PAPER • **OPEN ACCESS**

Application of response surface methodology to evaluate biodiesel production from spent bleaching earth by in situ transesterification process

To cite this article: R Sugiharto *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **230** 012074

View the article online for updates and enhancements.

IOP ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

This content was downloaded from IP address 180.242.69.69 on 19/02/2019 at 12:35

Application of response surface methodology to evaluate biodiesel production from spent bleaching earth by in situ transesterification process

R Sugiharto, S Hidayati and R Cholik

Department of Agricultural Product Technology, Faculty of Agriculture, University of Lampung, Bandar Lampung, Indonesia.

E-mail: ribut.sugiharto@fp.unila.ac.id

Abstract. Spent bleaching earth (SBE) is used bleaching earth from refining of crude palm oil (CPO). SBE still contains 20 to 40 percents oil. The oil contained in SBE is not food grade oil (non edible oil), but it can be converted into biodiesel. One method used to produce biodiesel is in situ transesterification. In situ transesterification is a biodiesel production process by integrating the oil extraction and biodiesel conversion in one continuous process, so that the process can reduce the time and the cost of biodiesel production. The aim of the study was to obtain the optimal in situ esterification/transesterification reaction conditions to produce biodiesel, investigated using the Response Surface Methodology (RSM). A central composite design with three independent variables: reaction temperature (51.6, 55.0, 60.0, 65.0, and 68.4°C); in situ transesterification time (0.4, 1.0, 2.0, 3.0, and 3.6 hours); and NaOH catalyst concentration (1.66, 2.0, 2.5, 3%, and 3.34% w/w) was used to study the response variable (yield of biodiesel). Based on the results of the experiment, it can be concluded that R^2 was 0.8813, lack of fit was 0.278, and the optimum condition for the in situ transesterification process to produce biodiesel was a heating temperature of 64.33°C, NaOH catalyst concentration of 2.39% (w/w), and a reaction time of 2.32 hours.

1. Introduction

One process of crude palm oil (CPO) refining is bleaching using bleaching earth as much as 0.5 to 2.0 percent of CPO weight. Indonesia's CPO production in 2016 reached 33.23 million tons [1], so the CPO bleaching process required about 664,600 tons of bleaching earth. This bleaching earth requirement will continue to increase along with the increase in the amount of purified CPO in Indonesia. The bleaching process will produce spent bleaching earth (SBE), and this SBE cannot be reused as a CPO bleaching material. Based on PP No. 101 of 2014, SBE can be classified as hazardous toxic waste (B3 waste), meaning that if left untreated has the potential as an environmental pollutant.

SBE is used bleaching earth from refining of CPO. The previous research stated that the CPO contained in SBE was quite large, ranging from 20 to 30% [2]. CPO contained in SBE is classified as nonedible oil, because it contains high levels of free fatty acids. But such CPO has the potential to become a biodiesel feedstock.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

Biodiesel (methyl ester) is an alternative fuel for diesel engines and is made from renewable sources such as vegetable oils and animal fats. Biodiesel consists of a mixture of mono-alkyl ester from a long chain of fatty acids, which is produced through the process of esterification of free fatty acids or the reaction of transesterification of triglycerides with methanol or ethanol and with the help of a catalyst. Methyl ester or ethyl ester is a relatively stable compound, which is liquid at room temperature, non-corrosive, and has a low boiling point [3, 4].

Biodiesel production process is usually carried out using two stages include oil extraction and biodiesel production process. With the two stages of the process, the biodiesel production process becomes less effective and efficient, so it is necessary to find an alternative biodiesel production processes such as in situ esterification/transesterification. In situ esterification/transesterification is a method developed to simplify the process of biodiesel production. In situ transesterification is a biodiesel production process by integrating the oil extraction and biodiesel conversion in one continuous process, so that the process can reduce the time and the cost of biodiesel production. In other words, the in situ transesterification process has better efficiency compared to conventional transesterification [5]. In the process of biodiesel production, there are several factors that can determine the biodiesel yield obtained, which are reaction time, reaction temperature, and catalyst concentration. The aim of the research was to obtain the optimal in situ esterification/transesterification reaction conditions to produce biodiesel, investigated using the Response Surface Methodology (RSM).

2. Materials and Methods

2.1. Materials

The main material used in this research was spent bleaching earth (SBE) obtained from PT. Bumi Waras, Tbk. Lampung. Other materials such as methanol, NaOH, hexane, H_2SO_4, indicators of phenolphthalein (PP), 95% ethanol, KOH, chloroform, Wijs solution, KI, $Na_2S_2O_3$, and HCl were obtained from J.T. Baker (Indonesia).

2.2. Experimental design

This research was conducted using the Response Surface Methodology (RSM) to determine the optimum conditions for biodiesel production process from SBE. The experiment uses 3 independent variables so that the ratability value was $(\alpha) = \sqrt[4]{(2^3)} = 1.68179 \approx 1.682$. Therefore, the value of ± 1.682 was used for coding during the data analysis process. Furthermore, Central Composite Design with 3 independent variables generates response surface. Response surface shows the number of 2^3 factorial design trials, 6 center points, and 6 axial points. The numbers of total trial units were 20.

The independent variables were coded according to the following equation: $\pm \alpha = (x_i + x_{ci})/\Delta x_i$, where x_i is the real value of an independent variable, $\square x_{ci}$ is the real value of an independent variable at the center point, and Δx_i is the step change of independent variable. Based on the equation above, it can then determine the level for independent variables which include reaction temperature, reaction time, and catalyst concentration. The independent variables used in this study are shown in Table 1. The dependent variable or response variable (parameter) is the yield of biodiesel, acid number, and cetane index. The results of the response variables were then analyzed using the Minitab 18.

Table 1. Experimental values and coded levels of the independent variables for central composite rotatable design.

Variables	Level				
	-1.682	-1	0	1	1.682
Reaction temperature (°C)	51.6	55.0	60.0	65.0	68.4
Reaction time (hours)	0.4	1.0	2.0	3.0	3.6
Catalyst concentration (%)	1.66	2.0	2.5	3.0	3.34

2.3. Biodiesel production

Biodiesel was produced through two stages processes, which were in situ esterification and in situ transesterification. The esterification in situ was carried out by mixing 100 grams of SBE with methanol and catalyst of H_2SO_4. Ratio of methanol to SBE was 6:1 (v/w) and the methanol utilized was 600 ml. The amount of H_2SO_4 catalyst added was 1.5% of SBE (v/b). Stirring was used during the process at a speed of 550 rpm and a reaction temperature was brought to 51.6, 55.0, 60.0, 65.0, or 68.4° C, respectively. In situ esterification lasted for 2 hours, followed by in situ transesterification.

The in situ transesterification process was carried out by adding a catalyst of NaOH as much as 1.66, 2.0, 2.5, 3.0, or 3.34% (b/b) to the weight of SBE. In situ transesterification process was carried out for 0.4, 1.0, 2.0, 3.0, or 3.6 hours, respectively, with the same temperature and stirring speed conditions as in the previous in situ esterification process. After the reaction was complete, the the SBE was separated with its liquid fraction by vacuum filtration. After that, the methanol was separated with methyl esters and glycerol using distillation. Furthermore, methyl ester (biodiesel) and glycerol were separated by a separating funnel. Methyl esters (biodiesel) are then washed with 60°C of distilled water until washing water was neutral (pH 7). Then the biodiesel produced was dried using an oven at 110°C to evaporate the remaining water and solvents. Biodiesel (methyl ester) resulted from the in situ transesterification reaction was then characterized to determine its yield, the acid number (AOCS Cd 3d-63, 2009), and the cetane index.

3. Result and Discussion

3.1. Characteristic of SBE

Preliminary research was carried out to determine characteristic of SBE, such as the oil content, free fatty acid content, and water content (Table 2). Characterization of SBE determined the stages of the biodiesel production process.

Table 2. Characteristic of spent bleaching earth (SBE).

Characteristics	Amount (%)
Oil (CPO) content	27.0
Free fatty acid content in oil (CPO)	9.24
Moisture content	0.14

The oil content obtained from spent bleaching earth (SBE) was 27%. The results obtained were in accordance with the research conducted by [2] which explained that the oil content contained in spent bleaching earth ranges from 20-30%. The amount of oil is caused by the nature of bleaching bleaching used in the oil refining process which has high oil absorbency. The results of this preliminary research indicated that SBE had the potential to be used as raw material in biodiesel production.

Based on the preliminary research, the free fatty acids and moisture content on the SBE were 9.24% and 0.14%, respectively. The free fatty acids content from SBE was very high. The high free fatty acid content will cause a saponification reaction (soap formation) which can cause problems in biodiesel production and result in a decrease in biodiesel yield [6]. Additionally, the high content of free fatty acids and water in SBE can reduce the effectiveness of catalysts in the reaction of biodiesel formation [7]. The free fatty acid level and water content have a great influence on the biodiesel production process. If the free fatty acids content in SBE is more than 2%, it is necessary to do an esterification process first to reduce the free fatty acid content in SBE [8, 9].

3.2. Biodiesel yield

Biodiesel yield was calculated on the weight of biodiesel produced compared to the weight of SBE. The results of the research showed that the yield was around 14.36% to 22.56% (w/w). The statistical analysis of the yield showed that the Lack of Fit Test has a significant effect ($P\ (0.009) < \alpha$), which means that the statistical model obtained is not acceptable. The concentration of catalyst affected the

yield of biodiesel linearly. While, the time of the in situ transesterification process affected the yield quadratically. Additionally, the temperature had no significant effect on biodiesel yield.

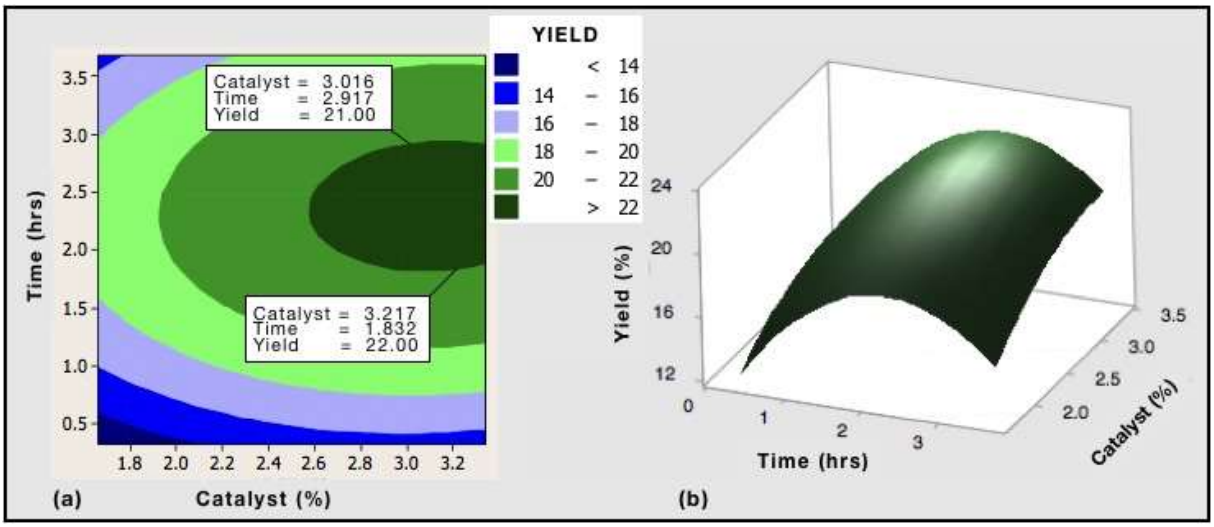

Figure 1. Surface response (a) and contour response (b) plot showing the time of in situ transesterification versus concentration of catalyst on the yield of biodiesel.

Figure 1 shows the optimum conditions of biodiesel production obtained at a catalyst concentration of more than 2.3%, the reaction time of 2.4 hours and the temperature of 64°C, which resulted in a biodiesel yield of around 21.5%. Figure 1 also shows that the greater the addition of NaOH catalyst concentration in the in situ transesterification process will result in increased biodiesel yield. This is because the addition of a catalyst in the reaction process will accelerate or increase the rate of the reaction, so that the results of the reaction obtained will be maximized [10].

The experimental results showed that the time of the in situ transesterification reaction had a significant quadratic effect on biodiesel yield. The figure 1 shows that the biodiesel yield increases until the reaction time of 2.4 hours. After the reaction time for maximum yield is achieved, the yield will be relatively constant. However, if the reaction continues the yield obtained will decrease again. The transesterification reaction will run slowly at the beginning of the reaction and reach a peak at a certain time [11]. The decrease of the yield after certain time was due to reversible reactions. Reversible transesterification reactions causes decrease biodiesel production, in which it is converted back to triglycerides [12].

3.3. Acid number

Acid number is an important parameter in biodiesel quality characteristics. The acid number is expressed by the number of milligrams of KOH used to neutralize free fatty acids contained in one gram of oil or fat. This parameter shows the amount of free fatty acids remaining after the transesterification process. The research showed that acid number of biodiesel ranged from 1.6746 to 3.9507 mgKOH/g. Statistical analysis of acid number showed that the Lack of Fit Test had a significant effect (P (0.000) <α), which means that the statistical model obtained cannot be accepted. Furthermore, the catalyst concentration and reaction time in the linear model had a P value of 0.002 for the catalyst concentration and 0.001 for the reaction time, respectively. It is smaller than α, which it means that the catalyst concentration and reaction time affect the biodiesel acid number linearly. The in situ transesterification reaction temperature has no significant effect on biodiesel acid number.

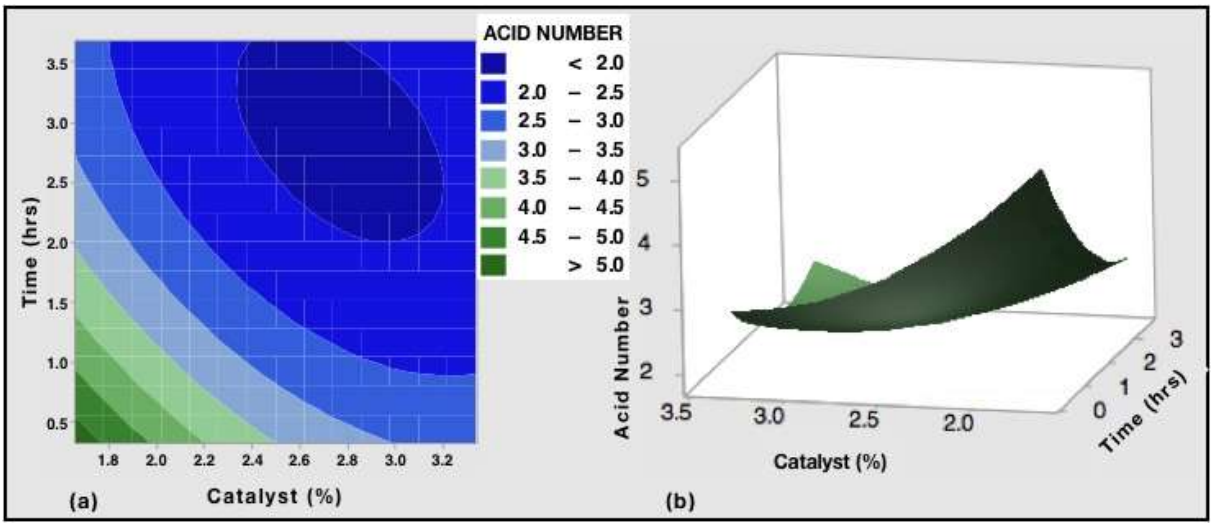

Figure 2. Surface response (a) and contour response (b) plot showing the time of in situ transesterification versus concentration of catalyst on the acid number of biodiesel.

Figure 2 shows that the longer the reaction time, the acid number contained in biodiesel will be lower. Additionally, the addition of catalysts can also reduce biodiesel acid numbers. This is due to the nature of the catalyst which can affect the rate of reaction in the transesterification process. The decrease in acid number along with the increase in catalyst concentration is caused by that the catalyst can accelerate the reaction between oil from SBE and methanol in the transesterification process. The addition of excess catalyst will cause a saponification reaction which will reduce the quality of biodiesel [13].

Decrease in acid numbers due to increasing in transesterification reaction time caused by that the longer the reaction time, the greater the chance of reactant molecules colliding with each other, which causes of fatty acids converted into esters, so that fatty acids in the biodiesel will decrease [14]. Decreasing the amount of acid number after the in situ esterification and transesterification process indicates that the process has proceeded as expected, so that the fatty acids in the SBE have reacted with methanol to form esters. The acid number in biodiesel which is not in accordance with Indonesian Standard for Biodiesel (SNI 7182:2015) is allegedly caused by the presence of free fatty acids in biodiesel still in high amount. The presence of free fatty acids in biodiesel can be caused by the incompleteness of the esterification process [15], which can reduce yield of biodiesel produced.

3.4. Cetane index

Cetane index or cetane number (CN) is an indicator to determine fuel quality, especially the combustion speed of diesel fuel and compression needed for ignition. Cetane number indicates how fast diesel engine fuel can be injected and burned spontaneously. The lower the cetane number, the lower the ignition quality because it requires a higher ignition temperature. Conversely, the higher the cetane number, the faster the combustion, the better the thermodynamic efficiency. A good quality of biodiesel fuel, according to Indonesian Standard for Biodiesel (SNI 7182-2015), must have a CN of at least 51. The biodiesel from experiment showed it has CN ranges from 65.86 to 84.97.

Statistical analysis of biodiesel cetane index showed that the Lack of Fit Test had a significant effect (P (0.044) <α), which means that the statistical model obtained is not acceptable. The catalyst concentration and reaction time in the linear model has a P value of 0,001 for the catalyst concentration and 0.018 for the reaction time, respectively, smaller than α, which means that the catalyst concentration and time affect the cetane index of biodiesel linearly. While the temperature of the in situ transesterification reaction does not significantly affect the index of biodiesel.

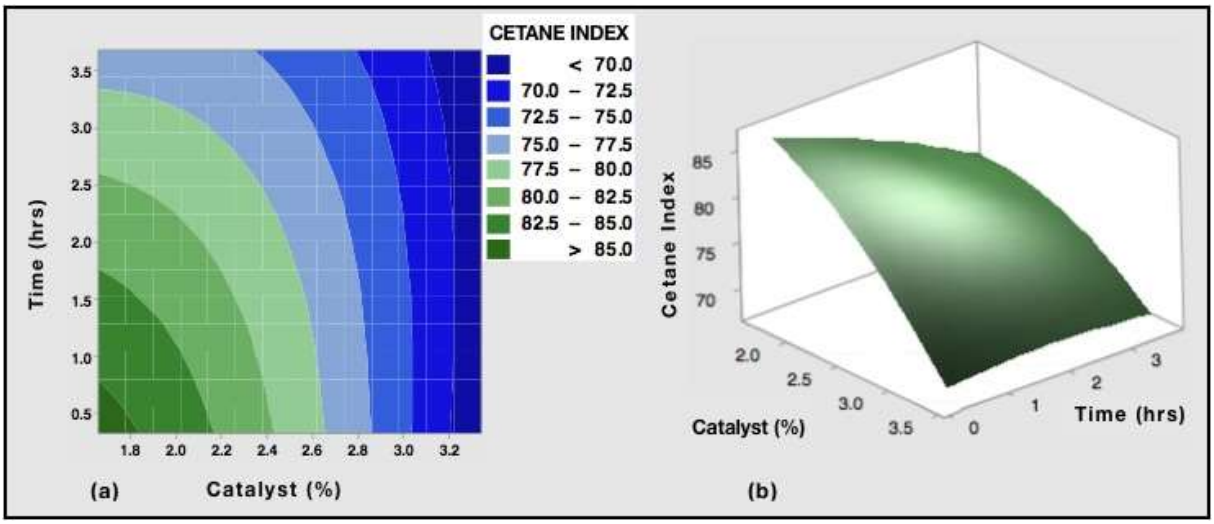

Figure 3. Surface response (a) and contour response (b) plot showing the time of in situ transesterification versus concentration of catalyst on the cetane index of biodiesel.

The cetane index response contour (Figure 3) shows that an increase in the catalysts concentration and an increase in reaction time can lead to an increase in the cetane index of biodiesel. The number of the cetane index is correlated with the number of the iodine number and the saponification number. The cetane index is inversely proportional to the saponification number and iodine number. Furthermore, the lower the saturation rate of the fatty acids that make up biodiesel, the cetane index is also lower [16]. Biodiesel cetane index is also related to the fatty acid composition that makes up the biodiesel. Saturated fatty acids with long carbon chains, such as lauric, myristic, palmitic, stearic, arachidic, contribute high cetane numbers to the biodiesel [17].

4. Conclusion

Based on the results of the research can be concluded that R^2 value was 88.13%, lack of fit was 0.278 and and the optimum condition for the in situ transesterification process to produce biodiesel from SBE was a heating temperature of 64.33°C, NaOH catalyst concentration of 2.39% (w/w, NaOH/SBE), and a reaction time of 2.32 hours. Such in situ transesterification produced a biodiesel yield of 21.45% (w/w, biodiesel/SBE), in which the biodiesel produced had an acid number of 2.28 KOH/g and cetane index of 78.10.

References

[1] Dirjenbun 2017 Statistik Perkebunan Kelapa Sawit Indonesia 2015-2017 (2015-1017 Statistic of the Indonesian Oil Palm Plantation) Direktorat Jenderal Perkebunan Kementerian Pertanian Republik Indonesia Jakarta. [In Indonesian]

[2] Kheang L S, Cheng S F, Choo Y M, Ma A N 2006 A study of residual oils recovery from spent bleaching earth: their characteristics and applications *J. Amer. Oil Chem. Soc.* **3** 10 2063-2067.

[3] Gerpen J V 2005 Biodiesel processing and production *Fuel Process. Technol*. **86** 1097-1107.

[4] Gashaw A, Getachew T, Teshita 2015 A review on biodiesel production as alternative fuel *J. For. Prod. Ind.* **4** 80-85.

[5] Haas M J, Scott K M, Marmer W N, Foglia T A 2004 In situ alkaline transesterification: an effective method for the production of fatty acid esters from vegetable oils *J. Amer. Oil Chem. Soc.* **81** 1 83-89.

[6] Sharma Y C, Sigh B, Upadhyay S N 2008 Advancements in development and characterization of biodiesel: a review *Fuel* **87** 12 2355-2373.
[7] Suryani A, Gustan P, Aswa A 2015 Proses reaktivasi tanah pemucat bekas sebagai adsorben umtuk pemurnian minyak sawit kasar dan biodiesel (Process of reactivation of spent bleaching earth as absorbent for purification of crude oil and biodiesel) *J. Teknologi Industri Pertanian* **25** 1 52-67. [In Indonesian]
[8] Qian J F, Wang S, Liu S, Yun Z 2008 In situ alkaline transesterification of cotton seed oil for production of biodiesel and non toxic cotton seed meal *Bioresour. Technol.* **99** 18 9009-9012.
[9] Ramadhas A S, Jayaraj S, Muraleedharan S 2005 Biodiesel production from high FFA rubber seed oil *Fuel* **84** 4 335-340.
[10] Leung D Y C, Guo Y 2006 Transesterification of neat and used frying oil: optimization for biodiesel production *Fuel Proces. Tecnol.* **87** 10 883-890.
[11] Leung D Y C, Wu X, Leung M K H 2010 A review on biodiesel production using catalyzed transesterification *Appl. Energy* **87** 4 1083-1095.
[12] Dharsono W 2010 Proses pembuatan biodiesel dari dedak dan metanol dengan esterifikasi in situ (Process of biodiesel production from oil rice bran and methanol by in situ esterification) Thesis (Semarang: Universitas Diponegoro). [In Indonesian]
[13] Shiu P J, Gunawan S, Hsieh W H, Kasim N S, Ju Y H 2010 Biodiesel production from rice bran by a two-step in situ process *Bioresour. Technol.* **101** 3 984-989.
[14] Maharani H N, Zuliyana 2010 Pembuatan metil ester dari minyak dedak dan metanol dengan proses esterifikasi dan transesterifikasi (Methyl ester production from rice bran and methanol by esterification and transesterification processes) Thesis (Semarang: Universitas Dipenegoro). [In Indonesian]
[15] Kartika I A, Yani M, Hermawan D 2012 Transesterifikasi in situ biji jarak pagar: pengaruh jenis pereaksi, kecepatan pengadukan dan suhu reaksi terhadap rendemen dan kualitas biodiesel (In situ transesterification of Jatropha seeds: the effect of reactant type, stirring speed and reaction temperature on yield and quality of biodiesel) *J. Teknol. Indust. Pertanian* **21** 1 24-33. [In Indonesian]
[16] Tazora Z 2001 Peningkatan mutu biodiesel dari minyak biji karet melalui pencampuran dengan biodiesel dari minyak jarak pagar (Improving the quality of biodiesel from rubber seed oil through mixing with biodiesel from jatropha oil) Thesis (Bogor: Institut Pertanian Bogor). [In Indonesian]
[17] Zuhdi M F A 2002 Aplikasi penggunaan limbah methyl ester pada high speed marine diesel engine (Application of methyl ester waste on high speed marine diesel engines) Seminar Nasional Teori Aplikasi Teknologi Kelautan FTK ITS Surabaya. [In Indonesian]