Research Article
Biodiesel Production from Bulk Frying Oil with Ultrasound Assisted

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Abstract: The objective of this research is to optimize of biodiesel production with ultrasound assisted. Optimization was used central composite design methods. Biodiesel was produced from frying oil with KOH catalyst and ultrasonic assisted. The variables were investigated temperature, catalyst concentration and ratio of methanol to oil. Biodiesel was separated from reactant and impurities with decantation process and distillation process. The results of research obtained optimum conversion 85.95% in operation condition are methanol/oil 5.05:1, catalyst concentration 1.65% and temperature reaction 50°C. Mathematic modeling for describe in this process like expressed; $Y = 86.2107 - 7.4287X_1 + 1.0661X_2 + 0.6289X_3 - 2.5319X_1^2 - 2.0603X_2^2 - 1.0618X_3^2$.

Keywords: ANOVA, biodiesel, central composite design, optimum, statistic, ultrasonic assisted, yield of biodiesel

INTRODUCTION

Nowadays, demands of fossil energy in Indonesia are significantly increasing while oil reserves will be diminishing within 20 years (Ibrahim *et al.*, 2010). As a consequence, there are serious attempts in finding new alternative energy i.e., hydrogen cells, solar energy and wind power. However, the above technologies are still at the development stage and still not feasible to be applied from economic point of view (Haeni *et al.*, 2008). The feasible option is developing the technology for biodiesel production as it is biodegradable and non-toxic product. Biodiesel also has low undesirable emission and environmental friendly. Biodiesel can be produce from vegetable oils which is generated from renewable resources. They practically have less sulphur content, offer no storage difficulty and they have excellent lubrication properties. Moreover, converting vegetable oils to become biodiesel indirectly can improve the absorption of carbon dioxide compare to the direct burning (conventional method in generating energy) (Ikwuagwu *et al.*, 2000). Some of the advantages of biodiesel is decrease the greenhouse effect, biodegradable, non-toxic and specifically to reduce levels of CO 65%, 78% CO_2 and SO_2 90% and 50% unburn carbon than fossil fuels. The Government of Indonesia has begun to support the development of biodiesel, bio-ethanol, bio-oil, bio-gas, the fuel of natural gas (Anonymous, 2005).

Biodiesel can be produced from vegetable oils or fats by transesterification-esterification reaction. The source materials are commonly used vegetable oils such as palm oil (*Elaeis*) (Kalam and Dan Masjuki, 2002), coconut oil (Jitputti *et al.*, 2006; Hadiyanto *et al.*, 2010), jatropha oil (*Jatropha curcas*) (Ginting *et al.*, 2011; Gubitz *et al.*, 1999) and rubber seeds oil (*Hevea brasilienis*) (Ikwuagwu *et al.*, 2000; Ramadhas *et al.*, 2005; Ragavan and Roy, 2011; Widayat and Suherman, 2012a; Widayat *et al.*, 2012b). Biodiesel production process can be conducted by using a homogenous acid catalyst process (Furukawa *et al.*, 2010), supercritical process (Deshpande *et al.*, 2010), enzymatic process (Sotoft *et al.*, 2010), heterogeneous acid catalyst (Ilgen *et al.*, 2007; Jitputti *et al.*, 2006) and ultrasonic assisted (Ragavan and Roy, 2011).

Today, have developed a new technique for solid-liquid extraction product that is ultrasonic waves assisted. Food processing are also not spared take advantage of this technique (Mason *et al.*, 1996). This technique is known as sono-chemical effects that is using ultrasonic waves to affect the changes that occur in chemical processes. The main advantage of the transesterification with the aid of ultrasonic waves in comparison with the conventional are greater efficiency and shorter operating time.

Ultrasonic technology can be used to increase conversion, improve selectivity, changing the reaction pathway and can also be used as an initiator in the reaction system of chemistry, biology and others. With the use of ultrasonic waves allows the process carried out at lower pressures and temperatures, reducing the consumption of raw materials and solvents, reducing synthesis steps to be performed and will simultaneously increase the selectivity of the end, allowing the use of raw materials and low-purity solvent and increasing the activity of catalysts and others (Garcia and Castro, 2003). With these advantages, the ultrasonic waves used in the industry is very promising because it offers

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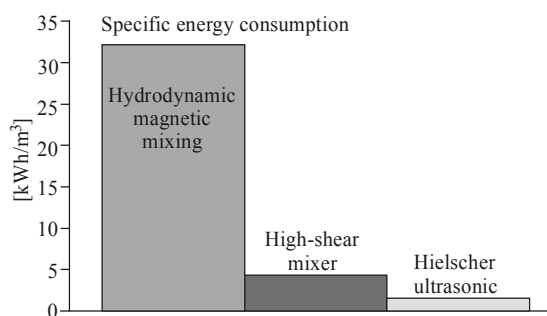
Fig. 1: Comparison of the energy usage of ultrasonic wave generating devices with conventional mixing

the potential for shorter reaction cycles leading to the formation of chemical plants are smaller and cheaper.

Sono-esterfication is term to express application of esterification assisted by ultrasound technology. At present, biodiesel is primarily produced in batch reactors in which the required energy is provided by heating accompanied by mechanical mixing. Since fats and alcohols are not totally miscible, the conventional transesterification reaction in batch processing is relatively slow and phase separation of the glycerin is time-consuming. Whereas, ultrasonic processing used in biodiesel production delivers a biodiesel yield in excess of 99% in five minutes or less, compared to one hour or more using conventional batch reactor systems. With the saponification of esters the reaction proceeds on the boundary between the aqueous acid or base phase and not in the water-soluble ester phase. Ultrasound accelerates the particle transition at the phase boundary and thus the reaction, compared with the classical reaction procedure with heating and stirring. Ultrasonic wave has the advantage in energy usage as shown in Fig. 1.

Biodiesel production process by ultrasonic waves assisted takes less time compared with mechanical systems. Researches conducted by Widayat *et al.*

(2012b) still use an ultrasonic cleaner for generate ultrasonic wave. Teixeira *et al.* (2009) stated that the biodiesel production process with ultrasonic wave takes time less than 1 hour, so the efficiency can be achieved with this process.

The objective of this study is to find optimum condition in biodiesel production from frying oil by ultrasonic waves assisted. The optimum conditions include of temperature, catalyst concentration and ratio of reactants. Optimization methods did use Central Composite Design (CCD).

MATERIALS AND METHODS

Materials: The raw material used is bulk frying oil that obtained from Banyumanik market, Semarang Central Java. Frying oil was analyzed of free fatty acid. The results analysis has shown free fatty acid content below 0.5%, so the biodiesel production just uses transesterification reaction (Kalam and Dan Masjuki, 2002). Potassium Hydroxide (KOH) as a catalyst has analytical specification (Merck). Methanol has industrial specification. Equipment for biodiesel production process as shown in Fig. 2 where the reactor using a capacity of 250 mL erlenmeyer (Pyrex) with bulk coconut palm oil. To generate ultrasonic waves using Ultrasonic Bronsonic with a frequency of 40 kHz capability. This equipment is equipped with a heater to reach operating temperature (which has been determined in accordance temperature variable) and degassing timer/ultrasonic. It is also equipped with a filter that serves to put the reactor equipment.

Biodiesel production processing: Experiment about biodiesel production was conducted in three stages involve methoxide reaction, transesterification reaction and biodisel separation. In methoxide reaction stages, methanol reacted with KOH in erlenmeyer and conducted in magnetic stirrer and 10-15 min. The addition of methanol, the operation variables and

Table 1: The operation condition and results of experiments

Run	Oil : methanol	V methanol (mL)	% catalyst	Mass of KOH (gr)	Reaction temperature (°C)	Yield of biodiesel (%)
1	1 : 6	28	1	1.22	40	81.972
2	1 : 6	28	2	2.44	40	82.792
3	1 : 10	46	1	1.37	40	83.611
4	1 : 10	28	2	2.70	40	84.431
5	1 : 6	28	1	1.31	55	76.104
6	1 : 6	46	2	2.60	55	76.836
7	1 : 10	46	1	1.46	55	77.567
8	1 : 10	46	2	2.90	55	78.299
9	1 : 8	37	1.500	2	45	83.511
10	1 : 8	37	1.500	2	31.77	93.648
11	1 : 8	37	1.500	2	58.20	77.326
12	1 : 4.5	21	1.500	1.80	45	85.831
13	1 : 11.5	53	1.500	2.30	45	86.604
14	1 : 8	37	0.618	0.80	45	87.377
15	1 : 8	37	2.382	3.30	45	88.151
16	1 : 8	37	1.500	2	45	88.924
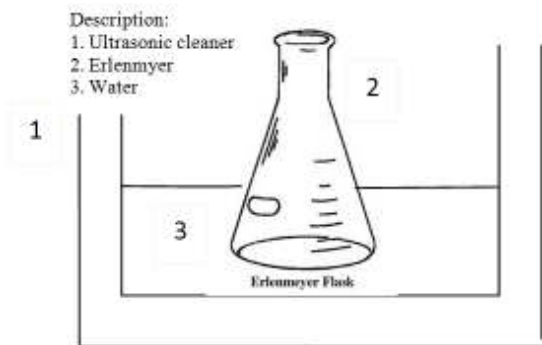
Fig. 2: Experimental apparatus for biodiesel production with ultrasonic assisted

Table 2: Experimental design for 3 variables with CCD methods

Run	Block	X_1	X_2	X_3	Y
1	1	-1	-1	-1	Y_1
2	1	-1	-1	1	Y_2
3	1	-1	1	-1	Y_3
4	1	-1	1	1	Y_4
5	1	1	-1	-1	Y_5
6	1	1	-1	1	Y_6
7	1	1	1	-1	Y_7
8	1	1	1	1	Y_8
9	1	0	0	0	Y_9
10	2	-1.76	0	0	Y_{10}
11	2	1.76	0	0	Y_{11}
12	2	0	-1.76	0	Y_{12}
13	2	0	1.76	0	Y_{13}
14	2	0	0	-1.76	Y_{14}
15	2	0	0	1.76	Y_{15}
16	2	0	0	0	Y_{16}

X_1: Coding for variable of ratio molar of bulk frying oil to methanol; X_2: Coding for variable of catalyst concentration; X_3: Coding for variable of temperature reaction; Y: Yield of biodiesel

the corresponding base catalyst for the transesterification reaction, where the variation of operation as shown in Table 1. Transesterification reaction stages, conducted with ultrasonics assisted (Fig. 2). Hundred gram of frying oil added with potasium methoxide and took in ultrasonic cleaner. Degassing time was adjust in 5 min and ultrasonic time in 30 min. The operation temperature/solution was adjust in experiments design (Table 1). These stages finished about in 35 min. In transesterification process, glycerol produced as by product. Biodiesel separated with decantation and distilation process. Glycerol was separated with decantation process as bottom product. Biodiesel as top product then separated with distilation as bottom product. Methanol was evaporated and obtained as top product. Glycerol and Biodiesel was analyzed viscosity, density, weght of biodiesel, acid number, iodine number and saponification number.

Central composite design methods: The method used to design this experiment is Response Surface Metodology (RSM). RSM is a combination of mathematics and statistical techniques that useful for modeling and analysis of problems where the observed response is influenced by several variables and aims to optimize the response. Response can be measured parameter or characteristic quality. To design the total number of experiment runs used the following equation:

$$\sum R = 2^k + 2k + n_o \quad (1)$$

where,
k = Number of independent variable
n_0 = Number of experiments that were repeated at the center point (in this case the value of n_0 = 2)

This experiment used Box-Wilson Central Composite Designed (CCD) that number of independent variable is 3 (Box *et al.*, 2005). The three independent variables are the ratio of methanol-bulk

frying oil, the percent of the catalyst and temperature reaction. So the response is the conversion of biodiesel or yield of biodiesel. Experimental design is presented in Table 2 and the realization of the experimental design as presented in Table 1. Yield of biodiesel was calculated with equations 2. Data processing is performed by software Statistica 6:

$$Y_{biodiesel} = \frac{\text{Mass of biodiesel}}{\text{Mass of raw material (Frying oil + methanol)}} \times 100\% \quad (2)$$

Furthermore, the data processing is done to obtain mathematical model equations to find out the most influential variable. Polynomial equations to model the CCD as follows Eq. (3) to (5):

$$Y_u = \beta_0 + \sum \beta_i X_{ui} + \sum \beta_{ii} X_{ui}^2 + \sum \sum \beta_{ij} X_{ui} X_{uj} + \varepsilon \quad (3)$$

$$X_i = \frac{[X_i - (X_{it} + X_{ib})/2]}{[(X_{it} - X_{ib})/2]} \quad (4)$$

where,
Yu = Predicted response to u
U = 1, 2, 3,........, n, in this experiments as yield of biodiesel
Bo = Average of response (yield of biodiesel average)
β_i = Linear coefficient
β_{ii} = Squared term
β_{ij} = interactions variable coefficient
x_i = Non dimension number of independent variables
X_i = The real price of an independent variable

In this experiment, Eq. (3) for three independent variables can be write follows:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3$$
$$+ \beta_{23} X_3 X_2 + \beta_1^2 X_1^2 + \beta_2^2 X_2^2 + \beta_3^2 X_3^2 + \beta_{123} X_1 X_2 X_3 \quad (5)$$

Table 3: Results of regression analysis and confidence level

Factor parameter	Regression coef.	S.E.	t (5)	p	-95% Cnf. limnt	+95% Cnf. limnt
Mean	86.21069	1.045967	82.42199	0.000000	83.52195	88.89944
Blocking	6.25707	0.745553	8.39253	0.000394	4.34057	8.17358
X_1	-7.42869	0.785309	-9.45957	0.000223	-9.44739	-5.40998
X_1^2	-2.53197	0.918533	-2.75654	0.039998	-4.89314	-0.17081
X_2	1.06612	0.785309	1.35758	0.232655	-0.95259	3.08482
X_2^2	-2.06031	0.918533	-2.24305	0.074928	-4.42148	0.30085
X_3	0.62893	0.785309	0.80087	0.459554	-1.38977	2.64763
X_3^2	-1.06180	0.918533	-1.15597	0.299925	-3.42296	1.29937
X_1X_2	-0.08795	1.046084	-0.08408	0.936259	-2.77699	2.60110
X_1X_3	-0.04397	1.046084	-0.04204	0.968096	-2.73302	2.64507
X_2X_3	0.00000	1.046084	0.00000	1.000000	-2.68904	2.68904

Table 4: Analysis of Variance (ANOVA)

Factor parameter	SS	Degree of freedom	MS	F	p
Blocking	154.1518	1	154.1518	70.43448	0.000394
X_1	195.8419	1	195.8419	89.48340	0.000223
X_1^2	16.6300	1	16.6300	7.59852	0.039998
X_2	4.0336	1	4.0336	1.84301	0.232655
X_2^2	11.0113	1	11.0113	5.03126	0.074928
X_3	1.4037	1	1.4037	0.64139	0.459554
X_3^2	2.9245	1	2.9245	1.33627	0.299925
X_1X_2	0.0155	1	0.0155	0.00707	0.936259
X_1X_3	0.0039	1	0.0039	0.00177	0.968096
X_2X_3	0.0000	1	0.0000	0.00000	1.000000
Error	10.9429	5	2.1886		
Total SS	386.7508	15			

The response selected, *Y*, was the yield of methyl ester/biodiesel. Independent variables in Eq. (5) are X_1; coding for ratio molar bulk frying oil to methanol; X_2 is coding for catalyst concentration and X_3 is coding for reaction temperature.

RESULTS AND DISCUSSION

Interactions between process variables: The coefficients of (5) were determined by multiple regression analysis with data for yield biodiesel (Table 1) and independent variables (Table 2). This analysis includes all the independent variables and their interactions, regardless of their significance levels. The best-fitting response surfaces found can be written as follows:

$$Y = 86.2107 - 7.4287X_1 + 1.0661X_2 + 0.6289X_3 - 2.5319X_1^2 - 2.0603X_2^2 - 1.0618X_3^2 - 0.0879X_1X_2 - 0.0439X_1X_3 \qquad (6)$$

Coefficients in Eq. (6) then evaluated with statistical. The results presented in Table 3. Table 3 show that interactions between variables have significant effect on the yield of biodiesel. Therefore, instead of studying single variable (as in conventional method) the interactions will be investigated which is significance and importance for a comprehensive optimization study. In Eq. (6) show Positive sign in front of the terms indicates synergistic effect, while negative sign indicates antagonistic effect. For a positive sign, the greater the value of independent variable can cause response variable (yield biodiesel) increase. Likewise for the negative sign, the greater the

value independent variable can decrease yield of biodiesel.

Table 3 also shows that the results of the t test and confidence level for each coefficient in the mathematical model is quite good. From Eq. (6), it can be seen that X_1 (ratio of methanol-frying oil) had the largest coefficient value, equals to -7.4287 so that the ratio of methanol is the most influential variable, X_2 (catalyst concentration) has the largest coefficient value after ratio methanol to bulk frying oil. X_2 coefficient is positive, this means that the greater percent of the catalyst used in the reaction will increase conversions, increase the amount of catalyst can enhance the catalytic activity of direct transesterification reaction, thereby increasing the amount of methyl ester.

Coefficients also evaluated of variance. The results of analysis presented Table 4. Table 4 show that single variable and quadratic variable have F value greater than the price p. For interaction variables have F value less than p value. Table 4 can also observed that the linear term of ratio molar methanol to frying oil (X_1) and catalyst concentration (X_2) has a large effect on the biodiesel yield significantly due to the high F-value. Ratio molar methanol to bulk frying oil, F-value 195.84 more significant than catalyst concentration, F-value 4.03. The quadratic term of ratio molar methanol to frying oil (X_1^2), F-value 16.63 is more significant than catalyst concentration (X_2^2), F-value 11.01. The effect influencing of variable on biodiesel yield, the model then analyzed with pareto chart.

Pareto chart is a simple frequency distribution (histogram) of the data which is based on categories of greatest to smallest. It is based on the principle that
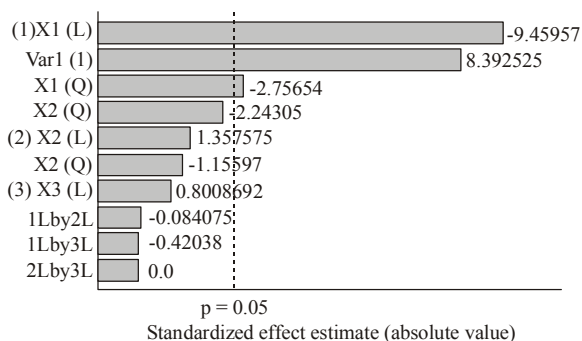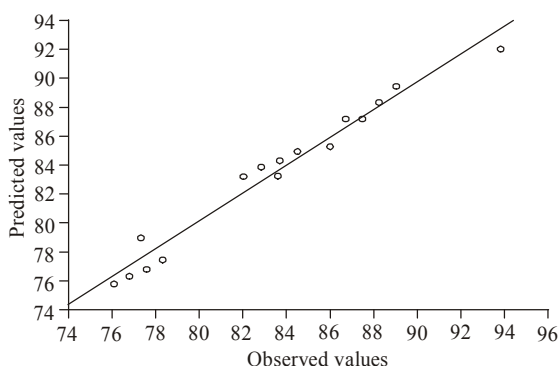
Fig. 3: Pareto chart

Fig. 4: Predicted versus experimental yield of biodiesel

there are many factors that affect anything but just a few important factors are taken into account the factors that cause the most significant impact. By placing the factors that were assessed according to the order, immediately recognizable factors are most important. Thus, pareto diagrams can assist in focusing efforts on the most important thing alone (Montgomery, 1991). The results of pareto chart presented in Fig. 3. Figure 3 show that the variables which pass the line p = 0.05 is a variable of ratio molar methanol to frying oil (L) and

quadratic variable. Value effects of variables which do not cross the line p = 0.05 is a powerful variable that can be overlooked, namely catalyst concentration (L and Q), temperature (L and Q) and all the interaction of two variables such as interactions. Each variable can be analyzed and optimized separately because the effect of each variable does not result in a increase yield of biodiesel significantly. For this analysis, mathematical model in Eq. (6) can be written follow as:

$$Y = 86.2107 - 7.4287X_1 + 1.0661X_2 + 0.6289X_3 - 2.5319X_1^2 - 2.0603X_2^2 - 1.0618X_3^2 \qquad (7)$$

To test the fit of the model, the regression equation and determination coefficient (R^2) were evaluated. In this case, the value of the determination coefficient ($R^2 = 0.9717$) indicates that the sample variation of 97.17% for FAME yield is attributed to the independent variables and only 2.83% of the total variations are not explained by the model. Figure 4 shows the predicted versus actual. A higher value of the correlation coefficient ($R^2 = 0.9205$) justifies an excellent correlation between the independent variables (Yuan *et al.*, 2008). Abdul Halim *et al.* (2009) also have determination coefficient ($R^2 = 0.9772$) in biodiesel production from waste cooking oil with packed bed reactor.

Figure 5 and 6 shows the effects of different reaction temperature and molar ratio of metanol to oil on the yield of biodiesel in three dimensional surface response and two dimensional interaction plots, respectively. From the figures, it is obvious that at any designated quantity of molar ratio, the yield of biodiesel increase proportionally with catalyst concentration and temperature. In contrast, the yield augmented when the molar ratio was reduced from 10 to 6 at any constant catalyst concentration within the range of 1-2%. The observed phenomenon occurred as increasing the
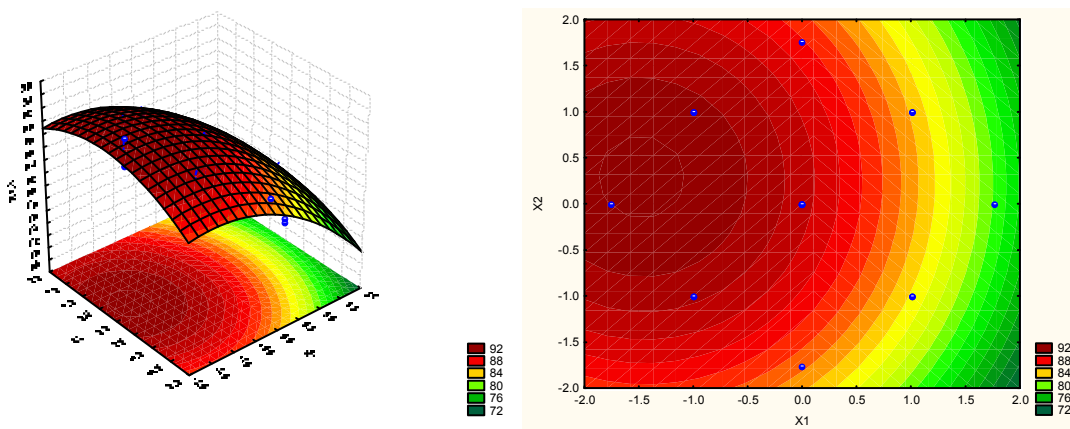

Fig. 5: Effect of catalyst concentration and ratio molar methanol to frying oil on the yield of biodiesel in three dimensional response surface
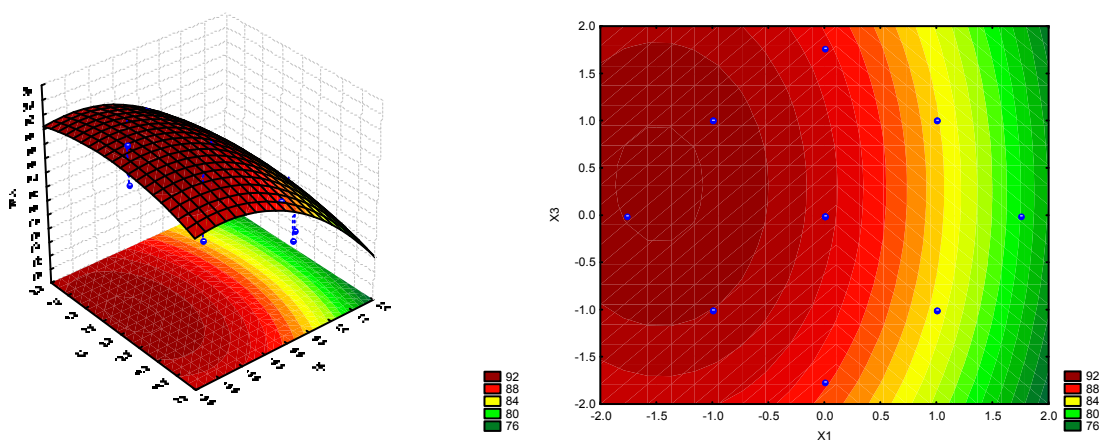
Fig. 6: Effect of molar ratio mathanol to frying oil and reaction temperature on the yield of biodiesel in three dimensional response surface
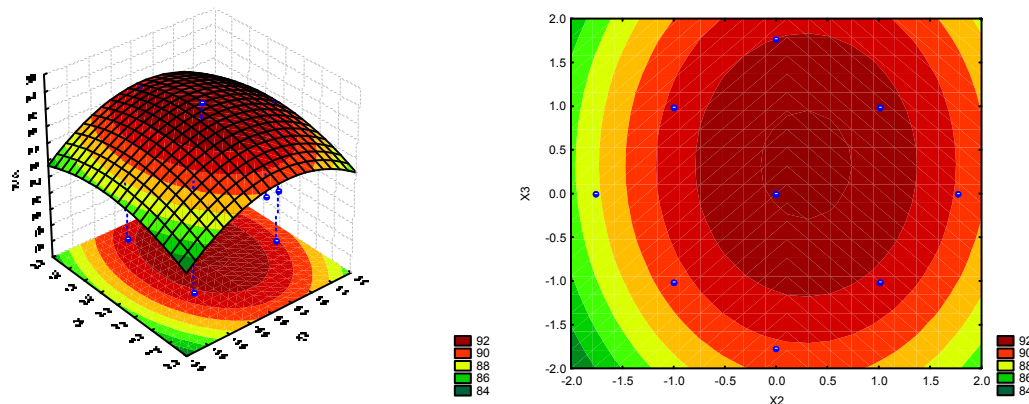

Fig. 7: Effect of catalyst concentration and reaction temperature of biodiesesl in three dimensional response surface

catalyst concentration enhanced the reaction rate of transesterification reaction and eventually the yield of biodiesel. On the other hand, the same trend was not applicable for molar ratio of methanol to oil. Although increasing the molar ratio will push this reversible reaction towards producing more products, but limitation of reaction equilibrium and difficulties in separating excessive methanol from biodiesel and glycerol will leads to lower yield.

Figure 6 represent the effect of interaction between molar ratio and reaction temperature. Figure 6 show that increasing of reaction temperature and decreasing of molar ratio cause the yield of biodiesel increase, but at higher molar ratio and higher reaction temperature, the yield of biodiesel decrease. As mentioned previously, the presence of excessive methanol in the reaction mixture required redundant separation process which is uneconomical and causes lower yield of biodiesel.

The effect of catalyst concentration and reaction temperature on the yield of biodiesel is shown in Fig. 7. At higher reaction temperature, its relevancy to the augmentation of yield is enormous. For instance, as can be seen in Fig. 7, the yield increases at higher catalyst concentration and higher reaction temperature. But when catalyst concentration increased at any constant reaction temperature, the yield will decreased. Reaction temperature plays a crucial role in determining the reaction rate in transesterification ultrasonic assisted reaction which influence the total yield of biodiesel produced. For instance, higher temperature induces faster reaction rate compared to lower temperature (Levenspiel, 1972).

Optimum operating conditions sought by looking at optimization 3-dimensional graph and surface contours graph. Optimization of three-dimensional graph consists of axis x, y and z, where x and y axis is the variable being tested while the z-axis shows the value of the conversion can be achieved from the interaction of two variables tested so from optimization of three-dimensional graphics can be seen the value of the conversion which can be achieved from the interaction of two variables that are tested and as well as optimal conditions. Surface contour graph consists of

Table 5: Optimization constrains used to obtain the optimum value for biodiesel yield

Variable	Observed min.	Critical values	Observed max.
X_1	-1.76000	-1.47485	1.760000
X_2	-1.76000	0.29021	1.760000
X_3	-1.76000	0.32670	1.760000

Min.: Minimum; Max.: Maximum

axis x and y, where x and y axes are the variables tested. In surface contours figuring in color areas, so it can be seen from this graph the points of interaction of two variables is clear, where most interactions are optimal in the red region of the oldest. The critical value in Fig. 5, 6 and 7 presented in Table 5 for X_1, X_2 and X_3 and in these condition obtained yield of biodiesel 85.95%. To obtain the actual value of the variable, use the Eq. (4). The optimum condition for yield biodiesel obtained in ratio molar methanol to frying oil 5.05:1, catalyst KOH concentration 1.65% and temperature 50°C.

CONCLUSION

The Central Composite Design (CCD) employed for optimization and analysis of transesterification of bulk frying oil with ultrasound assisted. The experiments conducted in ultrasonic cleaner and batch system. The optimum conditions of molar ratio methanol to bulk frying oil 5.05; 1, KOH catalyst concentration 1.65% and operation temperature 50°C. Biodiesel yield was determined under this condition and obtained 85.95%. Mathematical model that describe for biodiesel production with ultrasound assisted like expressed:

$$Y\ 86.2107 - 74287X_1 + 1.0661X_2 + 0.6289X_3 - 2.5319X_1^2 - 2.0603X_2^2 - 1.618X_3^2$$

ACKNOWLEDGMENT

REFERENCES

Abdul Halim, S.F., A.H. Kamaruddin and W.J.N. Fernando, 2009. Continuous biosynthesis of biodiesel from waste cooking palm oil in a packed bed reactor: Optimization using Response Surface Methodology (RSM) and mass transfer studies. Bioresour. Technol., 100: 710-716.

Anonymous, 2005, Buku Putih Program Pembangunan Iptek Bidang Ketersediaan Dan Pemanfaatan Sumber Energi Baru Dan Terbarukan 2005-2009.

Box, G.E.P., S. Hunter and W.G. Hunter, 2005. Statistics for Experimenters: Design, Innovation and Discovery. 2 Edn., John Wiley and Sons, New York.

Deshpande, A., G. Anitescu, P.A. Rice and L.L. Tavlarides, 2010. Supercritical biodiesel production and power cogeneration: Technical and economic feasibilities. Bioresour. Technol., 101: 1834-1843.

Furukawa, S., Y. Uehara and H. Yamasaki, 2010. Variables affecting the reactivity of acid-catalyzed transesterification of vegetable oil with methanol. Bioresour. Technol., 101: 3325-3332.

Garcia, J.L.L. and M.D.L. Castro, 2003. Ultrasound: A powerful for leaching. Trends Anal. Chem., 22: 41-47.

Ginting, M.S.A., M.T. Azizan and S. Yusup, 2011. Alkaline in situ ethanolysis of Jatropha curcas. Fuel, 93: 82-85.

Gubitz, G.M., M. Mittelbatch and M. Trabi, 1999. Exploitation of the tropical oil seed plant jatropha curcas L. Bioresour. Technol., 67: 73-82.

Hadiyanto, A.C.K., H. Bambang and Widayat, 2010. Process improvement of coco biodiesel production through three stage esterification. Proceeding International Seminar on Applied Technology Science and Arts LPPM ITS.

Haeni, J.H., C. Green, E. Setianto, I. Boyle, A.R. Indriyanto et al., 2008. Indonesia energy assessment. Report to USAID Indonesia.

Ibrahim, H.D., N.M. Thaib and L.M.A. Wahid, 2010. Indonesian Energy Scenario to 2050: Projection of Consumption, Supply Options and Primary Energy Mix Scenarios, Retrieved from: http:// www. sei. irk.ru/ symp 2010 /en/papers/ ENG/P3-04e.pdf.

Ikwuagwu, O.E., I.C. Ononogbu and O.U. Njoku, 2000. Production of biodiesel using rubber [Hevea brasiliensis] seed oil. Ind. Crops Prod., 12: 57-62.

Ilgen, O., A.N. Akin and N. Boz, 2007. Investigation on the Esterification of Fatty Acid Catalyzed by the H3PW12O40 Heteropolyacid. Universidade Federal de Vicosa, Brazil.

Jitputti, J., B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho and P. Jenvanitpanjakul, 2006. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. Chem. Eng. J., 116: 61-66.

Kalam, M.A. and H.H. Dan Masjuki, 2002. Biodiesel from palmoil-an analysis of its properties and potential. Biomass. Bioenerg., 23: 471-479.

Levenspiel, O., 1972. Chemical Reaction Engineering. 2nd Edn., Departement of Chemical Engineering, Oregon State University, John Willey and Sons, New York.

Mason, T.J., L. Paniwnyk and J.P. Lorimer, 1996. The uses of ultrasound in food technology. Ultrason. Sonochem., 3(3): 253-260.

Montgomery, D.C., 1991. Design and Analysis of Experiments. 3rd Edn., Wiley, New York.

Ragavan, S.N. and D.V. Roy, 2011. Transesterification of rubber seed oil by sonication technique for the production of methyl esters. Bio. Conver. Bioref., 1(2): 105-110.

Ramadhas, A.S., S. Jayaraj and C. Muraleedharan, 2005. Biodiesel production from high FFA rubber seed oil. Fuel, 84(4): 335-340.

Sotoft, L.F., B. Rong, K.V. Christensen and B. Norddahl, 2010. Process simulation and economical evaluation of enzymatic biodiesel production plant. Bioresour. Technol., 101: 5266-5274.

Teixeira, L.S.G., C.R.A. Júlio, R.M. Daniel, T.V.S. Iran, R.B.G. Paulo *et al.*, 2009. Comparison between conventional and ultrasonic preparation of beef tallow biodiesel. Fuel Proc. Technol., 90: 1164-1166.

Widayat, W. and S. Suherman, 2012a. Biodiesel production from rubber seed oil via esterification process. Int. J. Renewab. Energy Dev., 1(2).

Widayat, W., B. Fajar and T. Kiono, 2012b. Ultrasound assisted esterification of rubber seed oil for biodiesel production. Int. J. Renew. Energ. Dev., 1(1).

Yuan, X., J. Liu, G. Zeng, J. Shi, J. Tong and G. Huang, 2008. Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology. Renew. Energ., 33: 1678-1684.