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Optimization and Parametric Study of Free Fatty Acid (FFA) Reduction from Rubber Seed Oil (RSO) by Using Response Surface Methodology (RSM)

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ABSTRACT

Rubber seed plantations in Malaysia are one of the copious non-edible and un-utilized feedstock available for alkyl esters production. The free fatty acid content in feedstock needs to be in adequate limits for quality biodiesel. Current research was conducted on the reduction of FFA content in Rubber Seed Oil (RSO) by using experimental design software Design Expert 8.0. Central Composite Design (CCD) was implemented for experimental design and an optimized condition was found by RSM. Four basic parameters affecting acid esterification process were studied which comprise of alcohol to oil molar ratio, catalyst amount (wt %), reaction temperature (^{o}C) and reaction time (min). Parametric studied was conducted within the ranges of alcohol to oil molar ratio (from 10 to 15); catalyst amount (from 5-10 wt %); reaction temperature (from 45-65^{o}C); and reaction time (from 55-90 min). Statistical significance of each parameter was conducted by Analysis of Variance (ANOVA). Optimum conditions for an acid esterification reaction that reduce the FFA content of RSO to 0.82% was found to be at 15:1 alcohol to oil ratio, temperature of 45^{o}C, catalyst amount of 10wt% (oil basis) and reaction time of 90 min. The RSO feedstock was characterized and compared before and after acid esterification process.

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INTRODUCTION

Biodiesel is one of the renewable energy that is currently high in demand. Biodiesel has several advantages over petroleum diesel. It is renewable, biodegradable, nontoxic, environment friendly and has a lower cost of production. It helps to reduce CO_2 emission which is a greenhouse gas that harmful to the earth. (Demirbas, 2010) state in his book of Algae energy that as an alternative fuel, biodiesel is better that petroleum diesel in terms of sulphur content, cetane number, flash point, aromatic content and its biodegradability .

Biodiesel is a chemically modified alternative fuel which can be produced from non-edible vegetable oils, animal fats, and waste oils. These biodiesel is either in the form of triacylglycerols or trans-esterified with various monohydric alcohols (Klopfenstein *et al*., 1983). Vegetable oils are becoming a promising alternative to diesel fuel because they have practically no sulfur content, offer no storage difficulty, and they have excellent lubrication properties (Ramadhas *et al*., 2005). Examples of vegetable oils that can produce biodiesel are corn oil, canola oil, soybean oil, sunflower oil, palm oil, rubber seed oil, cotton seed oil, algae oil, and coconut oil (Mousdale and DM, 2010). Rubber seeds are an abundant source of low cost non-edible oil that is available in Malaysia (Khan and Yusup, 2009). Malaysia has estimated average of 1,028,840 hectares of rubber plantation in the year 2010 (MRB, 2012). Assuming the estimated production rate of 1000 kg seeds per hectare per year, the projected annual production of rubber seeds in Malaysia would be around 1 million metric tons. Since Malaysia has an abundant agriculture resource like rubber seeds, it would be beneficial and a good opportunity to expand the economy of the country by producing biodiesel from the rubber seed oil (RSO).

Most common methods to produce biodiesel was the transesterification technique in the presence of an alkali catalyst (Chen *et al*., 2005). However, according to Ramadhas *et al*., 2005, there is a problem when using alkaline-catalyzed trancesterification of the vegetable oils because they often contain a large amount of free fatty acids (FFA). These free fatty acids will quickly react with the alkaline catalyst to produce soaps that inhibit the

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separation of the ester and glycerin produced from esterification. Feedstocks with high FFA value must undergo acid esterification prior to transesterification for better results. The feedstock that has FFA content more than 2% cannot go directly for transesterification thus it should be reduced below 2% (Ramadhas *et al*., 2005) (Morshed *et al*., 2011).

MATERIALS AND METHODS

Rubber seed oil (RSO) was obtained from Vietnam Kinetics Chemiclas (M) Sdn Bhd Malaysia. All the chemicals used is in analytical grade. Methanol (99% pure), sulfuric acid (>97%), 2-propanol, toluene, potassium hydroxide phenolphthalein and sodium sulfate was purchased from Merck Germany.

An acid esterification experiment was conducted using 500ml three-neck round bottom flask placed in the water bath. A condenser was attached to the three-neck round bottom flask to avoid alcohol losses. The RSO was pour into the three-neck bottom flask and heated to the desired temperature using hot plate. Prepared mixture of alcohol (methanol) and catalyst (H_2SO_4) according to RSM design was then added to the reactor with the constant mixing rate of 350 rpm using magnetic stirrer.

The reaction is then started until the desired reaction time was reached. The product obtained was then separated using separating funnel after settled down for 24 hours. After 24 hours, two layers of product were obtained. The upper layer of the product consists of pre-treated RSO (desired product) while the lower layer of the product consists of excess catalyst, alcohol and glycerol. The excess catalyst, alcohol and glycerol were removed.

The desired product was then washed using deionized warm water until the water pH was found to be neutral. The remaining amount of water and alcohol in the desired product were removed using a rotary evaporator under vacuum condition. Approximately 10g of sodium sulfate (Na_2SO_4) was added to the desired product to absorb the remaining water and the remaining Na_2SO_4 was then filtered. Finally, the acid value was calculated using AOCS Cd 3d-63 method (AOCS, 5th Edition).

Design Expert 8.0 software has been used to design the acid esterification experiment. By implementing the Central Composite Design (CCD), four variables with two level design was employed in order to get the optimized reaction condition for FFA reduction. The CCD method gave the optimized conditions within the range of the experiment's design in an economic way and analyzes the relation between the reaction conditions and the response (Ahmad *et al*., 2014). The designed variables ranges and levels for the acid esterification are shown in Table 1.

Table 1: Experimental design variables using RSM.

Reaction Variable	Units	Low Value	High Value
Alcohol to oil molar ratio	-----	10	15
Catalyst Amount	wt%	5	10
Reaction Temperature	^oC	45	65
Reaction Time	min	55	90

RESULT AND DISCUSSION

The physical and chemical properties of RSO were analyzed and compared before and after the acid esterification conducted. Results for both physical and chemical properties of the analysis are shown in Table 2.

Base on the experimental design by RSM as shown in Table 1, the results of FFA reduction are shown in Table 3. The highest reduction of FFA value was found at trial number eleventh. The FFA value was reduced to 0.82% at the optimum condition by conducting the experiment at alcohol to oil molar ratio of 15:1; catalyst amount of 10wt%; reaction time of 90 min and reaction temperature of 45^{o}C.

Table 2: Physical and Chemical Properties of RSO.

Properties	Units	Before Treatment	After Treatment
Acid Value	mgKOH/ gOil	42	0.85
Iodine Value	I_2/g Oil	146	146
Peroxide Value	meg/kg	1.6	0.7
Saponification Value	mg/g	194	186
Calorific Value	kJ/kg	38.78	39.40
C	wt%	84.3	---
H	wt%	11.96	---
N	wt%	0.93	---
S	wt%	0.78	---
O	wt%	2.03	---

Table 3: Experimental Designed Runs by CCD.

Experimental Run	Alcohol to Oil Molar ratio	Catalyst Amount (wt%)	Reaction Time (min)	Reaction Temperature (^oC)	Response (FFA%)
1	8.3	7.5	72.5	55	3.12
2	12.5	7.5	72.5	38.2	1.16
3	16.7	7.5	72.5	55	0.85
4	15	5	90	65	0.91
5	12.5	7.5	72.5	55	1.12
6	12.5	7.5	72.5	55	1.12
7	15	10	55	45	1.23
8	15	5	55	65	1.09
9	10	10	90	65	1.21
10	10	10	10	55	1.99
11	15	10	90	45	0.82
12	10	5	90	45	2.58
13	12.5	7.5	72.5	55	1.11
14	12.5	7.5	101.9	55	0.86
15	12.5	7.5	43.1	55	1.60
16	12.5	7.5	72.5	71.8	1.55
17	12.5	7.5	72.5	55	1.11
18	12.5	11.7	72.5	55	0.89
19	12.5	3.3	72.5	55	4.96
20	10	5	55	45	2.20
21	12.5	7.5	72.5	55	1.12

Figure1 shows the perturbation plot for each of the parameters effect. Base on Figure 1, Catalyst amount (wt%) shows the maximum influence on the FFA reduction followed by alcohol to oil molar ratio, temperature (^oC) and reaction time (min).

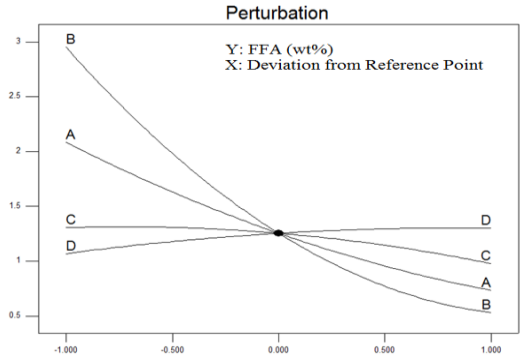

Fig. 1: Perturbation Plot for Acid Esterification Process for RSO.

Theoretically, only 3 mole of alcohol are required for 1 mole of oil conversion into triglycerides but excess amount of alcohol is needed to shift the reaction towards the product side. Base on Figure 2, the FFA percentage is decreased by increasing amount of alcohol used. Same effect of alcohol to oil molar ratio on the FFA percentage also reported by (Ramdhas *et al*., 2005) and (Khan M.A., *et al*., 2010).

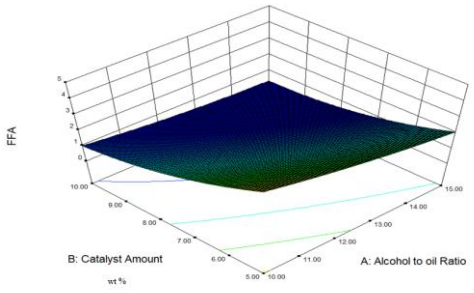

Fig. 2: Effect of Alcohol to Oil Ratio and Catalyst Amount on FFA.

Catalyst amount is the variable that gives second highest influence on the FFA percentage. Base on Figure 3, by increasing the catalyst amount, the FFA percentage is reduced. In this study, the maximum reduction of FFA percentage is at 10wt% of catalyst. Study on effect of catalyst amount to FFA percentage reduction has

been done by (Morshed *et al*., 2011) . It is reported that higher concentration of catalyst amount (5%-7%) is needed to reduce the FFA percentage of RSO from Bangladesh.

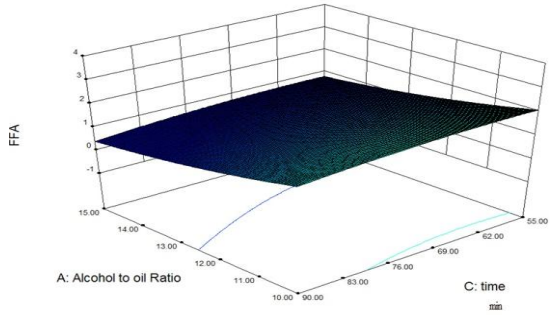

Fig. 3: Effect of Alcohol to Oil Ratio and Time on FFA.

Figure 4 shows the effect of reaction temperature towards the FFA reduction. Theoretically, rate of reaction is affected by the reaction temperature. Base on Figure 5, by increasing the reaction temperature, the reduction of FFA also increased. Reaction temperature higher than 65^{o}C leads to alcohol losses and darken the product produced which is not beneficial from economic point of view as reported by (Ramdhas *et al*., 2005).

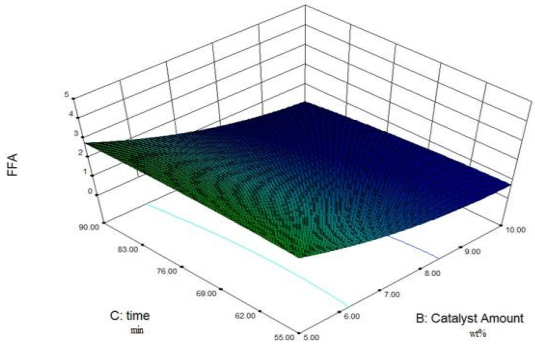

Fig. 4: Effect of Catalyst Amount and Time on FFA.

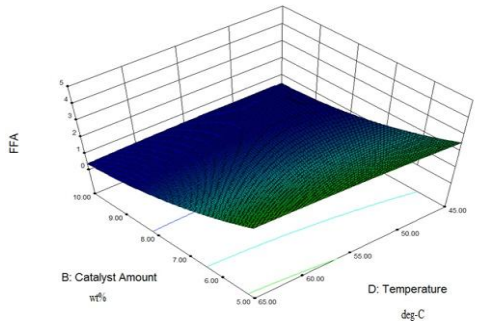

Fig. 5: Effect of Catalyst Amount and Temperature of FFA.

Figure 5 shows the effect of reaction temperature towards the FFA reduction. By increasing the reaction time, the FFA value is reduced. Base on study reported by (Kiem and G.I., 1945), the first hour of reaction time is sufficient to reduce the FFA value while by increasing the reaction time more than one hour will slightly effect the FFA reduction.

Conclusion:

Base on the experiment, the FFA content inside RSO can be reduced to be less than 1% using one step acid-esterification process by reacting the RSO with methanol and sulfuric acid at the optimum condition. The optimum condition are at alcohol to oil molar ratio of 15, catalyst amount of 10wt%, reaction time of 90 min

and at reaction temperature of 45^{o}C. Further analysis of the reaction parameters concluded that catalyst amount has the greatest effect over the FFA reduction followed by alcohol to oil molar ratio.

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REFERENCES

Ahmad, J., S. Yusup, A. Bokhari, R.N.M. Kamil, 2014. Study of fuel properties of rubber seed oil based biodiesel. Energy Conversion and Management, 78: 266-275.

Chen, M.J., K.N. Chen and C.W. Lin, 2005. Optimization on response surface models and for the optimal manufacturing conditions of dairy tofu. Journal of Food Engineering, 68: 470-480.

Demirbas, A.D., 2009. Algae Energy, Trabzon, Turkey: Springer.

Keim, G.I., 1945. Process of treatment of fatty glycerides. U.S. Patent, 2: 383-601.

Khan, M. and S. Yusup, 2009. Solvent extraction and characterization of rubber seed oil. International Journal of Postharvest Technology and Innovation. 1: 376-385.

Khan, M.A., S. Yusup and M.M. Ahmad, 2010. Acid esterification of high free fatty acid crude palm oil and crude rubber seed oil blend: Optimization and parametric analysis. Biomass and Bioenergy, 34: 1751-1756.

Klopfenstein, W.E. and H.S. Walker, 1983. Efficiencies of various esters of fatty acid for diesel fuels. Journal of American Oil Chemist Society, 60: 1596-1598.

Malaysia Rubber Board (MRB),"Available:http://www.lgm.gov.my/nrstat/nrstats.pdf.[Accessed: December, 2012].

Morshed, M., K. Ferdous, M.R. Khan, M.S.I. Mazumder, M.A. Islam, M.T. Uddin, 2011. Rubber seed oil as a potential source for biodiesel production in Bangladesh. Fuel, 90: 1981-1986.

Mousdale, D.M., 2010. Introduction to Biofuels, CRC Press.

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