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Biodiesel Production from Residual Palm Oil Contained in Spent Bleaching Earth by *In Situ* Trans-Esterification

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Abstract

Spent Bleaching Earth (SBE) is an industrial solid waste of vegetable oil industry that has a high residual oil to be potentialy converted to biodiesel. This study aims at developing a biodiesel production process technology by utilizing residual palm oil contained in SBE and to test the use of hexane in the trans-esterification process. Optimization process was done by using the Response Surface Method (RSM). The variables studied included catalyst concentration and reaction time. On the other hand, the deoiled SBE resulted from biodiesel production was tested as an adsorbent on biodiesel purification after being reactivated. The method used in the biodiesel production included an in situ acid catalysed esterification followed by in situ base catalysed trans-esterification. The results of RSM showed that the optimum process was obtained at NaOH concentration of 1.8% and reaction time of 104.73 minutes, with a predicted response rate of 97.18% and 95.63% for validation results. The use of hexane could also increase the yield of biodiesel which was obtained on the ratio of hexane to methanol of 0.4:1 (volume of hexane: volume of methanol). On the other hand, the reactivated bleaching earth was effective as an adsorbent in biodiesel production, which was still conform with the Indonesian National Standard.

Keywords: spent bleaching earth; palm oil; In Situ trans-esterification; biodiesel; optimization process

1. Introduction

Biodiesel is a renewable fuel produced from vegetable oils with methanol or ethanol reagent and acid or base catalyst. It is used in compression ignition engines as a direct fuel replacement, and as blends with petroleum (Knothe, 2010). As the largest crude palm oil (CPO) production in the world, with a total CPO production of 21.8 millions ton in 2011 (Oil World, 2012), biodiesel production from palm oil is very important for Indonesia. Indonesian biodiesel production increased significantly from 781 million liters in 2010 to 1.52 billion liters in 2011, and the total export was also increasing from 563 million liters in 2010 to 1.225 million liters in 2011 (USDA, 2012). To further increase its biodiesel production from CPO, Indonesia has been developing palm oil industrial clusters in three locations, namely Sei Mangkei, Dumai-Kuala Enok and Maloy (Pahan *et al*., 2011). In the palm oil industrial clusters, biodiesel is also expected to be produced from used cooking oil, while this study explored the possibility of developping biodiesel production process from residual oil contained in spent bleaching earth.

Spent bleaching earth (SBE) or spent clay is a solid waste generated from bleaching section of edible oil refining industry. Bleaching earth is used as an adsorbent to remove or to adsorb the color pigment or other impurities of crude palm oil (CPO) in the processing of cooking oil. The bleaching process leaves SBE still containing residual oil by 20 - 30% or even 40% by weight of SBE (Kheang et al., 2006; Taylor and Jenkins, 1999). Bentonit which is the common name for one of the bleaching earth, is not a renewable material. However, the need of bleaching earth as adsorbent in the refinery industry always increases with the increase of the demand of cooking oil.

In the cooking oil industry, the bleaching process typically uses bleaching earth with the levels of between 0.5% to 2% of the mass of CPO (Taylor and Jenkins, 1999). Generally, the production capacity of an Indonesian palm oil refining plant is 1.000 tons a day, so that the cooking oil industry will need 109.000 - 436.000 tons of bleaching agent annually. Therefore, it becomes an advantage to use SBE which is abundant in its availability and easy to find at the single palm oil refinery. In addition, based on Indonesian Government Regulation No 18, 1992, SBE is still classified as hazardous waste which can cause environmental pollution problems due to the bad odor, and is even classified as fire hazard material. The high content of residual oil in the SBE is challenging to be converted into biodiesel. While this issue is complex, Indonesian palm oil refineries have to take responsibility to manage this waste.

The purpose of this study was to optimize the biodiesel production process technology by *in situ* trans-esterification process using statistical approach of Response Surface Method (RSM). The experiment was then subsequently validated on a larger scale of the 10 liters reactor. Some variables studied in this study were the catalyst concentration and the time of reaction. Biodiesel production left deoiled SBE which could be utilized as an adsorbent in the biodiesel purification. The utilization and regeneration of SBE are important for refining industries, since it will enable SBE recycling and help in abating environmental pollution problems.

2. Materials and Methods

Spent bleaching earth was obtained from a palm oil refining industry (Asian Agri Group) located in Jakarta Indonesia. Methanol (>98% purity) and n-hexane (>98% purity) were supplied by Brataco Chemical Ltd (Indonesia). All solvents and chemicals for analysis were pure analytical grades obtained from Sigma-Aldrich, Fluka and J.T. Baker (Indonesia and France). Furthermore the experiments were divided into three section (i) spent bleaching earth characterization, (ii) opimization of biodiesel production, (iii) study on the effect of hexane on the yield of biodiesel and (iv) reactivated bleaching earth application on biodiesel purification.

Spent bleaching earth characterization covered the preparation and characterization of SBE as a raw material used in the study. Characterizations of raw material included moisture content, fat content and free fatty acid levels.

In situ esterification was performed by reacting 100 g SBE with 600 ml methanol and 1.5% (v/w) of sulphuric acid catalyst. This step was performed for three hours (Deli, 2011). Trans-esterification was performed by reacting alkali catalyst (NaOH).The reaction was carried out in a three-necked stirrer, a heater and condensor to prevent evaporation of methanol, under reaction condition of 625 rpm for the stirring speed, and at the temperature of 65°C. Upon achieving reaction period, the mixture was cooled to room temperature and was filtered to separate the filtrate from SBE. The filtrate was then evaporated using a rotary evaporator to recover methanol and n-hexane, and allowed to settle to be separated into two layers. The upper layer was then purified using fresh bleaching earth (FBE). Centrifugation was also done to separate the adsorben and the residual. The biodiesel yield was calculated using the following equation:

$$\text{Yield of Biodiesel} = \frac{m_1\,(g)}{m_2\,(g)} \times 100\%$$

m_1 = mass of biodiesel after washing
m_2 = mass of oil contained in SBE.

The response surface method with two replications and ANOVA (*α=0.05*) was apllied to investigate the optimum condition of the yield of biodiesel. The experimental range and levels of variables for biodiesel production are given in Table 1. On the other hand, the model resulted from this stage become the base of biodiesel production process at a scale of 10 liters reactors. The characterizations of biodiesel produced included yield, viscosity, density, acid number and saponification number.

Study on the effect of hexane on the yield of biodiesel was conducted to investigated the influence of hexane in the biodiesel production. Hexane was used in the study to extract the residual oil from SBE. Hexane is the best solvent that yielded lower percentage of free fatty acid presence in extracted oil (Lee *et al*., 2000). The volume of hexane addition was varied to investigate the increasing yield of biodiesel on the optimum condition, based on the first experiment resulted from optimization process model.

2.1. Reactivated bleaching earth application on biodiesel purification

This step aims at utilizing SBE left from the biodiesel production process as adsorbent in the biodiesel refining process. It was a further object of this study to provide regenerated bleaching earth with similar bleaching activity to that of fresh bleaching earth. Reactivation was done by using acid method. Reactivation process was carried out by mixing 200 g of SBE into the 400 ml solution of acid (HCl 16%) at a temperature of 80°C with a constant speed of 300 rpm

Table 1. Experimental range and levels of independet process variablesfor biodiesel production

Factor	Level				
	- α	-1	0	1	α
Catalyts Concentration	0.08	0.5	1.5	2.5	2.91
Time	47.57	60	90	120	132.43

for three hours. The next stage was to separate the acid solution from the adsorbent and followed by washing with distilled water to pH 3.5 to 4.0. Drying at 105°C was also conducted to eliminate the remnants of water.

Biodiesel purification was done by using an adsorbent (dry washing). This stage aims at testing the use of SBE as an adsorbent, meanwhile fresh bleaching earth was also used for doing analysis in the effort to compare the biodiesel purification results. The purification was done by mixing 3% of adsorbent by weight of biodiesel with stirring for 20 minutes. Centrifugation was later done to separate the adsorbent from biodiesel.

3. Results and Discussion

3.1. The characteristics of spent bleaching earth

SBE contains residual oil and impurities from degumming, decolourization, and deodorization processes. The oil content in SBE was 19.21% which was different from that of the range of 20-30% (Taylor and Jenkins, 1999; Ong, 1983) and was even up to 40% (Kheang *et al*., 2006; Lee *et al*., 2000). On the other hand, the free fatty acid content was 2.96%, the moisture content was 3.03% and the ash content was 65.82%. Moisture and fat contents were important parameters to know, since both parameters will influence the yield of biodiesel. The higher the fat content of the raw material, the higher will be the yield of biodiesel. The value of free fatty acid content was higher than 2%, so that the biodiesel production was conducted in two steps (esterification and trans-esterification).

On many cases, the free fatty acid tends to be higher than that of FFA contained in CPO. CPO contains about 3-5% FFA (Van Gerpen, 2005). The increase in FFA value could be atributable to the hydrolysis of some tryglirides, cataylzed by the acidic sites of SBE (King *et al*., 1991) occuring in the dump site. This dumping will led an oxidation reaction which might become the reason of increasing FFA value. A previous study reported that the FFA content of SBE may reach 21.6% (Deli, 2011).

3.2. Optimization of biodiesel production from residual oil contained in SBE.

Time of reaction and catalyst concentration are important parameters affecting the yield of biodiesel. By applying multiple regression analysis, the experimental results of the full factorial central composite design were fitted to the polynomial Equation 1. The coefficient of the empirical model and their statistical analysis, evaluated using Design Expert Software, are presented in Table 2. The final equation was derived in terms of coded factors for the biodiesel production as shown in Equation 1.

Table 2. Statistical analysis: regresion analysis

Std. Dev	1.21	Adj-R-Squared	0.8696
Mean	14.83	Pred-R-Squared	0.4857
R-squared	0.9239	Adeq Precission	11.607

Equation 1. $Y_{methyl\ ester} = 17.52 + 2.28\,X_1 + 1.027\,X_2 - 3.16\,X_1^2 - 1.20\,X_2^2 + 0.39\,X_1\,X_2$

This fit of the model was checked with the coefficient of determination R^2, which was calculated to be *0.923*, indicating that 92% of the response variability could be explained by the previously discussed model. The F-value of *17.00* with a 'Prob>*F*' less than *0.05* indicate that the model terms were significant at 95% level. The probability *p*-value was *0.0009*, indicating the significancy of the model specified previously. According to the analysis of variance, both catalyst concentration and reaction time show significant effect to the yield of biodiesel.

Y is the yield of biodiesel, X_1 is catalyts concentration (%) and X_2 is reaction time (minute). The regression equation above showed the linear and quadratic effects. Equation 1 was then used to facilitate plotting the response surface. The best condition based on this model were: 104.73 minutes of reaction time and 1.89% for catalyts concentration. The yield prediction of the response based on the model equation was 97.18%. The response surface contour (Fig. 1) shows the response model for interactive factors of catalyst concentration and time of reaction. As expected, it shows that biodiesel yield increases when high catalyst concentration was applied. The validation of the model in the laboratory scale resulted a number of 95.63% as the yield of biodiesel and 96.8% in the reactor scaleof 10 liters. On the other hand, the utilization of residual oil contained in SBE as biodiesel left deoiled SBE which could be utilized as an adsorbent.

With the same raw materials (SBE), the biodiesel yield from this study was higher than that of the results of previous studies (Kheang *et al*., 2006), namely 82% and (Lim *et al*., 2009) 90.4%. The increase of catalyst concentration (NaOH) can also increase the yield of biodiesel (Shiu *et al*., 2010). On the other hand, the addition of catalyst concentration that was too high can lead to triglyceride saponification, thereby reducing the yield of biodiesel. The optimum catalyst used *in situ* trans-esterification as reported by Shiu *et al*. (2010) was 2 ml NaOH 5 N or the same with 4% (w/w) by weight of the material. However, in this study, it was required less catalyst concentration to produce higher yield of biodiesel. On the other hand, the short time of rection

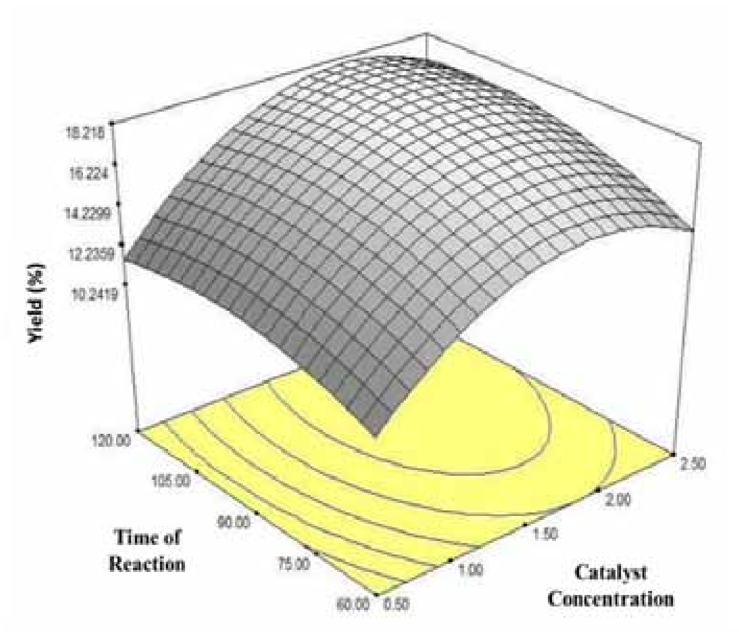

Figure 1. Response surface plot showing the time of reaction versus catalyst concentration on the yield of biodiesel % (w/w)

will not facilitate a perfect conversion of triglycerides into methyl esters.

3.3. Study on the effect of hexane on the yield of biodiesel

N-hexane is often used in the oil extraction process as an alcohol denaturant, or as a cleaning agent in the textile, furniture and leather industries (Faccini *et al*., 2011). Result shows that the best volume ratio of hexane and methanol of 0.4:1 could improve the mass transfer of oil into alcohol (methanol or ethanol) and also intensify the trans-esterification reaction between oil and alcohol (Hincapie *et al*., 2011; Shuit *et al*., 2010; Zeng *et al*., 2009).

Meanwhile, the increase of the hexane ratio to methanol will decrease the yield of biodiesel (Fig. 2). The reduction of biodiesel yield might be due to side reactions happening between methanol and hexane with the impurities in SBE, and consequently reduces the rate of reaction in trans-esterification process. Another reason for the decrease might be the solvency power of the n-hexane, for that reason part of the reagents can be dissolved in the n-hexane without reaction (Faccini *et al*., 2011).

3.4. Application of reactivated bleaching earth on biodiesel purification

In many cases, spent bleaching earth is used for disposal or even it is a general practice to recover the fatty matter from the spent bleaching earth and discard it (Baily, 1982). From this study, biodiesel production still leaves deoiled SBE having the potential to be reused

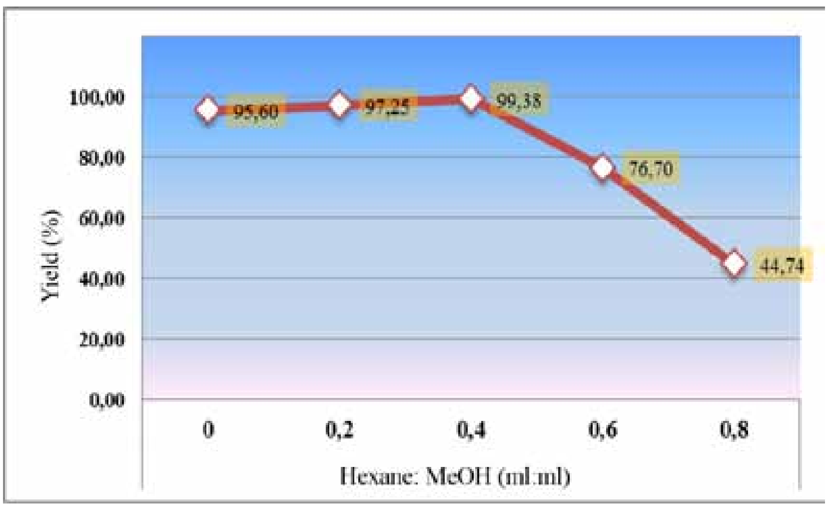

Figure 2. The effect of hexane on the production of biodiesel from SBE

Figure 3. The features of fresh bleaching earth (A), Spent bleaching earth (B), and Reactivated bleaching earth (C)

as an adsorbent. The deoiled spent bleaching earth may be reused in bleaching, either directly or after activation with acids (Alhamed and Zahrani, 2002). In this study, the deoiled SBE was reactivated with HCl. Activation is a treatment of the adsorbent aiming at enlarging the surface area by breaking hydrocarbon bonds or oxidize the surface molecules, so that enlarging the surface area and the effect on the absorption (Alhamed and Zahrani, 2002). The possitive sellection of dry washing is posible when a large amount of soap is present. The water washing causes emulsion problems, whereby the fatty acid esters, such as fatty acid methyl esters, will not separate from the water. In addition, water-washing does not eliminate effectively some of the other contaminants, such as sulfur, phosphorus, and any remaining free fatty acids (Abrams, 2009).

The purpose of reactivation was due to the pores of SBE which have been fully loaded by impurities, so that the active side of this material was closed. The reactivation will activate and increase the surface area and specific volume of SBE. Based on preliminary testing on the use of reactivated spent bleaching earth (RBE) among the concentration of 1%, 2% and 3%, the best concentration to reduce the acid number of biodiesel was 3%. On the other hand, the application of RBE in the biodiesel purification was also compared to the the FBE (Table 3). From this study, it was obvious that adsorbent made from SBE could still produce biodiesel which still conform with the Indonesian National Standard (with respect to viscosity, density, acid number and saponification number). Furthermore, the regeneration of spent bleaching earth shows that the process might be economically viable as reported previously by Alhamed and Zahrani (1999).

4. Conclusions

This study showed that the optimum condition based on RSM for the production of biodiesel was achived on the catalyst concentration of 1.8% and the reaction time of 104.73 minutes. Based on the study, the model predicted the highest respon for the yield of biodiesel was 97.18%. The regeneration of SBE using acid sollution (HCl 16%) could produce an adsorbent which can be used in biodiesel purification as required by the Indonesian Standard.

The use of hexane as an additional solvent in the biodiesel production has increased the yield at the ratio of hexane and methanol of 0.4:1. On the other hand, the use ratio of hexane to methanol of above 0.4:1 had caused a decreased in the yield of biodiesel. Furthermore, the biodiesel, purified by an adsorben which was produced from SBE, has the quality of 4.6 cSt for viscocity, 0.87 gr/cm^3 for density, 0.24 mg KOH/g for acid value and 280.50 mg KOH/g for saponification number.

Table 3. The comparison of biodiesel quality purified by FBE and SBE

No	Parameter	FBE	SBE	SNI*
1.	Viscocity (cSt)	4.60	4.98	2.3 - 6
2.	Dencity (gr/cm^3)	0.87	0.86	0.85 - 0,89
3.	Acid Value (mg KOH/g)	0.24	0.22	Max 0.8
4.	Saponification Value (mg KOH/g)	280.50	268.14	-
5.	Iodine Value (max. 115)	55.21	53.63	Max 125

* SNI-04-7182-2006 (Indonesian Standard)

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