysts

The major component of the calcined eggshell was CaO species, as demonstrated in the XRD pattern. The result reveals sharp XRD reflections (Fig. 1) with (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) orientations, implying that the calcined sample was well crystallized during the heat treatment process.XRD pattern for chicken eggshell before activation shows diffraction peaks at angles 2θ = 23º, 29,5º, 31,5º, 36º, 39,5º, 43,5º, 47,5º, 49º, 57º, 58º, 61º, 63º, 65º, 66º, 69.5º, 70,5º, 73º, 77º, 82º, 84º, 95º, 96º. As for the $CaCO_3$from eggshell after activation showed the formation of CaO at peak diffraction angle 2θ = θ: 32,2º, 37,4º, 53,9º, 67,4º, 88,6º, 91,5º; and $Ca(OH)_2$ at 2θ = 18º, 28.8º, 34.2º, 47.2º, 50.9º, 62,5º, 67,4º 38.5 °.

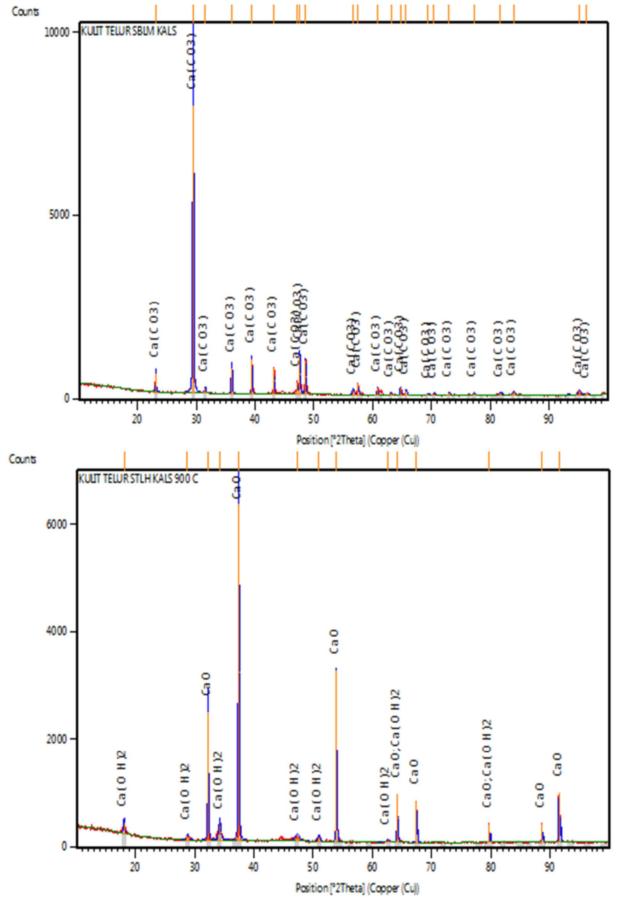

Figure 1: The XRD pattern for CaO from eggshell before and after activation

3.2 Characteristics of Biodiesel

Analysis of biodiesel characteristics of in this study is shown in Table 2, which shows the produced biodiesel has approximate value but does not exceed the standards set by SNI-2012 for biodiesel.

Table 2: Characteristics of biodiesel from off grade palm oil

No	Characteristics	Result	SNI-2012 for biodiesel
1	Acid number	0,24 mg-KOH/gr biodiesel	Max 0,6 mg-KOH/gr biodiesel
2	Density at 40°C	858,12 kg/m^3	850 - 890 kg/m^3
3	Viscosity at 40°C	2,35 mm^2/s	2,3 - 6,0 mm^2/s
4	Flash point	132°C	minimum 100°C

3.3 Development of regression model equation

Tabel 2 summarized the results regarding transesterification reaction yield. It can be noticed that this fluctuates between 62.3% and 87.41% depending on experimental conditions. It is worth mentioning that the presented values in Tabel 3 are the average of three repetitions and standard deviation is included in the last column of this Table.

Table 3: Experimental design of the experiments and their corresponding results

Standar	Run	Coded Process Variable			Yield (%)
		(X_1)	(X_2)	(X_3)	
1	17	-1	-1	-1	67,62
2	16	1	-1	-1	75,80
3	20	-1	1	-1	73,97
4	19	1	1	-1	87,41
5	4	-1	-1	1	62,30
6	9	1	-1	1	71,26
7	6	-1	1	1	69,12
8	13	1	1	1	86,67
9	3	-1,68	0	0	64,64
10	11	1,68	0	0	84,71
11	10	0	-1,68	0	72,64
12	8	0	1,68	0	85,35
13	12	0	0	-1,68	66,57
14	15	0	0	1,68	68,07
15	2	0	0	0	78,17
16	18	0	0	0	80,92
17	5	0	0	0	76,62
18	14	0	0	0	75,25
19	1	0	0	0	79,12
20	7	0	0	0	78,84

Based on coded factors, the quadratic regression model of experimental data was given as:

$$y = 78{,}18 + 6X_1 + 4{,}51X_2 - 0{,}97X_3 - 1{,}07X_1^2 + 0{,}46X_2^2 - 3{,}64X_3^2 + 1{,}73\,X_1X_2 + 0{,}61X_1X_3 + 0{,}54X_2X_3$$

where y is the methyl ester percentage (%), X_1 is reaction temperature (°C), X_2 is the methanol to oil ratio and X_3 is catalyst concentration (%). Positive sign in front of the terms indicates positive effect while negative sign indicates antagonic effect.

The statistical significance of the model equation was evaluated by the analysis of variance (ANOVA), which showed that the regression is statistically significant at 99% confidence level. The p-value of the model was smaller than 0.0001 and this indicates that the model is significantly suitable. In this case, the model was statistically significant since the model F-value was 3.02 for biodiesel production. This value implies that the lack of fit was not significantly related to experimental error. The p value of lact of fit was 0.1 (p value > 0.05), thus indicating that the lack of fit was insignificant. In this case, the vaue of the determination coefficient (R^2=0.96) indicates that the model expalins 96% of the variability. Thus, the value in Table 4suggest that the accuracy and general availability of the polynomial model was adequate. In consequence, this methodology allowed the formulation of the second order equation that describes the process.

Tabel 4: ANOVA and fit statistics for y

Varians	*Sum of Square*	*Degree of Freedom*	*Mean Square*	F_o	F_{tabel} ($F_{0.05;\,9;\,10}$)
Regresi	1020,59	9	113,40	25,39	3,02
Residual	44,66	10	4,47		
Total	1065,25	19			

Based on the results of the P-value test, the molar ratio methanol: oilhas a significant influence on the yield of biodiesel. The greater molar ratio methanol: oilincrease the yield of biodiesel. In addition to the molar ratio methanol: oil, the P-value test showed a significant effect on the quadratic molar ratio methanol: oilto yield biodiesel that can be seen on the curve surface curvature. Interaction of reaction temperature and catalyst concentration also has significant effect on the yield of biodiesel. Effect reaction temperature and molar ratio methanol: oilon the yield of biodiesel at catalyst concentration 1%wt depicted in the form of a curve surface in Figure 2. Increase in reaction temperature and molar ratio methanol: oiltends to increase yield of biodiesel. At 50°C and at molar ratio methanol: oil 7:1, resulting in low yield of biodiesel. When the reaction temperature and catalyst concentration was raised to 60 °C and 9:1, the yield of biodiesel is increasing. Yield biodiesel continues to increase at the reaction temperature and catalyst concentration at 70 °C and 11:1 (highest). The increase happens because at 70 °C methanol used is not evaporate yet and the higher the reaction temperature (still at the limit of methanol boiling point) will increase the reaction rate constant and the use of large molar ratio methanol: oilwill increase the rate of the transesterification reaction producing high yield biodiesel.

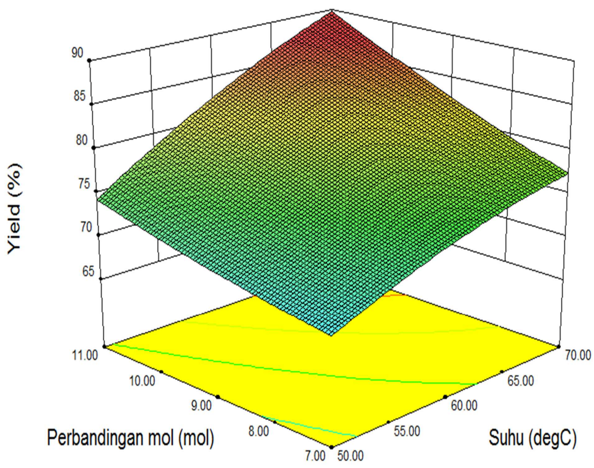

Figure 2: The surface curve, interactions of the reaction temperature and catalyst concentration to biodiesel yield at catalyst concentration 1%wt

4.0 CONCLUSION

Results of experiments that have been carried out can be concluded that biodiesel can be produced from a low quality oil-palm off grade which has high FFA concentration through two stages reaction using CaO from eggshell catalyst in transesterification stage. The highest biodiesel yield of 87.41% was obtained under the conditions of 70°C reaction temperature, molar ratio methanol: oil 11: 1, and the concentration of CaO from eggshell catalyst 2%wt. Process conditions that have significant influence on the yield of biodiesel is molar ratio methanol: oilwhere higher molar ratio methanol: oilwill increase the yield of biodiesel produced.

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