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Parametric Study of Esterification of Free Fatty Acids derived from *Ceiba Pentandra* Seed Oil using Microwave-assisted Technique via Response Surface Methodology

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Biodiesel is an alternative fuel to conventional petroleum diesel. Due to economic and social concerns, the use of edible vegetable oils and animal fats should be replaced by non-edible plant oils for biodiesel production. In this regard, the oil from tropical plant *Ceiba Pentandra* is an attractive potential feedstock. However, like other non-edible feedstocks, *C. Pentandra* seed oil contains high free fatty acids (FFA) which negatively affect the process of biodiesel production. In the present work, acid esterification process was applied as a pre-treatment to reduce FFA content. By using microwave-assisted technique, the optimum conditions for diminishing the FFA content in the seed oil to 0.388 % were found to be 2.0 wt% H_2SO_4 catalyst, 10:1 methanol to oil molar ratio at 60 °C within 12 minutes of reaction time. In addition, an investigation on the effect of different acid catalysts such as hydrochloric acid and phosphoric acid as well as different solvents such as ethanol, 1-propanol and 2-propanol to obtain the best result based on optimum conditions was carried out. Sulfuric acid and methanol were found to be the best option for pre-treatment of *Ceiba Pentandra* feedstock.

1. Introduction

Energy demands are always on the top priorities of government in most countries. Global energy developments, after the oil crises of the 1970s and the oil crisis of 2004, are showing the way to more serious steps towards sustainability in strategic energy planning, the improvement of energy efficiency, and the rational use of energy. Depletion and environmental concern have shifted the attention from fossil fuels towards renewable energy sources of fuel, with special emphasis on biodiesel. Biodiesel production processes have been reported by Alamu et al. (2008) as a very modern and technological area for researchers due to its environmental advantages. The biodiesel production from microalgae in the work of Wibul et al. (2012) and frying oil utilization used in restaurants of São Paulo according to Silva Filho et al. (2014) has been proven the contribution of biodiesel to the reduction of global warming potential.

There are several factors need addressing in choosing suitable feedstocks for biodiesel production such as availability, cost, stability and manufacturing method as mentioned by Vedharaj et al. (2013). In fact, the use of virgin vegetable oils for biodiesel production has a negative impact on the global imbalance to the market demand and the food resource by their high prices, the reduction of food storage and the growth of commercial edible oil crops' plantations. On the other hand, non-edible oils are grown in wastelands, which are widely available and further benefits as green cover to wastelands. Among these, *Ceiba Pentandra* emerges as a non-edible plant, containing about 22-25 wt% of oil in its seeds, which meets the requirement for current state (Salimon and Kadir, 2005).

Owing to the high free fatty acids content, *Ceiba Pentandra* needs to undergo a pre-treatment process called esterification reaction to improve the final yield in biodiesel. Nonetheless, this reaction reaches equilibrium state slowly, leading to a low conversion and high energy consumption. Microwave irradiation is an innovative energy source which has been extensively utilized for higher yield in shorter reaction time under mild reaction conditions. In sense, the microwave heating bases on dielectric heating, manifesting

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as heat through the interaction between microwave energy and the molecular dipoles and charged ions in the change of electric field (Sajjadi et al., 2014). As a result, these molecules or ions are able to align themselves through rotation and localized superheating is generated due to molecular friction, which increases the mass transfer between the two immiscible phases.
Biodiesel production from *Ceiba Pentandra* using microwave-assisted technique has not previously been reported in the literature. The objective of this work is to study the feasibility of using microwave-assisted technique for FFA reduction and to determine the optimum conditions for the process. In this study, the pretreatment process was conducted based on the approach which employed Central Composite Design (CCD). Furthermore, the present work also compares the findings of previous researches and the results obtained are improved based on the FFA content with different solvents and catalysts employed.

2. Materials and methodology

2.1 Materials

Solvents such as methanol (99.9 % purity), ethanol (99.9 % purity), 1-propanol (99.9 % purity), 2-propanol (99.5 % purity); acid catalysts which include H_2SO_4 (95 – 97 %), HCl (37 %), H_3PO_4 (85 %); titrant KOH pellet; drying agent Na_2SO_4 anhydrous (purity 99 %) and qualitative filter paper were purchased from Merck Chemical Company (Darmstadt, Germany) and Sigma Aldrich Chemical Company (United States). All chemicals obtained were used without any further purification. *Ceiba Pentandra* Seed Oil was purchased from BUNGAKEMBANG ENTERPRISE CV in Indonesia.

2.2 Experimental set up

The esterification of non-edible oil was conducted in a batch mode inside a microwave reactor. In this process, a 500 mL three-necked round-bottomed glass reactor was used. A stainless steel thermocouple probe was injected on the side neck of the column to maintain the desired temperature of the reactants with an accuracy of ±2 °C. To prevent the loss of methanol during the reaction, a reflux condenser was fixed on the main neck of the flask. A mechanical stirrer was put inside the reactor to attain a completely homogeneous mixture among the reactants at constant rate (Sivakumar et al., 2013).

2.3 Acid catalyzed esterification process

Initially, a fixed amount of the sample ie crude seed oil was transferred to the flask. A known amount of sulfuric acid was mixed with preset quantity of methanol and the mixture was stirred thoroughly until the acid was completely dissolved. Then, the resulting catalyst solution was added to the sample oil and esterification reaction occurred until a certain period of reaction time.
After completion of the reaction, the products were poured into a separating funnel and allowed to cool down to separate the excess alcohol, acid catalyst and impurities existed in the upper layer. Then the esterified oil at the lower layer was separated and washed with distilled water at 50 °C to remove impurities, including sulfuric acid and methanol. Next, anhydrous Na_2SO_4 was added to eliminate water and filter paper was used to filter any traces of Na_2SO_4. Finally, the product was poured into a rotary evaporator set at 60 ^{o}C under vacuum conditions for 1 hour to remove extra methanol and water.
In order to determine the conversion of FFA during the process, the acid value of treated oil was analyzed to evaluate the reduction in the FFA content before and after esterification. The conversion of FFA was calculated as referenced by Man et al. (2013) using the following Eq(1):

$$Conversion = \left(\frac{AV_i - AV_t}{AV_i}\right) x\ 100,\ \% \quad (1)$$

Where AV_i is initial acid value of the mixture and AV_t is the acid value at any “t” time.

2.4 Acid value test

The initial free fatty acids content of *Ceiba Pentandra* seed oil was 6.996 %. The higher the FFA content is, the higher likelihood of soap formation during transesterification reaction is. Therefore, pre-treatment process using acid catalyst was conducted to reduce the FFA content of *Ceiba Pentandra* below 1 %.
In this research, acid value test for *Ceiba Pentandra* seed oil was carried out to determine the amount of acid reduction through titration based on AOCS official method (Cd, 3d-63), as shown in equation (2) and equation (3). All the results were calculated using three decimal place.

$$Acid\ value = \frac{(A-B)\ x\ M\ x\ 56.1}{m}, \frac{mg\ KOH}{g\ oil} \quad (2)$$

Where,
A is the titrant solution volume used in the titration of the sample, mL
B is the titrant solution volume used in the titration of the blank, mL
M is the molarity of the titrant solution, mol/L
m is the mass of the sample, g

$$\% \, Free \, Fatty \, Acid = \frac{(A-B) x \, M \, x \, Mwt.}{m \, x \, 10} \quad (3)$$

Where,
A is the titrant solution volume used in the titration of the sample, mL
B is the titrant solution volume used in the titration of the blank, mL
M is the molarity of the titrant solution, mol/L
Mwt. is the molecular weight of fatty acid, g/mol

2.5 Design of experiment

Response Surface Methodology (RSM) is one of the multivariate techniques that is useful for developing, improving, and optimizing processes. It deals with experimental design and statistical modeling. In this study, RSM was applied to determine the optimized conditions using microwave technique for the esterification of *Ceiba Pentandra*. Central Composite Design (CCD) in RSM was used to develop a response surface quadratic model for describing the effect of four parameters on reduction of FFA. A full factorial experimental design of four parameters at five levels for the acid esterification is shown in Table 1. In terms of the coded variables, the low and high factors (with 16 factorial runs) were coded as -1 and 1 while the axial factors (with 8 axial runs) were coded as -2 and 2. In addition, 6 center runs coded as 0 is a very important design factor that needs to be considered to attain a more precise estimate of the quadratic part of the model.

Table 1: Process parameters for acid esterification

Process parameters	-2	-1	0	1	2
Catalyst concentration (wt%)	0.5	1.0	1.5	2.0	2.5
Methanol to oil (molar ratio)	4	6	8	10	12
Temperature (°C)	45	50	55	60	65
Time (min)	1.5	5.0	8.5	12	15.5

3. Results and discussion

3.1 RSM modeling

The possibility of using RSM for optimization of a process has also been discussed in the research of Dahmoune et al. (2014). Not only RSM is designed to optimize processes, but it is also used to investigate the interactions among various factors. Table 2 presents the results of ANOVA, which were used to analyze the four important variables affecting the FFA conversion. In the quadratic model, the p-Values and F values are used as tools to check the significance of the corresponding coefficients (Prakash Maran and Priya, 2015). At the confidence level of 95 %, the lower p-Value (<0.05) or the greater F value indicates that the model is statistically significant. The F value of 21.20 and p-Value less than 0.0001 imply a high degree of adequacy of this quadratic model.

As illustrated in Table 2, the goodness of fit of the model is evaluated by determination of coefficient (R^2 = 0.9519) which indicates that there is 95.19 % of correlation among all the variables and only 4.81 % of unexplained variance. The value of adjusted determination coefficient (R^2_a = 0.9070) is high and is in reasonable agreement with the predicted determination coefficient (R^2_p = 0.7240). This means the model provides a good prediction of the average outcomes. From the p-value of each model terms, all the first polynomial terms (A, B, C and D) and two second polynomial terms (A^2 and B^2) are highly significant at different levels of significance. In contrast, all the interactive terms (AB, AC, AD, BC, BD and CD) and two quadratic terms (C^2 and D^2) are insignificant. From the results, it can be concluded that there is no effect of the interactions of four factors on the conversion of FFA and factors A and B have noticeable impacts on the response as the quadratic terms of A and B remain significant when the sample population increases.

The acid esterification of *Ceiba Pentandra* was completed by varying four parameters using the Central Composite Design (CCD) method with 30 runs to get the optimum conditions. Based on the chosen parameter range chosen, Figure 1 indicates that factor A (catalyst concentration) is the most influencing factor towards the reduction of acid value, followed by factor B (methanol to oil molar ratio). This trend is similar to that reported by Ahmad et al. (2014). Temperature is the third factor which shows the effect of shifting the reaction equilibrium towards the product. Although the reaction time has been reduced significantly by using microwave, it appears to have the least influence among four variables invested. However, this trend changes slightly after the center point. While catalyst concentration continues gaining the marked influence on FFA conversion, methanol tends to lose its role in reducing the FFA content. At this range, it is evident the fact that acid catalyst is considered as a crucial factor in the esterification using microwave – assisted technique and increasing solvent does not really help this reaction.

Table 2: Results of ANOVA

Source	Sum of squares	Degree of freedom	Mean square	F value	p-Value Prob > F
Model	5.58	14	0.40	21.20	< 0.0001
A-Catalyst	2.80	1	2.80	148.84	< 0.0001
B-MeOH: Oil	0.72	1	0.72	38.47	< 0.0001
C-Temperature	0.85	1	0.85	45.01	< 0.0001
D-Time	0.49	1	0.49	26.08	0.0001
AB	0.018	1	0.018	0.98	0.3369
AC	0.018	1	0.018	0.98	0.3369
AD	0.015	1	0.015	0.79	0.3876
BC	1.322×10^{-4}	1	1.322×10^{-4}	7.036×10^{-3}	0.9343
BD	0.023	1	0.023	1.24	0.2835
CD	6.250×10^{-6}	1	6.250×106^{4}	3.325×10^{-4}	0.9857
A^2	0.46	1	0.46	24.72	0.0002
B^2	0.26	1	0.26	13.88	0.0020
C^2	0.028	1	0.028	1.50	0.2398
D^2	5.408×10^{-3}	1	5.408×10^{-3}	0.29	0.5996
Residual	0.28	15	0.019		
Lack of Fit	0.28	10	0.028	87.64	< 0.0001
Pure Error	1.599×10^{-3}	5	3.199×10^{-4}		
Cor Total	5.86	29			
Std. Dev.	**0.14**		**R-Squared**	**0.9519**	
Mean	**1.07**		**Adj R-Squared**	**0.9070**	
C.V. %	**12.82**		**Pred R-Squared**	**0.7240**	

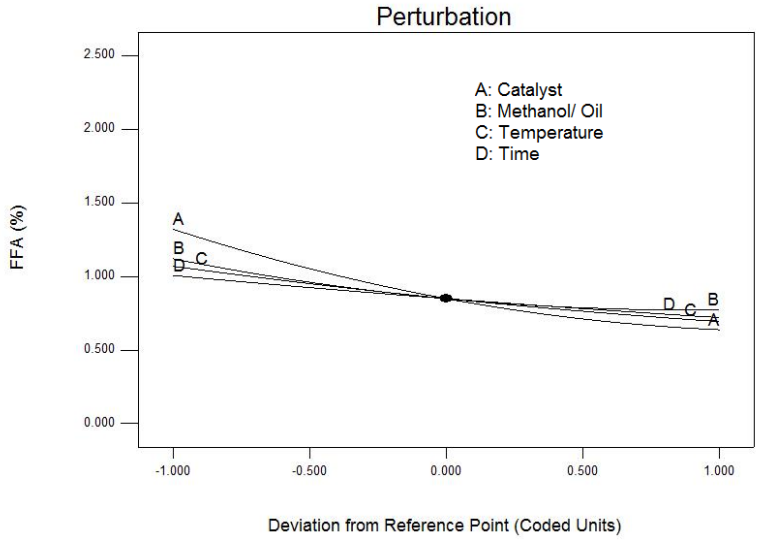

Figure 1: Perturbation plot for acid catalyzed esterification

3.2 Comparison

Table 3 describes the difference of the optimum conditions for *Ceiba Pentandra* between microwave and conventional technique. As can be seen from the table, the FFA conversion can reach up to 94.43 % in 12 minutes with the assistance of microwave while it takes 60 minutes with more amount of solvent to achieve 94.15 % of FFA conversion in conventional method. Besides, to attain higher FFA conversion, longer time as well as higher temperature needs to be set in conventional method.

3.3 Effects of different alcohol

After achieving the optimum conditions by using CCD method, the esterification reaction was performed with different alcohols at those conditions to compare the influence of solvents on FFA conversion. The results were an average of two repeated experiments. As shown in Table 4, the FFA reduction of methanolic system is around two times higher than that of the ethanolic one at the same conditions (0.388

% and 0.677 %). This is followed by using n-propanol which reduced the FFA content to 2.175 %. Isopropanol as an acyl acceptor shows the least effect on FFA reduction (4.675 %). Such results indicated that methanol has the strongest capability to absorb the microwave spectrum in comparison with other alcohols. As mentioned before, microwave energy can be transformed into heat via interaction with polar molecules. In this case, methanol as a simplest alcohol is more polar, which is easily affected by the variation in frequency. Sajjadi et al. (2014) reported that the dielectric constant decreases by increasing the length of the linear aliphatic groups in R–OH chain. Although, 1-propanol and 2-propanol have the same two methyl side chain, $–CH_3$, the FFA conversion of Ceiba Pentandra towards 2-propanol is lower than 1-propanol. This may be attributed to the steric hindrance of 2-propanol. Hence, the order for alcohols to reduce the FFA in esterification is methanol > ethanol > 1-propanol > 2-propanol.

Table 3: Comparison of process variables with previous studies

Parameters	**Microwave**	**Conventional**		
	This work	Ong et al. (2013)	Sivakumar et al. (2013)	Norazahar et al. (2012)
H_2SO_4 Catalyst (wt%)	2	1.84	1.834	1
Methanol to oil	10:1 (mol ratio)	10:1 (mol ratio)	8:1 (vol. ratio)	6:1 (mol ratio)
Temperature (°C)	60	60	65	65
Time (min)	12	180	60	180
FFA conversion (%)	94.43	96.41	94.15	98.1

Table 4: Alcohols used for esterification reaction assisted by microwave irradiation

Catalyst (wt%)	**Alcohol (oil mol ratio)**	**Temperature (°C)**	**Time (min)**	**FFA %**
H_2SO_4 (2 %)	Methanol (10:1)	60	12	0.388 ± 0.00014
H_2SO_4 (2 %)	Ethanol (10:1)	60	12	0.677 ± 0.00008
H_2SO_4 (2 %)	1-propanol (10:1)	60	12	2.175 ± 0.03608
H_2SO_4 (2 %)	2-propanol (10:1)	60	12	4.675 ± 0.03073

3.4 Effects of different acid catalysts

Similar to alcohol, different homogeneous acid catalysts were investigated in esterification reaction to determine the best catalyst for pre-treatment process. As it is mentioned by Liu et al. (2013), the role of acid catalyst in this reaction is to provide proton H^+ to carbonyl oxygen, increasing electrophilicity of carbonyl carbon and then facilitates the nucleophilic oxygen atom attack of alcohol. Due to that reason, the stronger the acidity of the catalyst is, the higher conversion is obtained. On the other hand, according to Patnaik (2003), the larger an acid dissociation constant is, the stronger an acid is, the more it easily loses a proton H^+. As reported in Table 5, among these acid catalysts, phosphoric acid has the smallest acid dissociation constant; therefore it does not bring a valuable help to reduce the FFA content. In contrast, hydrochloric acid and sulfuric acid with much larger acid dissociation constant greatly facilitate the reduction of FFA content. Even though hydrochloric acid and sulfuric acid are strong, this H_2SO_4 diprotic acid still appears to be the best acid catalyst to significantly decrease the FFA content to 0.388 % in 12 minutes ie two times higher than hydrochloric acid (0.897 %). This is also evidenced by Boucher et al. (2008) in their research. Higher concentration may lead sulfuric acid to remarkable performance as a role of catalyst for esterification reaction.

Table 5: Catalysts used for esterification reaction assisted by microwave irradiation

Catalyst (wt%)	**Acid dissociation constant (Ka)**	**Alcohol (oil mol ratio)**	**Temperature (°C)**	**Time (min)**	**FFA %**
H_2SO_4 (2 %)	$K_{a1} >> 1$ $K_{a2} = 1.2 \times 10^{-2}$	Methanol (10:1)	60	12	0.388 ± 0.00014
HCl (2 %)	$K_a >> 1$	Methanol (10:1)	60	12	0.897 ± 0.00682
H_3PO_4 (2 %)	$K_{a1} = 7.1 \times 10^{-3}$ $K_{a2} = 8.0 \times 10^{-8}$ $K_{a3} = 4.8 \times 10^{-13}$	Methanol (10:1)	60	12	5.552 ± 0.00261

4. Conclusion

The pre-treatment of biodiesel production from non-edible and underutilized *Ceiba Pentandra* seed oil via acid catalyzed esterification with the microwave-assisted technique was investigated in this work. The

optimum reaction conditions for the reduction of FFA content to 0.388 % were as follows: methanol to oil molar ratio of 10:1, catalyst concentration of 2 wt%, temperature of 60 °C and reaction time of 12 min. Response surface methodology (RSM) was successfully applied for designing and optimizing the experiments which showed the significance level of four parameters towards the response in the order of catalyst concentration > methanol to oil molar ratio > temperature > time. Moreover, methanol and sulfuric acid were proved to become the key factors for esterification reaction. The results showed notable improvement in terms of FFA conversion as well as energy, which clearly merits to become a practical application of biodiesel production. For further work, kinetic parameters of the esterification process from *Ceiba Pentandra* Seed Oil will be studied based on optimum conditions in this paper and transesterification reaction for biodiesel production will also be investigated.

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