Malaysian Journal of Analytical Sciences, Vol 21 No 1 (2017): 240 - 247
DOI: http://dx.doi.org/10.17576/mjas-2017-2101-28

MALAYSIAN JOURNAL OF ANALYTICAL SCIENCES
Published by The Malaysian Analytical Sciences Society

ISSN
1394 - 2506

CRUDE PALM OIL BIODIESEL BY TRANSESTERIFICATION PROCESS USING CHOLINE HYDROXIDE CATALYST

(Biodiesel Minyak Sawit Mentah Melalui Proses Transesterifikasi Menggunakan Mangkin Kolin Hidroksida)

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Received: 21 October 2015; Accepted: 14 June 2016

Abstract

Biodiesel is generally made by transesterification using alkaline catalyst. Choice of catalyst used greatly affects the biodiesel produced. Choline Hydroxide (ChOH) catalyst is a basic ionic liquid having excellent catalytic reactions in the synthesis of palm biodiesel from Crude Palm Oil (CPO). This catalyst is able to produce biodiesel without soap formation which at the end of the reaction, three layers formed. They are biodiesel, the catalyst itself and glycerol. This makes it easy to separate biodiesel from the by product. Several other important variables in addition to the choice of catalyst and is catalyst dosage, molar ratio of ethanol to CPO and reaction time. The highest yield of biodiesel produced is 99.84% with molar ratio of ethanol to CPO is 9:1, reaction time is 90 minutes, 5.5% catalyst (w/w) at 70 °C and 400 rpm stirring speed. The most influential variable is catalyst dosages that give the significant difference yield of biodiesel produced. It evidenced by more dosages of catalyst used will provide a higher yield of biodiesel.

Keywords: choline hydroxide, crude palm oil, ethanol, ionic liquid, palm biodiesel

Abstrak

Biodiesel umumnya dihasilkan secara transesterifikasi menggunakan mangkin beralkali. Pilihan mangkin yang digunakan sangat mempengaruhi biodiesel yang dihasilkan. Kolin hidroksida (ChOH) adalah cairan ionik bes yang memiliki tindak balas pemangkinan yang sangat baik dalam sintesis biodiesel sawit dari minyak sawit mentah (CPO). Mangkin ini mampu menghasilkan biodiesel tanpa pembentukan sabun di mana pada akhir tindak balas membentuk tiga lapisan. Lapisan tersebut adalah biodiesel, mangkin itu sendiri dan gliserol. Hal ini memudahkan pemisahan biodiesel dari produk sampingan tersebut. Beberapa pemboleh ubah penting selain pilihan mangkin adalah dos mangkin, nisbah molar etanol terhadap CPO dan masa tindak balas. Hasil tertinggi dari biodiesel adalah 99.84% dengan nisbah molar etanol terhadap CPO adalah 9:1, masa tindak balas 90 minit, 5.5% mangkin (w/w) pada 70 °C dan kelajuan putaran 400 rpm. Pemboleh ubah yang paling berpengaruh adalah dos mangkin yang memberikan perbezaan hasil yang signifikan terhadap biodiesel yang dihasilkan. Ini membuktikan dengan semakin banyak dos mangkin yang digunakan akan memberikan hasil biodiesel yang lebih tinggi.

Kata kunci: kolin hidroksida, minyak sawit mentah, etanol, cecair ionik, biodiesel sawit

Introduction

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial [1]. According to the statistics, 70% of manufacturing cost in producing biodiesel is contributed by feedstock [2]. Indonesia has a big potential for producing biodiesel because the developments in Indonesia's Crude Palm Oil (CPO) production is increasing every year.

Biodiesel is mostly produced by a transesterification reaction, from oil with an alcohol and the presence of a catalyst to generate mono-alkyl esters and glycerol, which are then separated and purified [3]. Alcohols such as methanol and ethanol are the most commonly used. The yield of biodiesel using ethanol as alcohol reactant and ChOH catalyst is higher than using methanol as alcohol reactant [4]. In addition, ethanol can be produced from renewable agricultural resources [5]. So the use of ethyl esters is more environmentally friendly than the use of methyl ester.

Ionic liquids have been successfully used as a catalyst to catalyze transesterification reaction towards biodiesel production with good performance, higher conversion and selective production of biodiesel and glycerol conversion [6]. Ionic liquids are organic salts with a low melting point and very low vapor pressure [7]. Choline hydroxide (ChOH) catalyst exhibited better catalytic activity compared with other basic ionic liquid catalysts [8]. Ionic liquid-based catalyst choline does not cause the formation of soap. Reaction conditions such as temperature, time, molar ratio and dose of catalyst are optimized to obtain highest conversion in producing biodiesel [9]. The structure ChOH shows the presence of ion OH^- in Figure 1.

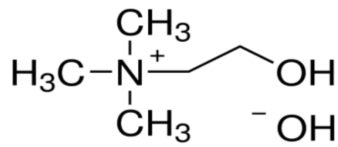

Figure 1. The ionization structure of choline hydroxide

Materials and Methods

The raw materials used are crude palm oil (CPO) obtained from PT Perkebunan Nusantara IV (PTPN IV). Alcohol used is ethanol (C_2H_5OH) and choline hydroxide (ChOH) was used as catalyst. Transesterification reaction is carried out by the stirring speed 400 rpm and a constant temperature of 70°C with process variables as follows: 1) dose of catalyst, 2) the molar ratio of ethanol:CPO and 3) reaction time.

CPO with a certain amount of weight is weighed and followed by the preparation of ethanol and a catalyst ChOH. CPO and ethanol were mixed at a specific molar ratio in a flask equipped with reflux condenser, thermometer and stirrer. Afterwards, ChOH was added and the mixture was stirred and heated using a hot plate till a constant temperature was reached. After that, the mixture was separated using a separator funnel until 2-3 layers were formed, then washed until the washed water is clear. Analysis can be performed after the ethyl ester prepared.

Factors that influence the reaction such as catalyst dosage, molar ratio of ethanol toward CPO and reaction time were analyzed systematically with the response surface methodology (RSM) with a central composite design (CCD). Level code and the combination of research can be seen in Table 1 and Table 2, respectively. Design equation models offered during the three factors which are as follows [10].

$$Y = \beta_1 + \beta_2\chi_1 + \beta_3\chi_2 + \beta_4\chi_3 + \beta_5\chi_1\chi_2 + \beta_6\chi_2\chi_3 + \beta_7\chi_1\chi_3 + \beta_8\chi_1^2 + \beta_9\chi_2^2 + \beta_{10}\chi_3^2 + \varepsilon \tag{1}$$

Table 1. Level code on experimental design

Variables	Code	Levels				
		-1.673	-1	0	1	1.673
Catalyst Dosage (w/w)	X_1	2.5	3	4	5	5.5
Molar Ratio Ethanol:CPO	X_2	4:1	6:1	9:1	12:1	14:1
Reaction Time (min)	X_3	40	60	90	120	140

Table 2. Central Composite Design for Three Variables

No	Dose of Catalyst (w/w)	Molar Ratio Ethanol:CPO	Reaction Time (minute)
1	-1	-1	-1
2	-1	1	1
3	1	-1	1
4	1	1	-1
5	0	0	0
6	-1	-1	1
7	-1	1	-1
8	1	-1	-1
9	1	1	1
10	0	0	0
11	-1.673	0	0
12	1.673	0	0
13	0	-1.673	0
14	0	1.673	0
15	0	0	-1.673
16	0	0	1.673
17	0	0	0

Results and Discussion

Free fatty acid (FFA) and water content

Analysis free fatty acids and moisture have been done to raw materials CPO. Comparative analysis of the levels of free fatty acids for CPO against palm oil degummed (DPO) can be seen in Figure 2.

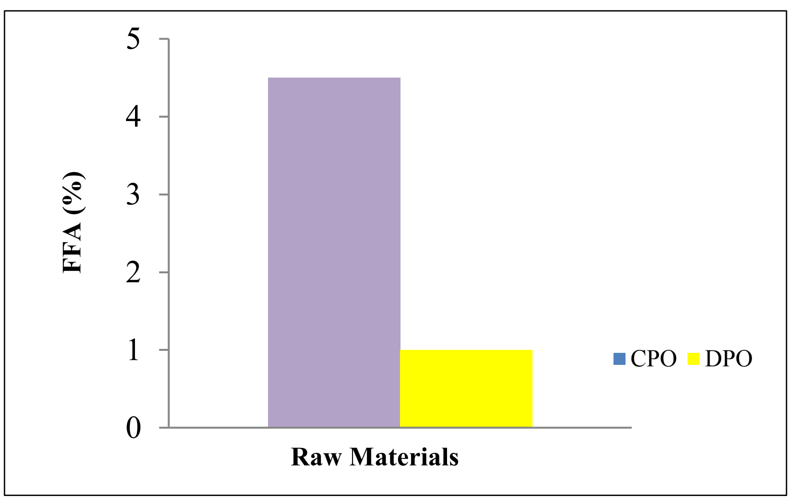

Figure 2. Free fatty acid level

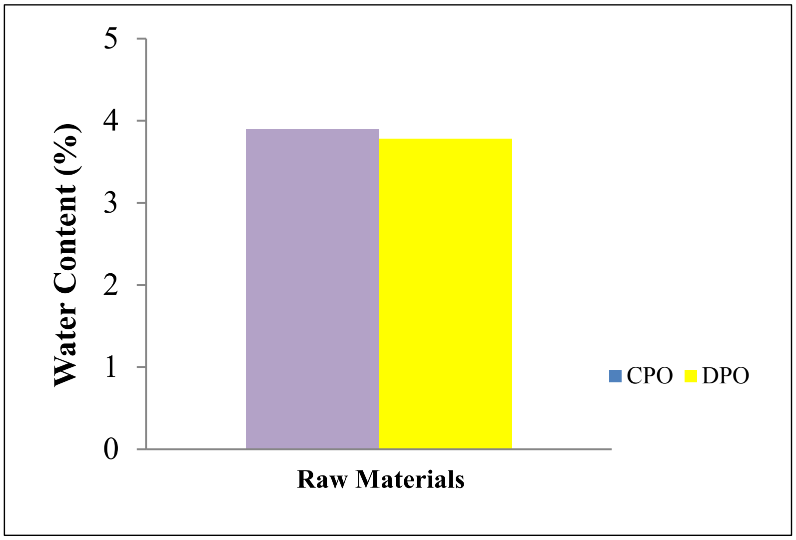

Figure 3. Water content

Low water content can generate higher products conversion. In addition to FFA and water, CPO also contain gum that can interfere the performance of the catalyst, therefore CPO needs to be degummed.

CPO as the raw material

Preliminary research has been done on CPO and DPO as basic of raw material selection. With the same reaction conditions, % yield of the ethyl ester of CPO and DPO can be seen as shown in Figure 4.

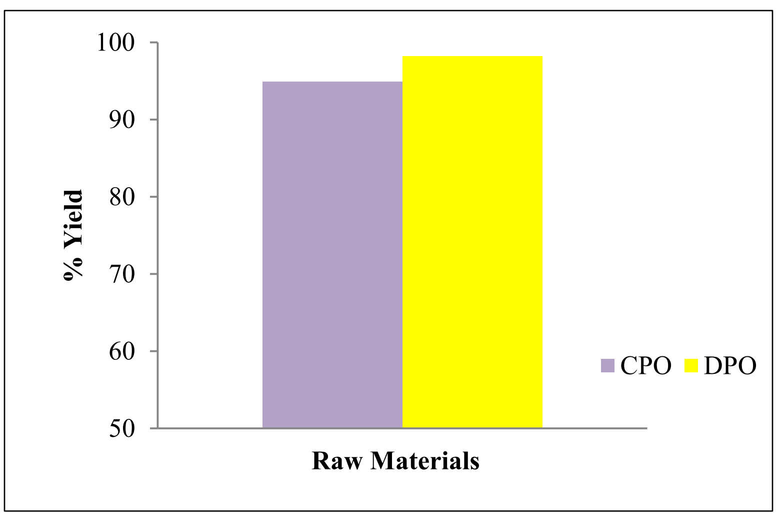

Figure 4. Percentage yield ethyl ester of CPO and DPO

Figure 4 shows the percentage yield of ethyl ester of CPO and DPO with reaction temperature at 70 °C and a stirring speed 400 rpm. Catalyst dosage used was 4% (w/w), molar ratio of ethanol against the raw material is 9:1

and reaction time is 90 minutes. Percentage yield of DPO is 98.17 and 94.92 for CPO. Based on the data above, the raw materials are selected in this study is the CPO as percentage yield obtained from the experiment is not too far difference from DPO. With the high FFA and high water content of CPO, the ionic liquid ChOH able to catalyze the transesterification reaction very well, with percentage yield of ethyl ester is 94.92%.

Manufacturing biodiesel from CPO, as raw materials without pre-treatment is able to lower production costs. The cost of raw materials contributes about 70% of the total cost of production. Pre-treatment CPO make the preparation of raw material more complex, so the cost of it as raw material higher than no pre-treatment CPO. Therefore, using CPO as raw material for biodiesel production was instrumental in lowering the total cost of production so that the price of biodiesel can be predicted cheaper.

Effect of process variables toward percentage yield

Following the experimental results data in a central composite design and the combination of the research can be seen in Table 3.

Table 3. Yield ethyl ester in central composite design

No	Dose of Catalyst (w/w)	Molar Ratio Ethanol:CPO	Reaction Time (minute)	% Yield
1	-1	-1	-1	63.578
2	-1	1	1	95.318
3	1	-1	1	97.930
4	1	1	-1	97.070
5	0	0	0	98.174
6	-1	-1	1	60.500
7	-1	1	-1	97.569
8	1	-1	-1	97.002
9	1	1	1	97.538
10	0	0	0	98.174
11	-1.673	0	0	61.296
12	1.673	0	0	99.845
13	0	-1.673	0	99.505
14	0	1.673	0	98.907
15	0	0	-1.673	96.653
16	0	0	1.673	65.870
17	0	0	0	98.174

Experimental data were analyzed using STATISTICA program, to get the parameters from the model that will provide the estimation of influence of variables against ethyl ester percentage yield. Statistical analysis to determine the significant influence of variables is shown in Table 4.

Table 4. Regression coefficients

Model Parameter	**Parameter Estimate**	**Standard Error**	**Computed T-Value**	***P*-Value**
Intercept	97.617	5.188	18.813	2.35×10^{-7}
X_1	20.863	5.148	4.052	0.004
X_2	-13.147	6.377	-2.061	0.078
X_3	9.957	4.943	2.014	0.083
X_1^2	2.459	5.408	0.454	0.662
X_2^2	-8.149	4.943	-1.648	0.143
X_3^2	-10.460	5.408	-1.934	0.094
X_1X_2	-17.282	6.435	-2.685	0.031
X_1X_3	1.681	6.435	0.261	0.801
X_2X_3	0.091	6.435	0.014	0.989

Based on the Table 4, the most significant parameter is the dose of the catalyst and combination of catalyst dosage and molar ratio ethanol to CPO. Since p-value is 0.05, the other parameter is considering as insignificant. Polynomial equation is expressed as equation 2 below.

$$Y_{yield} = 976179 + 208637X_1 - 131470X_2 + 24599X_1^2 - 172828X_1X_2 \quad (2)$$

The experimental data are shown in graphical form contour plot that showing the relationship the two variables against percentage yield (see Figure 5, 6 and 7). Figure 5 shows the relationship between the dose of the catalyst and the molar ratio of ethanol to CPO against percentage yield of ethyl esters. Based on the graph, it shows that the effect is given by catalyst dosage to the percentage yield of ethyl esters greater than molar ratio. The greater dose of the catalyst makes the process of converting oil into ethyl ester higher. Low doses of catalysts can also produce biodiesel with high yields but is followed by the amount of the molar ratio of ethanol: CPO. The use of catalysts with high enough doses followed by the high molar ratio of ethanol to CPO can raise percentage yield of ethyl ester.

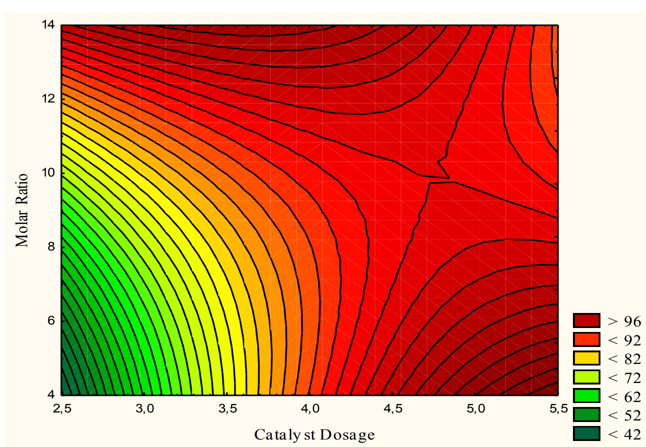

Figure 5. Contour plot of catalyst dosage and molar ratio ethanol: CPO against percentage yield

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Figure 6 shows the relationship between the dose of the catalyst and reaction time against percentage yield. In this figure, it can be seen that the use of catalysts ChOH with high enough doses, the conversion of triglycerides into biodiesel is also high, but must be followed by the optimal reaction time. If the transesterification reaction time is too long exceeding the optimum time, the conversion of the resulting biodiesel can be low. For a short time, the biodiesel produced is high enough so that the use of catalysts ChOH is very advantageous in biodiesel transesterification reaction. The catalyst dosage and reaction time effect on yield greatly significant.

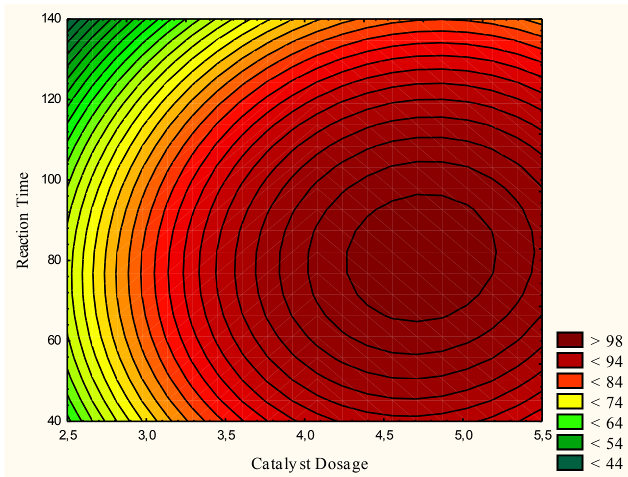

Figure 6. Contour plot of catalyst dosage and reaction time against percentage yield

Figure 7 shows the relationship between the molar ratio of ethanol: CPO and reaction time against percentage yield of ethyl ester. From this contour plot, it can be seen that the high molar ratio of ethanol to CPO, can produce biodiesel with a high percentage yield. As for the reaction time, on the contrary, the long reaction times, can cause biodiesel produced is low. Transesterification short reaction time is sufficient to produce the high percentage yield of ethyl ester. Effect of reaction time on biodiesel is more dominant than the molar ratio of ethanol to CPO.

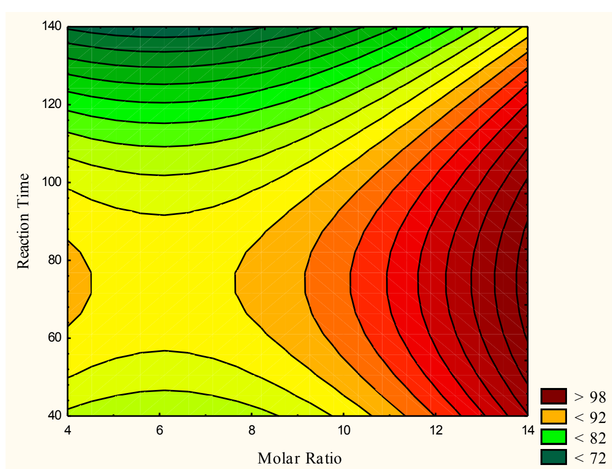

Figure 7. Contour plot of molar ratio ethanol: CPO and reaction time against percentage yield

Conclusion

CPO as feedstock in biodiesel production without going through the pre-treatment can produce good enough yields of biodiesel using a basic catalyst ionic liquid choline hydroxide (ChOH). Ethanol has great potential in biodiesel production as a reactant alcohol because it is renewable and included in agricultural cycle. The optimum point in biodiesel production is 99.84% at 70 °C with a molar ratio of ethanol against crude palm oil was 9:1, the catalyst dosage 5.5% (w/w) and the reaction time is 90 minutes. The variables that most influence are the catalyst dosage followed by reaction time and the molar ratio. The lower of catalyst dosage and more doses of catalyst and molar ratio of ethanol: CPO will produce higher percentage yield.

Acknowledgement

The facilities supports from Chemical Process Laboratory, Department of Chemical Engineering, Faculty of Engineering, University of Sumatera Utara, North Sumatera, Medan 20155, Indonesia.

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