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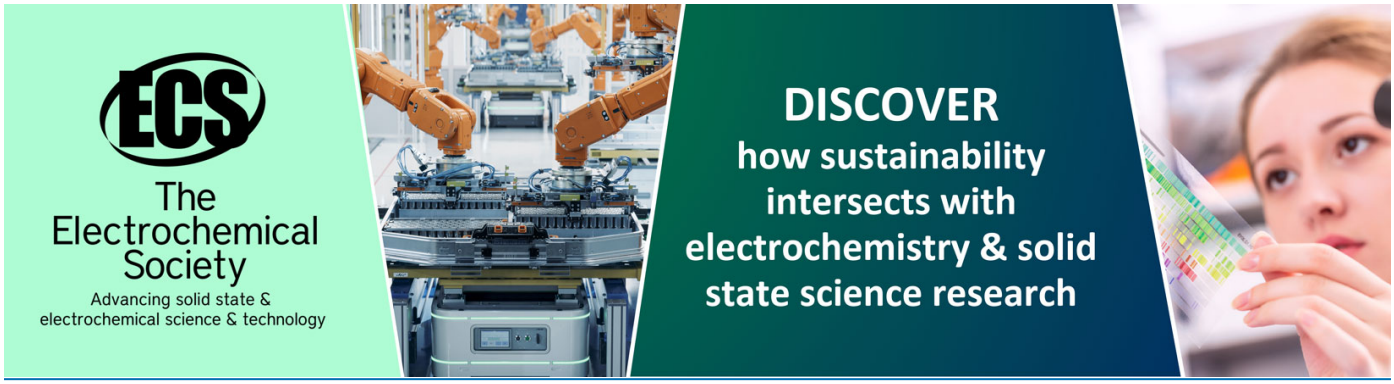

Analysis of process variables on biodiesel transesterification reaction using Taguchi Method

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Abstract. Continuous process for biodiesel production using homogeneous catalysts finds many constraints. Heterogeneous catalysts are the solution for the production of continuous biodiesel. One of the heterogeneous catalysts is zeolite/KIO_3. Determination of operating conditions for heterogeneous catalysts, especiallyzeolite/KIO_3 is required to obtain appropriate process conditions in order to the continuous system. The Taguchi method is one of experimental design that focuses on the variable approach to product quality improvement by control operation condition.Taguchi method is designed using 4 independent variables with 2 levels (4x2), which are temperature, mole ratio, time reaction and heterogeneous catalyst ratio. The Taguchi method can provide an analysis of the influence of each process variable significantly.This study aims to determine optimal operating conditions for the production of biodiesel with the KIO_3 heterogeneous catalyst. Biodiesel is synthesized by esterification (pre-treatment) and transesterification following the Taguchi method. The source of triglyceride is crude palm oil while the alkyl source comes from methanol. Based on the result of analysis Taguchi method known that all process variables have an effect to transesterification reaction. But, variable temperature and reactant mole ratio give the most significant influence and show the interaction with p-value value 0.000 (temperature) and p-value 0.001(reactant mole ratio).Thus, for the production of biodiesel using the KIO_3 heterogeneous catalyst obtained optimal operation conditions at temperature 65^{o}C, mole ratio 1:6, time reaction 120 minutes and heterogeneous catalyst ratio at 5% (w/w). ANOVA gave result decided to reject Ho, and decided the reaction model influence by the variable process.

1. Introduction

After receiving a patent application on machine creations at the Paris Exhibition in 1912, Rudolf Christian Karl Diesel has expressed his thoughts on predicting the use of vegetable oil as a future fuel in exchange for petroleum and coal products. The current shift in fuel use to biofuel is a phenomenon that cannot be denied any longer and has been predicted several years ago. The availability of fossil fuels is dwindling, accompanied by increased in energy consumption, especially in the automotive industry and the acceleration of bio fuel development that requires industrial scale upgrading. Biodiesel is a kind of biofuel in addition to bioethanol and biogas that have the potential to replace the presence of diesel. Biodiesel is expected to be one of the best diesel because of its superior characteristics, such as

biodegradability, renewability, lower toxicity and reduced harmful combustion emissions.[1-3].

Biodiesel from crude palm oil (CPO) is one of the largest palm oil producers in the Asian country. Given that Indonesia is the second largest palm oil producer in the world after Malaysia. Indonesia's palm oil production is currently 6.5 million tons per year and it will increase to 15 million tons per year in land development. Indonesia's oil palm plantations are spread across the islands of Sumatra and Kalimantan.The high cost of producing biodiesel from other vegetable oils is actually an advantage for the development of crude palm oil (CPO) as an alternative fuel. Because when compared with other types of vegetable oils as alternative fuel producers, the use of palm oil as a raw material will be much cheaper. [4]

Biodiesel synthesis usually used homogeneous catalysts, such as acids and bases. The use of homogeneous catalysts causes problems with the resulting product, including still contain catalysts, which require a separation process to purify biodiesel products.In addition, the use of a basic catalyst can also cause a side reaction that is a saponification reaction that affects the process of making biodiesel.Soap should be separated by washing and flooring methods that will add to the process stage and production costs. this makes the biodiesel industry difficult to develop continuously.

Reviewing these conditions, various studies were developed to find heterogeneous catalysts to change the tendency of conventional catalyst use (homogeneous catalysts). It is known that zeolite can be used as a heterogeneous catalyst in biodiesel synthesis but has not been optimally utilized. Zeolite can be used as a heterogeneous catalyst through the activation process using acid compounds and the addition of an impregnator compound in the form of a strong base. Zeolite exhibits no activity, but when loaded with compounds such as NaOH, KNO_3, KF, KI or K_2CO_3 and activation at high temperature, the supported solid catalyst show high catalytic activities. Also, it is found that the supported has an effect on the activity of the heterogeneous catalyst.[5-6].

There are many study done to observe the advantage of zeolite. [7-9]. In this study, used zeolite/KIO_3 as a heterogeneous catalyst obtained by impregnation of zeolite with compound KIO_3.The study aimed to determine the optimum operating conditions for the production of biodiesel with the KIO_3 heterogeneous catalyst. The observed variables are temperature, mole ratio, time reaction, heterogeneous catalyst ratio. The Taguchi method is used as an experimental method with two levels for each process variable, so that variable approach can be used to obtain optimal production process variables.

2. Material and Method

2.1. Raw Material

The raw materials used are crude palm oil (CPO) as the triglyceride source, Methanol (p.a), zeolite/KIO_3 as the heterogeneous catalyst, H_2SO_4 98%, NaOH (p.a), hexane, ethanol. CPO as the main ingredient analyzed free fatty acid to know the initial free fatty acid content.

2.2. Esterification

At first, crude palm oil (CPO) was performed free fatty acid (FFA) analysis to determine the free fatty acid content before esterification reaction was performed. CPO is reacted with methanol and an H_2SO_4 as the acid catalyst. It is added with a ratio of 15% (w/v). The esterification reaction is pre-treatment process for CPO to reduce free fatty acid (FFA). The reaction lasts for 120 minutes, at temperature 65^oC and 400 rpm on stirring speed (scale of

1000 rpm). If CPO as trigliceride source contains many FFA, it will interferethe formation of ester bonds with methanol.

2.3. Transesterification

The transesterification reaction is also called alcoholization, is the conversion stage of triglyceride (vegetable oil) to alkyl ester, reacted with the alcohol to produce a by-product of glycerol. The CPO from esterification reaction is referred to crude ester. It is used as a feedstock in the transesterification reaction. crude ester is reacted with methanol with the addition of zeolite/KIO_3 heterogeneous catalyst, temperature, mole ratio and reaction time according to the Taguchi design Reactan are stirring at speed of 400 rpm (scale 1000 rpm).

2.4. Experimental Design

Taguchi method can be done approach to make improvements to product quality or reaction. in this design used 4 variable processes and 2 level. There are 8 arrays with 5 replications, and the total samples are 40 products. The variablesare temperature, mole reactan, time reaction and heterogeneous catalyst ratio, with the initial hypothesis (Ho) the reaction model is not influenced by the process variable, with the final hypothesis (H_1) the reaction model being influenced by the process variable. Ho will be rejected if p-value <0.05.

Table 1. Data Design of Taghuci Experimental Method

Temperature (°C)	Mole Ratio	Time Reaction (Minutes)	Heterogeneous Catalyst Ratio (w/w)	Ester Content (%)				
				1	2	3	4	5
65	6	90	5	Y_n	$Y_{..}$	$Y_{...}$	$Y_{...}$	$Y_{...}$
75	8	120	10	$Y_{..}$	$Y_{..}$	$Y_{.}$	$Y_{..}$	Y_{n+1}

The variables observed in this research are the factors that influence the production of biodiesel. Each process variable consists of 2 levels, i.e. level 1 (low level) and level (high level). For variable temperature, level 1 is at 65°C and level 2 is at 75°C. The Taguchi method uses 2 levels (low and high) as an approach technique for optimizing the operating conditions of biodiesel production.

3. Result and Discussion

Biodiesel synthesis from CPO and methanol as an acil source by transesterification reaction. In transesterification used zeolite/KIO_3 as heterogeneous catalyst to change the conventional homogeneous catalyst. The heterogeneous hasa different phase with the reactans, so it came more easily to separated at the end of product. If homogeneous catalyst used, at the end of production, it had to be separated from the soap. It was by product of transesterification and had to removed from biodiesel because it can give effect to the quality of biodiesel especially flash point.

In this research, used Taguchi method as experimental design by involving variable with two levels. The independent variable is a factor which influences the transesterification reaction, i.e temperature, mole ratio, time reaction and heterogeny catalyst ratio. Two levels are used in each variable that aims to determine the significant influence of each of the independent variables. The result of the statistical test of Minitab 14 in Figure 1 shows the Taguchi model gives significant p-value response on the 4 free variables (p-value <0.05, reject Ho). It shows that variable temperature, mole ratio, time reaction and heterogeneous catalyst ratio give influence to transesterification which formed biodiesel. The S/N ratio

means a signal to noise ratio is a measure of robustness which can be used to identify the control factor setting that minimizes the effect of noise on the response. Minitab program calculates a separated signal to noise (S/N) ratio for each combination of control factor levels in the design. For this research, used S/N ratio larger is better, because higher ester content in the composition of biodiesel product, show good quality of biodiesel. Large ester content shows high reactant conversion to biodiesel. Ester content also affects the characteristics of biodiesel produced.

Estimated Model Coefficients for SN ratios

Term	Coef	SE Coef	T	P	
Constant	36.3241	0.006042	6012.339	0.000	
Temperat 65	0.4112	0.006042	68.069	0.000	
Mole Rat 6	0.1331	0.006042	22.031	0.002	
Time Rea 90	-0.0564	0.006042	-9.335	0.011	
Heteroge 5	0.0918	0.006042	15.191	0.004	
Temperat*Mole Rat 65 6	-0.1063	0.006042	-17.595	0.003	

S = 0.01709 R-Sq = 100.0% R-Sq(adj) = 99.9%

Figure 1. Taguchi data analysis results

This condition is amplified through the ANOVA output in figure 2, which shows a consequent decision with the S/N ratio. The ANOVA gave the same p-value for SN ratio at p-value 0.00 for temperature constant, p-value 0.002 for reactant mole ratio, p-value 0.011 for time reaction and p-value 0.004 for heterogeneous catalyst ratio. The p-value for each variable is below the significant value of <0.05, giving the decision to reject the initial hypothesis (Ho). In the Taguchi method, the S/N ratio is used as the product quality performance or the characteristics used as the test response.

Analysis of Variance for SN ratios

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Temperature	1	1.35299	1.35299	1.35299	4633.42	0.000
Mole Ratio	1	0.14172	0.14172	0.14172	485.34	0.002
Time Reaction	1	0.02545	0.02545	0.02545	87.15	0.011
Heterogen Catalyst Ratio	1	0.06739	0.06739	0.06739	230.78	0.004
Temperature*Mole Ratio	1	0.09040	0.09040	0.09040	309.58	0.003
Residual Error	2	0.00058	0.00058	0.00029		
Total	7	1.67854				

Figure 2. ANOVA output for S/N ratio

As for the linear regression model analysis, the average model and ANOVA estimate obtained in Figure 3 show the linearity of the model to the independent variables, with R-sq (adj) = 97.8.

Estimated Model Coefficients for Means

Term	Coef	SE Coef	T	P
Constant	65.5875	0.03185	2059.057	0.000
Temperat 65	3.0885	0.03185	96.960	0.000
Mole Rat 6	0.9680	0.03185	30.389	0.001
Time Rea 90	-0.4305	0.03185	-13.515	0.005
Heteroge 5	0.6970	0.03185	21.882	0.002
Temperat*Mole Rat 65 6	-0.7600	0.03185	-23.859	0.002

S = 0.09009 R-Sq = 100.0% R-Sq(adj) = 99.9%

Analysis of Variance for Means

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Temperature	1	76.3107	76.3107	76.3107	9401.34	0.000
Mole Ratio	1	7.4962	7.4962	7.4962	923.52	0.001
Time Reaction	1	1.4826	1.4826	1.4826	182.66	0.005
Heterogen Catalyst Ratio	1	3.8865	3.8865	3.8865	478.81	0.002
Temperature*Mole Ratio	1	4.6208	4.6208	4.6208	569.27	0.002
Residual Error	2	0.0162	0.0162	0.0081		
Total	7	93.8130				

Figure 3. Linier Model Analysis For Mean Average

Figure 4 is the response for SN and average shows the sequence of independent variables that affect the formation of biodiesel. From the Taguchi model, it is known that the reaction temperature is the variable that most influence the formation of biodiesel, followed by the mole ratio of reactant and heterogeneous catalyst ratio, while time reaction does not give significant influence when compared with the other three independent variables. The Taguchi method gives the rank for each variable, which involved in the reaction.

The first rank that influences the biodiesel production process is the reaction temperature. The use of heterogeneous KIO_3 catalysts has increased the activation energy of the reaction so that the use of the reaction temperature decreases. Chai (2007), had conducted research to observe the effect of increasing the reaction temperature level. Known reaction temperature at range 60ºC-65ºC gives the formation of content ester. But, the reaction above temperature 65ºC decreased the conversion of the content ester. [10]. This is due to the loss of methanol because it forms a vapor phase due to the reaction temperature above the boiling point of methanol. In this study, the optimum reaction temperature was at 65°C.

The second rank is given by the mole ratio of reactants, which shows that the use of excess mole ratios above 1: 3 (general reaction) has a significant effect on the increase of content ester.

$$\text{Triglyceride} + 3CH_3OH \rightarrow CH_3\text{-}COOR + C_3H_8O_3$$

This corresponds to Jacobson's (2008) study which observed an increase in ester yield with an increase in the mole ratio from 1: 6 - 1:18. [11]. The results showed that the content ester increased up to 81% after 10 hours of reaction in a various mole ratio of reactants.

Response Table for RatiosLarger is better

Level	Temperature	Mole Ratio	Time Reaction	Heterogen Catalyst Ratio
1	36.74	36.46	36.27	36.42
2	35.91	36.19	36.38	36.23
Delta	0.82	0.27	0.11	0.18
Rank	**1**	**2**	**4**	**3**

Response Table for Means

Level	Temperature	Mole Ratio	Time Reaction	Heterogen Catalyst Ratio
1	68.68	66.56	65.16	66.28
2	62.50	64.62	66.02	64.89
Delta	6.18	1.94	0.86	1.39
Rank	**1**	**2**	**4**	**3**

Figure 4. Response For Ratio Lager Is Better With Rank Variable Process

Heterogeneous catalyst ratio gives the highest ester content at 5% (w/w). An increase in the heterogeneous catalyst ratio above 5% (w/w) did not show an increase in the ester content. This result is contemporaneous to our research, which states that the use of a heterogeneous catalyst ratio in the 0.5% -3% ranges (w/w) provides increased the content ester. While an increase in the heterogeneous catalyst ratio above 5% (w / w) did not provide an increase in the content ester. Insufficient amounts of catalyst resulted in a lower content of methyl ester and a high amount of monoglyceride and diglyceride intermediates. It is also recognized that the catalyst loading, the proton concentration in the interface of oil and methanol will increase, so the reaction will be enhanced. However, there was no significant increase in the biodiesel yield when the content of catalyst increased from 3.0 wt.% To 5.0 wt.%. In this case, enhancing mass transfer becomes more important than increasing the amount of catalyst [12].

Time reaction has an effect on the increase of content ester. According to the research results of Moushoul et.al, the conversion of the reaction takes place at 1 hour of reaction. This is due to the presence of heterogeneous mass transfer systems due to slow reaction. On the other hand, it could be seen that gradually after 2 hours of reaction time. [13]. In this study, the optimum condition of transesterification reaction time lasted for 120 minutes.

Table 1. The Experimental Result Measured By Ester Content

Temperature (^oC)	Mole Ratio	Time Reaction (minutes)	Heterogeneous Catalyst Ratio (w/w)	Ester Content				
				1	2	3	4	5
65	6	90	5	69.32	69.30	69.32	69.20	68.80
65	6	120	10	68.57	68.70	68.73	68.70	68.20
65	8	90	10	67.29	67.32	67.25	67.50	67.60
65	8	120	5	69.89	69.70	69.34	69.56	69.23
75	6	90	10	63.24	63.00	62.00	63.40	63.60
75	6	120	5	65.67	65.20	65.12	65.34	65.70
75	8	90	5	61.23	61.33	61.20	61.11	60.13
75	8	120	10	60.60	60.45	60.32	60.57	60.77

Figure 5 shows the interaction of each independent variable in the conversion of biodiesel. The slope of the variable temperature is very high indicating that the variable is very influential to the transesterification reaction of biodiesel. Independent variable that has the least influence is the reaction time because the slope form is very small. Whereas in interaction plot data for means in Figure 6,show the influence of interaction between temperature and mole ratio. But based on the slope scale formed, it is interpreted that the interaction between temperature and mole ratio gives low effect.

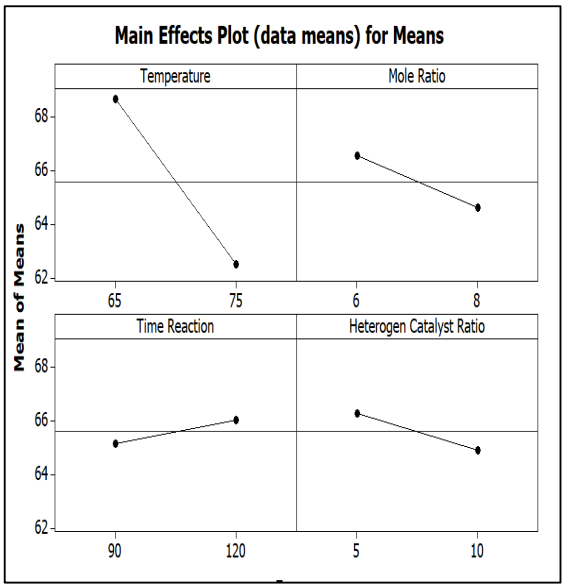

Figure 5. Main Effect For Means

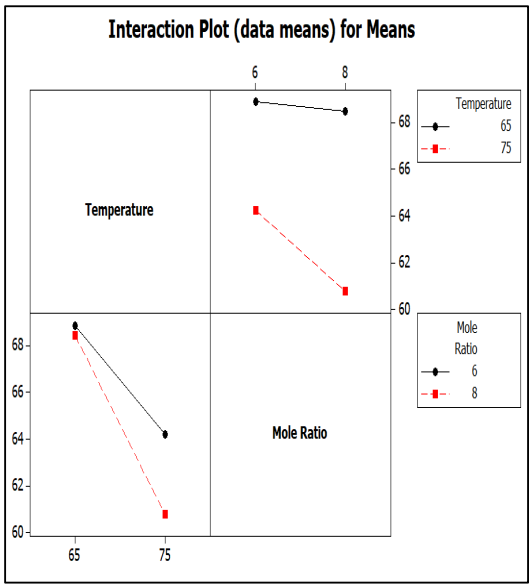

Figure 6. Interaction Plot For Means

Biodiesel produced by transesterification reaction was tested using GC-MS method to determine ester content which show the amount of reactant converted to biodiesel. From GCMS analysis, it was found that the content of ester was 69.89%, DG (diglyceride) was 22.21%, MG (monoglyceride) was 4.04% with the remaining TG (triglyceride) 3,856%. Through the obtained of biodiesel composition shows that many TG forming to DG and MG.

The formation of methyl ester bonds can be continued by increasing the mole ratio of reactants and temperature. Because by increasing the mole ratio of reactans, then the energy needed to break the TG bond sourced from crude palm oil to becomes higher and the increased amount of reactant will give an opportunity to form methyl ester bond.

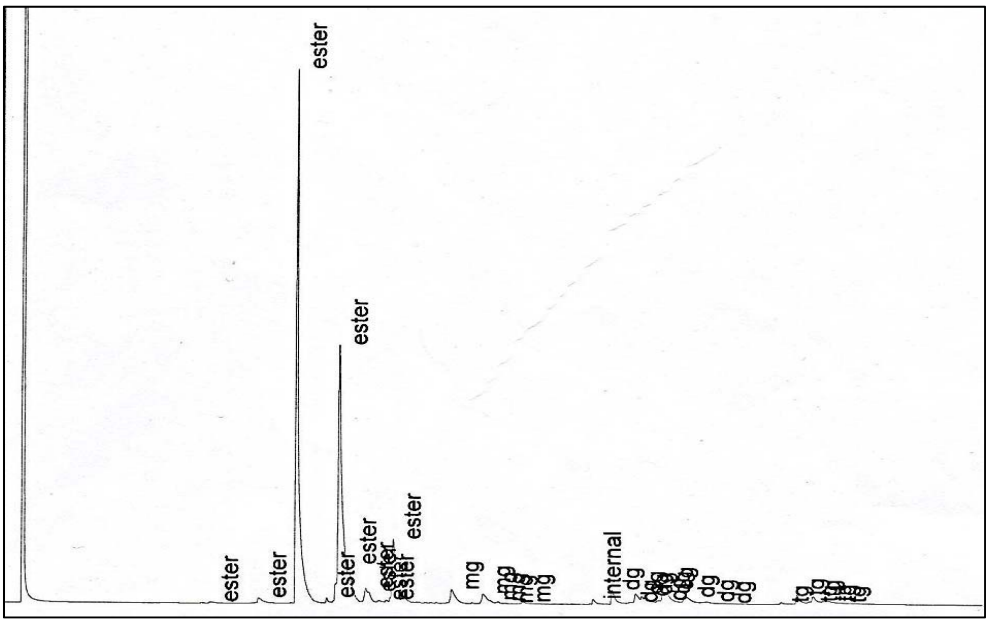

Figure 7. Chromatogram of biodiesel at 65°C, mole r Ratio (1:6), time reaction 120 minutes, heterogeneous catalyst ratio 5.0 % (w/w)

The results of the methyl ether component analysis correspond to the ANOVA output, which provides a possible interaction between the reaction temperature and the mole ratio of reactants. Time reaction gives the lowest significant effect than the other variables. It means, increasing time reaction more than 120 minutes would not give much effect for increasing ester content. Many studies had proven that biodiesel quickly formed at 1-2 hours time reaction. After 2 hours, transesterification gives decreased formed reaction.

Figure 8. Production and purification biodiesel by transesterification reaction

4. Conclusion

Based on the ANOVA analysis for experimental Taguchi method design, which gives p-value <0.05 so that reject Ho and receive H1, all process variables affect the production of biodiesel using KIO_3 heterogeneous catalyst. But, variable temperature and mole ratio have the most significant influence among the four variables and show the reaction

interaction. These results were confirmed with GCMS for biodiesel product with the optimum condition and obtained ester content of 69.89%, DG 22.21%, MG 4.04%. The interaction between the temperature level and the mole ratio will provide an increase in the ester content.The optimal operation condition to transesterification of biodiesel done attemperature 65^{o}C, mole ratio 1:6, time reaction 120 minutes and heterogeneous catalyst ratio at 5% (w/w).

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