FAME Production from Jatropha Curcas seed oil via Calcium Oxide Catalyzed Transesterification and its Purification using Acid Activated Bentonite

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Abstract— This paper presents the study of transesterification of Jatropha curcas oil (JCO) via environmentally benign process using calcium oxide as heterogeneous catalyst. Response surface methodology (RSM) based on central composite design (CCD) was performed to optimize three reaction variables in this study. The transesterification process variables were reaction time, $x1$ (60 minutes-120 minutes), molar ratio of methanol: oil, $x2$ (5:1 – 13:1), and amount of catalyst, $x3$ (0.5 % –1.50 % of mass fraction). Since water washing method is not suitable to purify CaO synthesized fatty acid methyl esters (FAME), the purification of as-synthesized FAME with acid-activated bentonites to eliminate the remaining calcium was also investigated. It was found that the yield of JCO FAME could reach up to 94.35 % using the following reaction conditions: 79.33 minutes reaction time, 10.41:1 methanol:oil molar ratio and 0.99 % catalyst at reaction temperature 65oC. Among bentonites used in the purification, 2.5% of H_2SO_4-activated bentonite shows a good performance as decalcifying agent for FAME purification. The properties of purified jatropha FAME were comparable to those of diesel and satisfied the international standard.

Keywords—FAME; biodiesel; Jatropha curcas; transesterification; bentonite purification; calcium oxide; heterogeneous catalyst

I. INTRODUCTION

Biodiesel has been widely accepted as an alternative energy source. It is very popular due to its renewable, non-toxic, biodegradable and non-flammable properties besides its low emission profiles and environmentally beneficial characteristics. Biodiesel can be used either in a pure form or as blends on conventional petro-diesel in automobiles without any major engine modifications [1-5]. There are various non-edible and edible oils which can be used for as alternative source for engine fuel. However, the use of non-edible oil is preferable since it is inapplicable as a food source. Among the non-edible oils, *J. curcas* has remarkable potentials for biodiesel production [6].

The production of biodiesel or more commonly known as FAME can be classified into homogeneous, heterogeneous and non-catalytic methods, depending upon the type of catalyst used in the process. Traditionally, homogeneous method is used in many commercial production of FAME. However, this method has many disadvantages. In this method, the reactants, catalyst and FAME are all in the liquid phase. This results in a complex liquid–liquid separation process. Besides, the recovery of the homogenous catalyst is also difficult, thus resulting in loss of useful material. Moreover, the catalyst dissolves fully in the glycerin layer and partially in the FAME layer. This makes FAME need to be cleaned through a slow, tedious and an environmentally unfriendly water washing process. In addition, catalyst contaminated glycerin has little value in today's market and is increasingly becoming a disposal issue [7]. In contrast, heterogeneous transesterification method proved to be more superior as compared to the homogenous transesterification method especially on the separation and purification of the product (FAME) [8-11]. The heterogeneous method, which uses solid catalyst, does not face the same limitations. Solid–liquid separation process is relatively easy as compared to liquid–liquid separation process. This makes the recovery of solid catalyst a lot easier.

In addition, heterogeneous catalyzed method eliminates the formation of soap. This omits the need of wash water. Elimination in the formation of soap then prevents the formation of emulsion which could complicate the separation and purification processes in the mixture [12]. Recently, there are many feasible heterogeneous catalysts

suitable for transesterification process. Among them are metal oxides [13-17], metal complexes [18], active metals loaded on supports [19,20], zeolite [21], resins [22,23], membranes [24,25], lipases [26], and hydrotalcites [27]. Some of these catalysts are already used in commercial production of FAME and patented [28]. They have been proven to have high activity in the reaction of transesterification. Among alkalic heterogeneous catalysts, CaO is one of the most investigated compounds because of its high basicity, low solubility, low price, and possibility of production from cheap sources. Moreover, it is easier to handle than homogeneous catalyst such as KOH or NaOH [29,30].

There has been various experiments on CaO catalyzed transesterification. Most of these catalysts, however, are used on oils such as soybean oil [31-34], sunflower oil [16,35-37], rapeseed oil [38-40] and microalgae [41]. A single case of using CaO catalyst on JCO transesterification was reported by Zhu [29]. But, the catalyst must be treated with ammonium carbonate before calcinations at high temperature. Thus, the main objective of this study is application of CaO without ammonium carbonate treatment as heterogeneous catalyst to optimize the production of fatty acid methyl esters (FAME) from JCO.

This study is supplemented by a statistical design of experiment using response surface methodology (RSM). It is used to accumulate and analyze information on the effect of three process variables on the yield of transesterification in a rapid and efficient manner using minimum number of experiments. As water washing method is not suitable for purifying CaO-treatment [29], the procedure employing the acid-activated bentonites was also investigated. It is expected that FAME production process will be simple, low cost, and environmentally friendly.

II. MATERIALS AND METHODS

A. Materials

Mature seeds of J. *curcas* were collected from South Lampung District, Lampung Province, Indonesia (LN 5°29', LO105°30', 120 m above sea level, annual rainfall 2500 mm, soil type: inseptisol). The seeds were selected in such a way that, the damaged seeds were discarded and the seeds in good condition were cleaned, de-shelled and sundried and dried at a temperature of 70 °C for 24 h before pressing using hydraulic jack press. The oil extraction was carried out at room temperature and oil was stored in the ice room at -5 °C until needed for analysis. The seed cakes, by-product of oil extraction, was sun-dried and stored in the ice room at -5°C until needed for further studies on toxicity.

Fatty acid composition of JCO are given in Table 1. Anhydrous methanol (MeOH), 99.8%; potassium hydroxide (KOH), sulfuric acid (H_2SO_4), and 37%-38% hydrochloric acid (HCl), were purchased from ChemAR®. A calcium-rich bentonite (CaB) sample was obtained as powder from PT. Superintending Company of Indonesia. Chemical composition of bentonite are: SiO_2 (64.15%); TiO_2 (0.47%); CrO_3 (0.003%); Al_2O_3 (0.70%); Fe_2O_3 (0.10%); MgO (0.70%); CaO (0.03%); Na_2O (0.20%); K_2O (0.50%) and 22.61% of loss on ignition (LOI). The pulverized limestone ($CaCO_3$) as a source of CaO was obtained from Sago Halaban, West Sumatra-Indonesia (LN 0°16', LO100°42', 676 m above sea level). Elemental composition analysis with ED-2000 XRF spectrometer indicated that the limestone contained CaO (54.85%), Fe_2O_3 (0.32%), MgO (0.65%), SiO_2 (2.46%), Al_2O_3 (0.31%), and LOI (43.8%).

TABLE I
FATTY ACID COMPOSITION OF JATROPHA OIL

Acid Common Name	Formula	Structure	Systemic name	Percentage (%)
Palmitic	$C_{16}H_{32}O_2$	C16:0	Hexadecanoic	14.07
Palmitoleic	$C_{16}H_{30}O_2$	C16:1	*Cis-9-*Hexadecanoic	0.94
Stearic	$C_{18}H_{36}O_2$	C18:0	Octadecanoic	6.03
Oleic	$C_{18}H_{34}O_2$	C18:1	*Cis-9-*Hexadecanoic	43.55
Linoleic	$C_{18}H_{32}O_2$	C18:2	cis-9,cis-12-Octadecedianoic	34.50

B. Preparation of CaO catalyst

The CaO catalyst (in powder form) was prepared by calcination of pulverized lime stone ($CaCO_3$) for 1.5 h, at 900°C [32]. CaO was stored under vacuum in desiccator that contains silica gel and KOH pellets to remove H_2O and CO_2 of residual atmosphere. Before it was used, CaO was pretreated by outgassing at 700°C [35] for 30 minutes. The properties of CaO compared to those of $CaCO_3$ as a source of CaO catalyst are summarized in Table 2.

TABLE III
PROPERTIES OF THE CaO CATALYSTS IN COMPARISON TO THOSE OF CaCO3

	BET surface area[a] (m^2/g)	Basic strength[b] (H_)
CaO	13	15.0 < H_ < 18.4
$CaCO_3$	10	7.2 < H_ < 9.3

[a] Calculated by BET method on the data from adsorption of nitrogen
[b] Determined by using Hammett indicators

C. Preparation of acid activated bentonite adsorbent

Acid activated Bentonite were prepared by aqueous impregnation technique. Either 5.3 kmol m^{-3} aqueous solution of HCl or 400 kg m^{-3} of aqueous solution of H_2SO_4 was applied to bentonite by aqueous impregnation (at 80 °C and 4 h). The material was washed with deionized water until Cl^{-1} and SO_4^{-2} ions were not detected. Then, it was dried overnight and calcinated at 500 °C for three hours. The surface area of bentonite was measured with multipoint Brunauer, Emmett and Teller (BET) method from the Quantachrome Surface Analysis Instrument (Autosorb 1-C, Boynton Beach, Florida, USA). This was done using nitrogen adsorption/desorption isotherms at liquid nitrogen temperature and relative pressures (P/Po) ranging from 0.04-0.40, where a linear relationship was maintained.

Five adsorbents for decalcination of as synthesized FAME were used, they were: (A) "untreated" bentonite; (B) 5.3 kmol m^{-3} aqueous solution of HCl-activated bentonite; (C) 5.3 kmol m^{-3} aqueous solution of HCl-activated and calcinated at 500 °C bentonite; (D) 400 kg m^{-3} of aqueous solution of H_2SO_4-activated bentonite; (E) 400 kg m^{-3} of aqueous solution of H_2SO_4-activated and calcinated at 500

°C bentonite. Physical parameters of bentonite and acid-activated bentonites is shown in Table 3.

TABLE IIIII
PHYSICAL PARAMETERS OF BENTONITE AND ACID-ACTIVATED BENTONITES.

Physical parameter	Adsorbent				
	A	B	C	D	E
BET surface area (m^2/g)	50.6496	239.3534	210.1829	252.2536	248.3601
Langmuir surface area (m^2/g)	79.1939	374.8640	329.6299	393.8833	389.3721
External surface area (m^2/g)	46.6242	226.2408	199.0738	232.8391	233.6701
Micropore area (m^2/g)	4.0254	13.1128	11.0990	19.4145	14.6900
Micropore volume (m^3/g)	0.0018	0.0052	0.0044	0.0085	0.0060

D. Evaluation of catalytic activity of CaO catalyst

1) *FFA removal by esterification : Jatropha curcas* oil with high content of FFAs cannot be directly used in an alkali catalyzed transesterification because FFAs will react with alkali catalyst to form soaps, which result in serious emulsification and separation problem. Esterification catalyzed by homogeneous acids, such as sulphuric acid, phosporic acid, or sulphonic acid, is a conventionally used method to reduce the FFAs. This makes possible transesterification of raw oils by an alkalic catalyst [39,40]. FFA removal in this study was done by esterification reaction using the method of Tiwari et al [42]. At a constant stirring rate 3.3 Hz, 200 ml of jatropha oil was pretreated with 280 dm3 m-3 solution of methanol using 1.43% volume fraction of H_2SO_4 as a catalyst in 88 mins reaction time, and reaction at 60 °C.

2) *Level-2 Heading:* The CaO catalyst and methanol were added into a 250 ml three-neck flask and stirred for 20 mins. Then, the temperature was raised to the desired level reaction temperature (65°C). Subsequently, 30 g of JCO was added through a constant press dropper. After the reaction, the solid catalyst was separated by centrifugation using Compact Tabletop Centrifuge 2420 (Kubota Corporation, Japan). The liquid was put into a separating funnel and was kept at ambient temperature for 4 hours. Afterwards, two liquid phases appeared: the upper layer was FAME and the lower was glycerol. Synthesized FAME was purified before analysis. The analysis of FAME for each sample was carried out by dissolving 1.0 g of FAME sample and 0.2 g of methyl salicylate which was added as a reference into 8 mL of n-hexane and injecting 1 μL of this solution in the Shimadzu-GC17A Gas Chromatograph, Japan. The sample injected was separated in a BPX 70 capillary column (30m × 0.25mm × 0.25μm) and a flame ionization detector (FID). The oven temperature of the GC was programmed 180°C (isothermal) for 15 min. The injector's and detector's temperatures were 280°C and 250 °C respectively. The purity of FAME samples was calculated based on the area of FAME over the reference by the following equation:

$$Purity\ (\%) = \frac{(area\ of\ FAME)/area\ of\ reference) \times (weight\ of\ reference)}{Weight\ of\ FAME\ sample} \times 100 \quad \text{(1)}$$

E. Purification of the as-synthesized FAME

Twenty milliliters of as-synthesized FAME followed by the adsorbent were added into a 50 ml conical flask, and the mixture was stirred for 15 min. The product was centrifuged at 50 Hz for 10 mins. As a result, purified FAME appeared at the upper layer.

The quantity of calcium ions that remained in the FAME was analyzed using spectrophotometric method. Less than 0.5 g FAME sample was digested with hydrogen peroxide and nitric acid using *MLS-120 Mega Microwave* for 18 mins. The samples then were analyzed with *AAS/ICP-OES/ICP-MS (GBC 906 Elite)*.

The performance of the adsorbent was evaluated by determining the change in concentration of the calcium ions in FAME before and after the decalcification. The decalcification efficiency and FAME yield were calculated using the equations:

Decalcification efficiency = 1–(remaining calcium ions /total calcium ions) × 100%.. (2)
and,
Yield = (volume of the refined FAME / volume of the synthesized FAME) × 100%.. (3)

Six methods for the purification step in FAME production were compared: (A) adsorption on "untreated" bentonite; (B) adsorption on HCl-activated bentonite; (C) adsorption with HCl-activated and calcined at 500 °C bentonite (D) adsorption on H_2SO_4-activated bentonite; (E) adsorption on H_2SO_4-activated and calcined at 500 °C bentonite; and (F) citric acid, as a control treatment.

F. Fuel properties

The fuel properties namely density, kinematic viscosity, flash point, cetane number, and acid value of jatropha oil, jatropha FAME and conventional diesel were determined according to the recommended methods and compared with the latest *American and European standards* [29].

G. The design of the experiments

The experimental design selected for this study is a central composite design (CCD) that helps in investigating linear, quadratic, cubic and cross-product effects of the three transesterification process variables (independent) on the conversion of JCO FAME (response). The three transesterification process variables studied are reaction period, ratio of oil to methanol and amount of catalyst. Table 4 lists the range and levels of the three independent variables studied. The complete design matrix of the experiments employed and results are given in Table 5.

TABLE IVV
INDEPENDENT VARIABLES AND LEVELS USED FOR CCD IN TRANSESTERIFICATION

Variable	Coding	Unit	Levels				
			-α	-1	0	+1	+α
Reaction time	x_1	min	60	75	90	115	120
Molar Ratio of Methanol/oil	x_2	mol mol^{-1}	5:1	7:1	9:1	11:1	13:1
Mass fraction of catalyst	x_3	%	0.50	0.75	1	1.25	1.50

TABLE V
CCD ARRANGEMENT AND RESPONSES FOR TRANSESTERIFICATION PROCESS.

No	Random	Point Type	Levels of variables			Conversion (%)	
			Reaction time (mins)	Ratio of Methanol/ Oil (mol mol^{-1})	Mass fraction of catalyst (%)	Experimental	Predicted
1	8	Fact	(-1)75	(-1)7:1	(-1)0.75	86.12	82.24
2	16	Fact	(+1)115	(-1)7:1	(-1)0.75	80.92	76.60
3	4	Fact	(-1)75	(+1)13:1	(-1)0.75	89.67	88.71
4	11	Fact	(+1)115	(+1)13:1	(-1)0.75	80.76	82.82
5	9	Fact	(-1)75	(-1)7:1	(+1)1.25	36.21	40.91
6	18	Fact	(+1)115	(-1)7:1	(+1)1.25	36.68	44.40
7	13	Fact	(-1)75	(+1)11:1	(+1)1.25	79.71	90.79
8	19	Fact	(+1)115	(+1)11:1	(+1)1.25	83.40	94.04
9	20	Axial	(-α)60	(0)9:1	(0)1.00	87.33	85.24
10	17	Axial	(+α)120	(0)9:1	(0)1.00	87.51	82.84
11	14	Axial	(0)90	(-α)5:1	(0)1.00	22.62	23.89
12	7	Axial	(0)90	(+α)13:1	(0)1.00	88.03	80.00
13	1	Axial	(0)90	(0)9:1	(-α)0.50	83.17	90.00
14	6	Axial	(0)90	(0)9:1	(+α)1.50	73.67	59.98
15	3	Center	(0)90	(0)9:1	(0)1.00	90.16	89.24
16	10	Center	(0)90	(0)9:1	(0)1.00	92.01	89.24
17	2	Center	(0)90	(0)9:1	(0)1.00	89.20	89.24
18	12	Center	(0)90	(0)9:1	(0)1.00	90.21	89.24
19	15	Center	(0)90	(0)9:1	(0)1.00	89.75	89.24
20	5	Center	(0)90	(0)9:1	(0)1.00	90.89	89.24

Each response of the transesterification process was used to develop a mathematical model that correlates the conversion of JCO FAME to the transesterification process variables studied through first order, second order and interaction terms, according to the following second order polynomial equation,

$$y = \beta o + \sum_{j=1}^{3} \beta j x j + \sum_{ij=1}^{3} \beta_{ij} X_i X_j + \sum_{j=1}^{3} \beta_{jj} x_j^2 + e_1 \ldots\ldots\ldots\ldots \quad (4)$$

where y is the predicted conversion of JCO FAME; x_i and x_j represent the variables; β_o is a constant coefficient; β_j is the linear effect; β_{ij} is first order interaction effect; β_{jj} is a squared effect and e_1 is the error.

H. Model fitting and statistical analysis

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 the statistical significance of the equation developed.

III. RESULTS AND DISCUSSION

A. Development of regression model equation

The final equation in terms of uncoded (actual) factors for conversion of JCO FAME is,

Conversion (%) = 15.87+0.41 * x_1 +27.45*x_2 -166.66*x_3 -5.78E^{-003}
*x_1^2 -2.33 *x_2^2 -56.82 * x_3^2 -2.04E^{-003} *x_1*x_2
+0.61*x_1*x3 +21.71 *x_2* x_3, with R^2 = 95.56
………..…….. (5)

Positive sign in front of the terms indicates synergistic effect, while negative sign indicates antagonistic effect. Eq. (5) shows that the yield of JCO FAME has a linear and

quadratic effect on the three transesterification process variables studied. High R^2 value illustrates good agreement between the calculated and observed results within the range of experiment. The optimized critical values were found to be 79.33 minutes reaction time, 10.41:1 methanol:oil molar ratio and 0.99% catalyst at reaction temperature 65°C. It was found that the conversion of JCO oil to FAME could reach up to 94.35 % in this optimized conditions.

Fig.1 shows the experimental values versus predicted values using the model equation developed. A line with the slope of 1, which corresponds to a perfect fit with zero deviation from the experimental points, is also shown. This plot therefore visualizes the performance of the model in an obvious way. The results in Fig.1 demonstrate that the regression model equation describes the experimental data with sufficient accuracy, indicating that it was successful in capturing the correlation between the four transesterification process variables to the yield of JCO FAME.

B. Effects of transesterification process variables

Data from the reaction experiment of Kouzu et al [33] gain the yield of FAME catalyzed by $CaCO_3$ was less than 10% at 4 h of the reaction time. This yield indicated that $CaCO_3$ seemed to be ineffective in catalyzing the transesterification [33]. It was evident that the decrease in the catalytic activity was corresponded to that of the basic properties and BET surface area, as shown in Table 2 [34].

As can be seen from Table 6, the model *F*-value of 11.67 and a low probability value (P > *F* < 0.0001) indicate that the model was significant for predicting the conversion of FAME from *J. curcas* oil. It was observed that among the three individual variables studied, the molar ratio of methanol/oil (x_2) has the largest effect on the yield of JCO FAME (due to the highest F value) followed by the amount of catalyst (x_3) whereas the reaction time (x_1) has otherwise insignificant effect (Table 6).
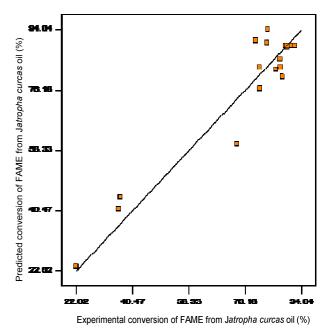

Fig.1 – Predicted versus experimental conversion of JCO FAME.

Source	Sum of square	Degree of freedom	Mean of squares	F-test	Probability (P) >F
Model	7320.51	9	813.39	11.67	<0.0001**
x_2	3148.05	1	3148.05	45.18	<0.0001**
x_3	907.06	1	907.06	13.02	<0.0001**
x_2^2	2186.26	1	2186.26	31.38	<0.0001**
x_2x_3	942.43	1	942.43	13.53	<0.0001**
Residual	696.79	10	69.68		

** Significant at 1% level.

Bajpay and Tyagi reported that the conversion rate increase with time, but the conversion were almost the same after 1 h transesterification of soybean, beef tallow and sun flower [44]. Insignificant effect of reaction time caused by the observed reaction time in this study ranged from 60 mins-120 mins.

The quadratic term of (x_2) was significant for the yield of JCO FAME. The other significant terms include the effect of interaction between variables, particularly between variables (x_2) and (x_3). The results in Table 6 illustrate that there is a great possibility in improving the yield of JCO FAME with proper selection of transesterification process variables using CaO as the catalyst.

The interaction terms with a significant effect on the yield of JCO FAME was found to be the product of x_2 and x_3. Fig. 2 and Fig.3 shows the changes in yield with varying methanol/oil ratio at 0.75% and 1.25% catalysis. It is generally perceived that higher methanol/oil ratio used will result in higher yield of FAME because increasing methanol shifts the equilibrium towards the products [43]. However, the effect of methanol/oil ratio on the yield of FAME was significantly different at different amount of catalyst.

The yield of FAME was increased at 0.75% catalysis if compared to 1.25% according to the data in Fig.2 and 3.A more probable reason for lower activity of 1.25% CaO compared to 0.75% is that the catalyst (produced from a crude lime stone) contains some impurities which hinder the reaction or deactivate CaO when reaching some critical level. The FAME yield could be improved by introducing excess amounts of methanol to shift the equilibrium to the right-hand side. The experimental results, illustrated in Fig. 3, indicate the molar ratio of methanol to oil has a significant impact on the FAME yield. The FAME yield increased from 42% to 94% when the molar ratio was increased from 7:1 to 11:1 at 1.25% catalysis. In comparison, the FAME yield was 80% at a 7:1 molar ratio of methanol to oil at 0.75% catalysis. However, the yields were slightly reduced when the ratio of methanol to oil was higher than 10:1, and the biodiesel yield was only 88% at 11:1. The reason is that the catalyst content decreased with increase of methanol content. Therefore, the optimum molar ratio of methanol to oil depends on amount of catalyst loaded [31]
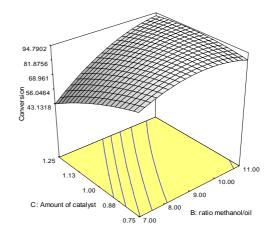

Fig. 2 – Response Surface Plot of Effect of methanol oil ratio and amount of catalyst on the conversion of JCO to FAME
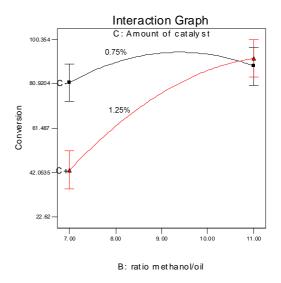

Fig. 3 – Two dimensional drawing on effect of methanol oil ratio and amount of catalyst on the conversion of JCO to FAME

C. Purification of as-synthesized FAME

When calcium oxide is used for the transesterification of vegetable oil with methanol, it is very likely that the reaction is catalyzed not only by basic sites on the surface but also by soluble substance from the solid base catalyst [45]. When basic catalyst is employed to prepare FAME, some cations will remain in the products. Because of the leaching of the solid base catalyst, purification of the produced FAME must be carried out. It is found that strong acidity is one of the desirable properties for the cation-exchange resin to remove the soluble substance [46].

Water washing is not suitable for purifying CaO-catalyzed FAME. The operability of the purifying process is poor if water is used and the effect of the purifying is not obvious if the stirring speed is too low. Contrarily, too high stirring speed leads to emulsification. The yield of the product is decreased and a large amount of the product is lost and the quality of the product cannot meet the standard of FAME [29]. The strategy for purifying the as-synthesized FAME using bentonite (2.5 % of mass fraction) was employed as

complexing agents to remove calcium ions in this study. Six methods for the purification step in FAME production were compared: (A) adsorption on bentonite; (B) adsorption on HCl-activated bentonite; (C) adsorption on HCl-activated and calcinated at 500 °C bentonite (D) adsorption on H_2SO_4-activated bentonite; (E) adsorption with H_2SO_4-activated and calcinated at 500 °C bentonite; (F) adsorption on citric acid (1.5 % of mass fraction); and (G) without adsorption. The results are listed in Table 7.

As shown in Table 7, the application of H_2SO_4-activated bentonite resulted in best removal for the soluble substance, which was reflected by the calcium content remaining after purification. H_2SO_4-activated bentonite has a better efficiency than HCl-activated bentonite caused by the higher surface area and pore volume (Table 3). Since H_2SO_4-activated bentonite is more porous than the other adsorbent, it is best suitable for removal of the soluble substance. The performace of this adsorbent is similar to citric acid, a complexing agent which was also previously used by Zhu et al [29].

The acid-activated and calcinated bentonite method can also remove the calcium ions in the as-synthesized FAME containing 1,666. 67 mg/ml of Ca^{2+}, but the yield of the purified biodiesel is low. The probable reason is that surface and pore properties of the acid-activated and calcinated bentonite was lower than acid-activated bentonite without calcinations (Table 3). In summary, acid-activated and calcinated bentonite is not suitable for decalcifying agent.

It was interesting to note that, even though the surface area and pore properties of non-activated bentonite was lower than H_2SO_4-activated bentonite, the decalcification efficiency was unsignificantly different. The probable reason is that beside surface and pore properties, CEC is also a desirable properties for FAME purification. CEC of the raw and acid treated bentonite showed that they vary with the concentration and and type of activating acid. CEC also followed the same trend as the acidity. The optimum condition (pH) from previous study for higher CEC is 3.72 for H_2SO_4–activated bentonite and 3.82 for HCl-activated bentonite [46].

Even though decalcification efficiency between H_2SO_4-activated bentonite and non-activated bentonite was non-significantly different, the remaining calcium was different significantly. Non-activated bentonite has remaining calcium was higher than H_2SO_4-activated bentonite (Table 7). During the experiments, it was observed that when non-activated bentonite was used, the density of the purified biodiesel obtained still higher than standard of FAME. Therefore, the non-activated bentonite method is not suitable for our purification process.

Beside the increasing of FAME yield and decalcification rate, the application of H_2SO_4-activated bentonite for purification is also environmentally friendly compared to water washing methods where a large amount of water is needed. The volume ratio of oil to water should be 2:1–5:1, which is inevitable to produce a huge of polluted water [29].

TABLE VII
DECALCIFICATION EFFICIENCY OF DIFFERENT TYPE OF PURIFICATION METHOD

Code	Purification Method	Remaining Ca^{2+} (µL/ L)	Decalcification efficiency (%)	Yield (%)
D	H_2SO_4-activated bentonite	92.37 [a]	94.57 [a]	92.50 [a]
F	Citric acid	93.49 [a]	93.51 [a]	92.27 [a]
A	Non-activated bentonite	112.37 [b]	93.46 [a]	91.69 [ab]
B	HCl-activated bentonite	213.88 [c]	88.46 [b]	85.30 [c]
E	H_2SO_4-activated and calcinated bentonite	272.57 [d]	83.67 [d]	81.20 [d]
C	HCl-activated and calcinated bentonite	290.58 [e]	85.49 [c]	80.38 [e]
G	Control	1666.67 [f]		

Values with similar superscripts in a column do not deffer significantly (p≤0.05)

D. Fuel properties of jatropha FAME

Several key properties of the purified biodiesel have been characterized, and the results are shown in Table 8. Most of the properties of the purified biodiesel meet the criteria of Indonesian standard (SNI- 04-7182-2006), Indian standard (IS 15607 : 2005), Germany standard (DIN E 51606) and USA standard (ASTM D6751-02), except for the slightly lower purity of FAME at optimized condition (94.35%). An European standard (EN 14214) require the FAME purity of 96.5%, but Germany standard (DIN E 51606) and USA standard (ASTM D6751-02) contains no such restriction (Table 8).

TABLE VIII
FUEL PROPERTIES OF JATROPHA FAME

Property	Unit	Jatropha oil before treatment	Jatropha oil after pre-treatment	Jatropha FAME	Diesel	FAME Standard		
						ASTM D 6751-02	DIN E 51606	EN14214
Density	kg/m³	919	910	870	850	-	875-0.900	860-900
Viscosity	mm²s⁻¹	38.0	25.3	4.80	2.60	1.9-6.0	3.5-5.0	3.5-5.0
Flash point	°C			172	68	>130	>130	>120
Cetane number	-	-	-	55.2		>40	>49	>49
Acid value	mg KOH/g	9.91	0.78	0.43	-	<0.80	<0.50	<0.50
Ester content	%mass			94.35				96.5 min

IV. CONCLUSIONS

Based on the experimental results obtained, it can be concluded that CaO could be used as an effective catalyst for the conversion of JCO to FAME. The optimized critical values were found to be 79.33 minutes reaction time, 10.41:1 methanol:oil molar ratio and 0.99 % mass fraction of catalyst at reaction temperature of 65°C. Among bentonites used for purification, H_2SO_4-activated bentonite shows the best performance, resulting in the yield of jatropha FAME above 90%, with properties satisfying the standard for FAME. The whole process is simple and seems promising for practical application.

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