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Cite as: AIP Conference Proceedings **2059**, 020047 (2019); https://doi.org/10.1063/1.5085990
Published Online: 11 January 2019

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Oil Palm EFB supported Solid Acid Catalyst for Esterification Reaction: Optimization and Parametric Effects Study

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Abstract. An acid esterification of free fatty acid (FFA) from high acid content palm oil and methanol has been investigated. This study describes an optimization study on the esterification reaction using Oil Palm EFB supported solid acid catalyst. A statistical experimental design of L_9 orthogonal array using Taguchi method was implemented to optimize the esterification reaction conditions to maximize FFA conversion. Three main reaction conditions include methanol to oil molar ratio, reaction duration (min) and percentage of catalyst loading were investigated. Based on the results, the optimum conditions were obtained as follows: molar ratio of methanol to oil of 30:1, reaction duration of 120 min, catalyst loading of 5 wt%, constant temperature of 60 ^oC. At these reaction conditions, the highest FFA conversion was achieved with 87.20%. Notably, methanol to oil molar ratio has the most significant effect on the FFA conversion followed by reaction duration. Catalyst loading has minimal effect on FFA conversion throughout the reaction. Thus this study showed that methanol to oil molar ratio has the strongest influence in FFA conversion.

INTRODUCTION

In the concern of current environmental issue and limited fossil fuel resources, biodiesel has been a good solution for these problems. Biodiesel is one of the common biofuels produced from vegetable oil and animal fats via transesterification of triglycerides or esterification of high free fatty acid (FFA) oil in the presence of alcohol to produce fatty acid methyl alkyl [1]. Generally, biodiesel being obtained is dependent on edible oil as the primary feedstock because they exhibit high biodiesel yield with alkali catalyst due to low FFA content [2]. However, the major disadvantage of edible oil is high cost and cause imbalance supply between food industry and biodiesel production [3]. Therefore, the use of non-edible oil has gain more important as it is low cost and can reduce the biodiesel production cost. But, the high content of FFA and not available sufficiently in quantity as may lead to lower yield of biodiesel and insufficient source for biodiesel production [4]. In addressing this issue, the idea to produce biodiesel from a mixture of palm oil with oleic acid can be an alternative solution. The use of mixture of oil for biodiesel production can reduce the utilization of food supply which leads to an economical process [5]. Therefore, the mixture edible oil or refined oil with high acid oil considered as 'bridging gap' that solve the existing problems on high production cost using refined oil and omit the issue on insufficient supply of non-edible oil. To the

Proceedings of the 3rd International Conference on Automotive Innovation Green Energy Vehicle
AIP Conf. Proc. 2059, 020047-1–020047-7; https://doi.org/10.1063/1.5085990
Published by AIP Publishing. 978-0-7354-1787-8/$30.00

best knowledge, the use of biomass supported heterogeneous catalyst on esterification of mix oil still rare. Besides, understanding the effects of process parameters such as percentage of catalyst loading, methanol to acidified oil molar ratio, reaction time and reaction temperature is essential to determine the significant of parametric effect.

Statistical experimental designs are beneficial in optimization of multiple parameters to achieve the best response with minimal number of experiments. Taguchi's orthogonal array method is a statistical method of designing experiments that provide sufficient results with reduced number of experiment trials [6].This method is able to identify controllable factors that minimize the effect of noise factors. The major tools used in this method are signal to noise (S/N) ratio that measures the quality with emphasis on the variation between the levels and orthogonal array provides number of experiments [7]. It also offers three categories to measure the quality characteristics such as smaller is better, nominal is the best and larger is better. The scientific advantage of Taguchi method has been well utilized in biodiesel industry to achieve high quality results. In the study, esterification is employed to esterified high acid oil blend of refined palm oil and oleic acid. The reaction various esterification process parameters (catalyst loading, methanol to acidified oil molar ratio and reaction time) for the esterification of acidified oil applying Taguchi L9 orthogonal array design.

EXPERIMENTAL SECTION

Materials

Industrial oleic acid (196 mg KOH/g) from R&M, Malaysia, refined palm oil purchased from local hypermarket and methanol (Dulab) were used as model materials for esterification reaction. All chemicals used in the study were analytical grade. The list of materials used in the experiment tabulated as shown in Table 1.

Table 1. List of materials

Materials
Oleic acid
Refined palm oil
Methanol
Potassium hydroxide
Phenolphthalein

Catalyst Preparation

Pre-treated EFB fibers were used as the support material in synthesis of solid acid catalyst using transition metal sulfates, $Fe_3(SO_4)_2$ via direct impregnation method. The method was performed at 60 ^oC with continuous stirring for 2 hours. The impregnated samples were oven-dried at 105 ^oC for 24 h to remove excess water. The dried sample was powdered well and calcined at 500 ^oC for 3 hours. The catalyst was denoted as FS-SAC.

Process Design of Experiment

The Taguchi design process flow has been represented in the form of flow diagram in Fig 1. The Taguchi L9 orthogonal array experimental design was used with three independent process parameters was selected as independent parameters while conversion of acidified oil acts the dependent factor as shown in Table 2. Taguchi method was used to study the effects of different process parameters and to obtain the optimal reaction condition with high conversion of acidified oil considering S/N ratio. The L9 experimental design was extracted using MINITAB-14:MinitabInc.USA with the mean of three replications value and calculated S/N ratio. The value of S/N ratio (larger is better) was calculated from equation 1. The S/N ratio values corresponded to the conversion were calculated on the basis of larger is better characteristics since the objective of the study was to maximize the FFA conversion yield.

$$\frac{S}{N} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \quad (1)$$

where i is the number of replicate and n is the number of trial experiments performed.

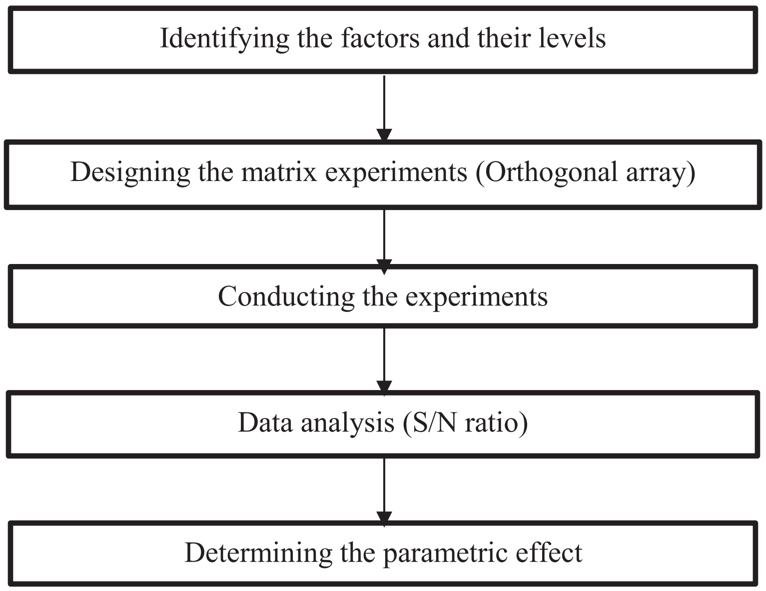

FIGURE 1. The Taguchi design process flow-diagram

TABLE 2. Parameters involved in the optimization study

Factors	**Range**		
	low	**intermediate**	**High**
Catalyst loading, wt%	5	10	15
Methanol : oil	10:1	20:1	30:1
Duration, min	60	90	120

TABLE 3. L9 orthogonal array design of experiment

No. of experiments	**Catalyst loading, %**	**Methanol : oil**	**Duration, mins**
1	5	10:1	60
2	5	20:1	90
3	5	30:1	120
4	10	10:1	90
5	10	20:1	120
6	10	30:1	60
7	15	10:1	120
8	15	20:1	60
9	15	30:1	90

Esterification Reaction

The esterification of 85% (mass/mass) refined palm oil with 15% (mass/mass) oleic acid [5] was conducted in 100 ml three-necked flat bottom flask equipped with magnetic stirrer with thermocouple to maintain the desired temperature throughout the experiment and condenser. Table 3 depicts the L9 Orthogonal array design of experiment for esterification of acidified oil. The range of parameters was specified based on the preliminary laboratory experiments and in all sets of experiments the reaction temperature was kept constant at 60^oC. The catalyst loading indicates the amount of catalyst to be loaded in esterification together with methanol to oil molar ratio represent quantity of alcohol with specific amount of oil. Meanwhile, the reaction will be monitored at a time range which indicates the duration required for the catalyst and alcohol react in the acidified oil.

Characterization of the Acidified Oil

The acid value (AV) of acidified oil was calculated based on the ASTM D664 method where it was calculated to be 28.0 mgKOH/g and raw palm oil with AV of 0.18 mgKOH/g.

Characterizations of the Products

The free fatty acid (FFA) conversion was evaluated using potassium hydroxide (KOH) titration method. The acid value ‘Equation (2)’ and FFA conversion equation 3 were calculated using the equation shown below.

$$\text{Acid value (mg KOH/g)} = \frac{V_{KOH} \text{ x } 56.1 \text{ x } C_{KOH}}{m_{sample}} \tag{2}$$

where V_{KOH} (ml) is the consumed volume of standard KOH, 56.1 $gmol^{-1}$, C_{KOH} is the concentration of standard KOH and m_{sample} (g) is the weight of the sample used in every titration.

$$\text{Esterification conversion (\%)} = \frac{AV_0 - AV_t}{AV_0} \text{ x } 100 \text{ \%} \tag{3}$$

where AV_o (mg KOH g^{-1}) is the initial acid value of high acid value oil and AV_t (mg KOH g^{-1}) is the acid value of esterified samples.

RESULTS AND DISCUSSIONS

After the esterification reaction, the free fatty acid (FFA) conversion was calculated to determine the product yield. According to the OA_9 matrix, nine experiments were carried out and the product yield results were shown in Table 4. The esterification reaction was conducted using EFB supported FS-SAC calcined at 500^oC. All the experiments were repeated twice to indicate the average mean value. The table shows that the range of product yield varies from 40.55% to 87.20%. Despite that all the experiments have proved reduction in FFA content, the highest reduction was found in the experiment number 3 where it has achieved 87.20%. The maximum conversion rate was recorded at the optimized conditions with catalyst loading of 5%, methanol to oil molar ratio 30:1 and reaction temperature of 60^oC for 120 mins. Taguchi method helped to evaluate the effect of parameters on esterification reaction. The effect of each parameter on FFA conversion was studied based on the results obtained in Table 4. The average signal to noise ratio for each parameter was shown in Table 5. Over the range of parameters studied, methanol to oil molar ratio have the highest effect in comparison to the other parameters, followed by percentage of catalyst loading and reaction duration in min. The main effects plots for *SN* ratio is shown in fig 2. The plots indicate that S/N ratio increases with methanol to oil molar ratio and reaction time in the entire reaction while there was a slight reduction in catalyst loading at 10% and with an increment at 15%. This slight reduction could be contributed from the effect of other factors during the reaction especially methanol to oil ratio which has a significant effect in the esterification reaction. The methanol to oil molar ratio dominate the overall reaction with intermediate effect of duration.

The increase in methanol to oil molar ratio resulted in FFA conversion through esterification reaction and was the most influential parameter as shown in the Table 4. Various molar ratio were used in this optimization study includes 10:1, 20:1 and 30:1. The corresponding effect was recorded in Table 4 as conversion rate. It can be seen that increasing amount of methanol as excess amount of methanol could shift the equilibrium towards the side of products [8,9]. Based on the equation 4, an excess amount of alcohol is required to drive the reaction to the right which consequentially increases the FFA conversion [10]. Besides that, increasing methanol to oil molar ratio could reduce the viscosity of reacting mixture which could attributed for a better mixing between the reactants and catalyst hence enhances higher conversion rate [11].

$$\underset{\text{Fatty acids}}{R_1COOH} + \underset{\text{Alcohol}}{R_2OH} \underset{\Delta}{\overset{H^+}{\longleftrightarrow}} \underset{\text{Alkyl ester}}{R_1COOR_2} + \underset{\text{Water}}{H_2O} \quad (4)$$

The reaction time was observed to exhibit a significant effect in the FFA conversion rate. Based on the results, the lowest conversion rate was observed 40.55% with reaction time of 60 min and the highest rate was achieved at 120 min. The conversion increased at longer reaction time being maximum at 120 min. This might be due to the longer reaction time allows interaction of more acid sites before its saturation point thus more esters would be produced [12,13]. The amount of catalyst loading also contributed to the effect of FFA conversion where lowest catalyst loading of 5% resulted high conversion rate compared to 10% and 15%. Generally, an increase in catalyst dosage implies the availability of more active sites, however high dosage of catalyst might cause increase in viscosity of the reaction mixture and limits the interaction between reactants and catalyst [14–16]. Hence, 5% catalyst loading has shown most significant in conversion rate. After the orthogonal experiments and analysis, the optimal level for each parameter was determined as follows: methanol to oil molar ratio 30:1, reaction time 120 min, catalyst loading 5% and reaction temperature, 60^{o}C.

TABLE 4. FFA conversion in Taguchi L9 orthogonal design of experiments

No. of experiments	Catalyst loading, %	Methanol:oil	Duration, mins	Trial 1	Trial 2	Mean	Standard deviation
1	5	10:01	60	37.95	43.15	40.55	3.68
2	5	20:01	90	63.27	70.10	66.69	4.83
3	5	30:01	120	83.30	91.09	87.20	5.51
4	10	10:01	90	38.61	44.24	41.43	3.98
5	10	20:01	120	68.61	73.95	71.28	3.78
6	10	30:01	60	64.60	70.91	67.76	4.46
7	15	10:01	120	49.24	54.21	51.73	3.51
8	15	20:01	60	60.60	66.05	63.33	3.85
9	15	30:01	90	70.27	76.91	73.59	4.70

TABLE 5. Average of signal to noise ratio for each parameter

Level	Catalyst loading, %	Methanol:oil	Duration, min
1	35.82	32.93	34.94
2	35.34	36.52	35.39
3	35.88	37.59	36.71
Δ	0.54	4.66	1.78
Rank	3	1	2

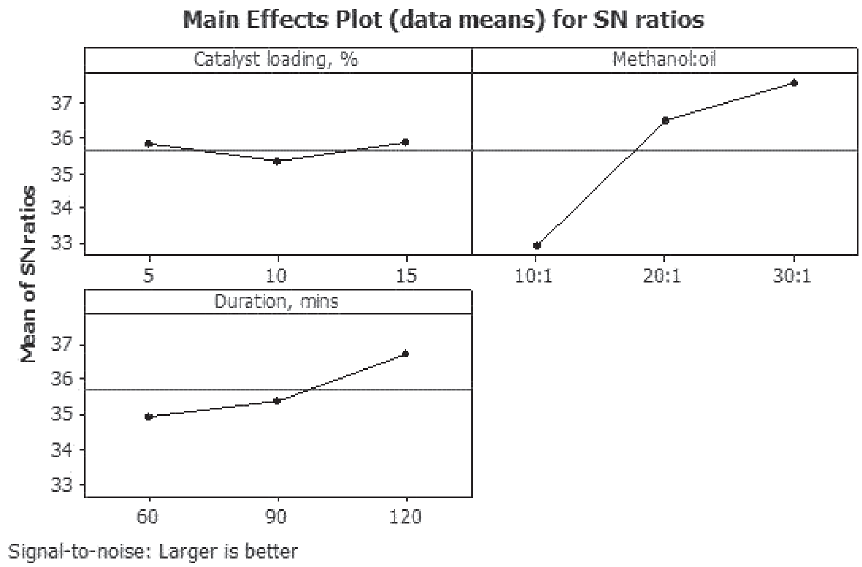

FIGURE 2. Main effects plots for 'larger-is-better' *SN* ratio analysis of each parameter.

CONCLUSION

The present study has explored to optimize and study the significant of parametric effect in the esterification of acidified oil (refined palm oil/oleic acid) with EFB supported FS-SAC. The optimum reaction conditions for FFA conversion were investigated orthogonal array, OA_9 matrix based on Taguchi method and exhibited to be 30:1 methanol to oil molar ratio, 5% catalyst loading and 120 min reaction time where the highest conversion was resulted 87.20%. According to the parametric analysis, methanol to oil molar ratio had the highest effect on FFA conversion followed by duration of reaction in min while percentage of catalyst loading had the lowest effect.

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support offered by the Ministry of Higher Education (MOHE) Fundamental Research Grant Scheme (20140118FRGS) and the financial support given by Universiti Tenaga Nasional for the 2017 BOLD Research Grant (10289176/B/9/2017/21). In addition, we gratefully thank for the support and the facilities provided by the Institute of Sustainable Energy, UNITEN.

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