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HETEROGENEOUS TRANSESTERIFICATION OF RUBBER SEED OIL BIODIESEL PRODUCTION

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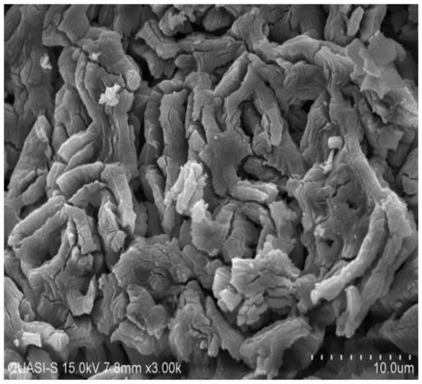
Graphical abstract



Abstract

An experimental investigation was conducted to explore the effects of using waste cockle shells as a heterogeneous catalyst on the transesterification process of very high free fatty acid (FFA) rubber seeds oil with methanol. The waste cockle was calcined at 900°C for 4 hours and was employed as a source of calcium oxide (CaO). SEM, XRD and XRF were adopted to analyze the catalyst characterization. The process variables namely oil molar ratio, catalyst concentration and reaction time were optimized using response surface methodology (RSM) based on central composite design (CCD) method. The optimum yield of 88.06% was obtained for the final product of biodiesel with optimal conditions was obtained as: molar ratio of methanol to oil of around 15.57:1, 9 % catalyst weight percentage with 2.81 hours reaction time. All the fuel properties were analyzed according to the ASTM D6751 and EN-14214 standards in terms of viscosity, acid value, density and flash point.

Keywords: Biodiesel, heterogeneous catalyst, transesterification, non-edible oil

Abstrak

Satu kajian dijalankan untuk mengkaji kesan penggunaan pemangkin hetorogen daripada sisa kulit kerang dalam proses transesterifikasi minyak biji getah yang tinggi kandungan asid lemak bebas (FFA) bersama metanol. Sisa kerang dipanaskan pada suhu 900°C selama 4 jam dan berfungsi sebagai sumber kalsium oksida (CaO). SEM, XRD dan XRF digunakan untuk mengkaji ciri-ciri pemangkin. Proses parameter seperti nisbah molar minyak, konsentrasi pemangkin dan tempoh tindak balas dioptimumkan menggunakan kaedah tindak balas permukaan (RSM) berdasarkan kaedah reka bentuk komposit pusat (CCD). Hasil optimum sebanyak 88.06% diperolehi dari produk akhir dengan kondisi optimum: nisbah molar metanol minyak sekitar 15.57:1, 9 % peratus berat pemangkin dengan tempoh tindakbalas selama 2.81 jam. Kesemua sifat bahan api telah dianalisis berdasarkan piawaian ASTM D6751 dan EN-14214 dari segi kelikatan, nilai asid, ketumpatan dan takat kilat.

Kata kunci: Biodiesel, pemangkin heterogen, transesterifikasi minyak tidak boleh dimakan

1.0 INTRODUCTION

Biodiesel, an alternative fuel can always be considered as a sustainable fuel for a greener future. Due to the food crisis, a 2nd generation of biodiesel or also familiar as nonedible sources is becoming widely recognized as one of the efforts to reduce the dependency on edible sources. These inexpensive 2nd generation feedstock have recently attracted a great deal of attention. Some examples of non-edible oils that have recently been extensively reviewed are *Jatropha curcas*, *Calophyllum inophyllum*, *Madhuca indica* (mahua), Linseed, *Pongamia pinnata* (karanja), *Hevea brasiliensis* (rubber seed) and many more [1].

The heart of biodiesel chemistry is the process of transforming the vegetable oil esters into the biodiesel esters by adding alcohol (methanol or ethanol), to form fatty acid alkyl esters and glycerol. At this stage, transesterification process is used in order to reduce the high viscosity and at the same time increase the volatility of the vegetable oils as well as animal fats to the desired level. Reversible process is a key feature of transesterification starting with converting the triglycerides into diglycerides and followed by converting diglycerides to monoglycerides. In the last process, monoglycerides are converted to glycerol. Three esters are obtained from one triglycerides molecule, one ester molecule for each glyceride at each step [2].

In recent years, the production of biodiesel has undergone a number of changes both in terms of technology or raw materials used. However, there are some constraints that have been identified limiting the quality of biodiesel production. One of the major concerns among biodiesel producers in commercializing biodiesel is the cost of the feedstock and the production process [3]. One of the possible alternatives is by performing transesterification method using heterogeneous catalysts from waste sources which allows simple product separation and purification and does not required neutralization process [4]. Even though homogeneous catalyst is said to be dominating the biodiesel industries due to their simple usage and very high yield production this method still has a few drawbacks such as generates water and soap formation which will consume more catalyst and in turns reduce the yield of biodiesel [5]. Heterogeneous catalyst act in a different phase from the reaction mixture, usually as a solid. Heterogeneous catalytic reaction converts triglycerides into methyl ester and glycerol as a byproduct slowly but produces biodiesel in a very feasible way due to the reusability of catalyst. It is also economical and cost effective due to easy separation. Basically, there are two types of heterogeneous catalyst that are currently used in biodiesel production; solid base and solid acid catalyst. The solid base is found to be more active compared to solid acid catalyst which required relatively shorter reaction time and lower reaction temperature. Calcium oxide (CaO), catalyst is one among the most promising heterogeneous catalyst that can be classified having an eco-friendly characteristic and value added to the green biodiesel process [6]. Apart from the low in cost, it also can withstand high temperatures and their performances are reported is comparable to homogeneous catalyst biodiesel production [7].

This work is attempted to study the performance of selected process parameters that influence the optimization process on the transesterification of high FFA rubber seed oils. The variables affecting the transesterification reaction such as effect of reaction time, reaction temperature and molar ratio of alcohol to oil are also addressed. A statistical method using response surface methodology (RSM) based on central composite design (CCD) was employed to analyze the optimization process parameters.

2.0 METHODOLOGY

2.1 Material and Chemicals

The crude rubber seed oil (RSO) with FFA value of 39.69 % and acid value of 78.9 was purchased from Kinetics Chemical (M) Sdn Bhd, Malaysia. The physical characteristics of the crude rubber seed oil were conducted and the test result was tabulated as in Table 1. All tests were determined according to the ASTM D-6751, EN-14214 and AOCS (American Oil Chemists' Society) method. The crude RSO is sent for the gas chromatography analysis to determine the composition of the crude oil. All chemicals that were used in this research were obtained from various sources namely Polyscientific Chemicals (methanol 99.9 % purity, KOH pellets, n-hexane HPLC grade, sulphuric acid of 95-98% and methanol of 99% purity) and Sigma- Aldrich (phenolphthalein). The catalyst was prepared from natural waste cockle, purchased from local seafood restaurant in Melaka, Malaysia.

2.2 Catalyst Preparation and Characterization

The waste cockle shells were washed with tap water to remove all the impurities. Then, the cleaned samples were dried for 24 hours in the oven at 100 °C for 3 to 4 hours to remove the excess water. The dried waste shells were then calcined in a furnace at 900 °C with a heating rate of 10 °C/min for 4 hours to convert calcium carbonate, $CaCO_3$ into calcium oxide, CaO [8]. The samples were later crushed and grounded into different particles sizes (2 mm - 4 mm) using pestle and mortar. All the produced catalyst samples were then stored in a highly sealed glass jars (desiccator) to prevent contamination from carbon dioxide, CO_2 and atmospheric water moisture.

X-ray diffractometer, XRD (Shimadzu diffractometer model XRD6000 using Cu-Kα radiation) was used to measure the crystalline phase of the calcined sample. JCPDS (Joint Committee of the Powder Diffraction Standard) was used to identify the phases present in the samples. X-ray fluorescence spectroscopy (XRF-Oxford, ED-2000) is used to obtain the elemental chemical compositions of the calcined sample for more precise measurement. The SEM-EDS technique was used to obtain the information of the morphology and elemental composition of the samples. Themorphology of the catalysts was carried out using a HITACHI scanning electron microscope model SUI510.

Table 1 Properties of methyl ester of crude Rubber seeds oil

Test	Unit	Method	Results
Acid Value	mg KOH/g	ASTM D664	78.9
Iodine Value	(g I_2/100 g)	AOCS Id 3-92	129.8
Saponification value	mg KOH/g	AOCS Cd 3-25	180.9
Water Content	% wt	EN ISO 12937	0.44
Kinematic viscosity @ 40°C	mm^2/s	ASTM D7042	32.96
Density@ 15°C	kg/L	ASTM D4052	0.9248

2.3 Esterification

The esterification process is a pre-treatment process for the feedstock oil with the aim to reduce the free fatty acid (FFA) content. High FFA content may contributed to some negative effects on the production namely higher saponification level that lead to low yield production. 50 g of crude RSO was placed in a 250 ml three-necked round-bottomed flask with reflux condenser to avoid any loss of methanol. The reaction mixture was heated up to 60 °C while stirred with magnetic stirrer under atmospheric conditions. A mixture of 10 wt% sulphuric acid (H_2SO_4) in reference to the mass of oil and methanol with different methanol-oil molar ratios (6:1, 9:1, 12:1 and 15:1) was added to the preheated oil and again stirred for specific time. The sample was then put into the separating funnel to separate the pre-treated oil, excess of methanol and catalyst. The treated oil was separated and collected and the amount of FFA content remaining and the acid value is determined before conducting the transesterification process.

2.4 Transesterification

The acid value of crude RSO reduced from 78.9 mg KOH/g to 1.45 mg KOH/g after conducting the esterification process. Transesterification process is carried out by heating 50 g of rubber seed oil to a selected temperature which ranges from 60 to 64 °C on a constant temperature with magnetic stirrer. Methanol and the catalyst (cockle) were added and mixed and heated up to 60 ºC to 65 ºC. The process parameters and ranges are shown in Table 2. The mixture was stirred at all-time throughout the transesterification process. Upon the reaction completion, the catalyst is filtered out and the end product was poured into a separation funnel and was left overnight for separation of ester and glycerol to occur. After separation, the lower layer which is glycerol is drawn out of separation funnel and the excessive amount of methanol was evaporated. The product obtained which is the biodiesel was taken out for further properties analysis. The yield obtained was calculated using the formula shown below:

$$FAME\ Yield\ (\%) = \frac{Total\ weight\ of\ FAME}{Total\ weight\ of\ oil} x100 \qquad (1)$$

For optimization, few tests were performed by varying the methanol to oil ratio, the catalyst weight percentage and the reaction time in order to find the optimum parameters for the best yield using Minitab software.

2.5 Statistical Analysis

Methanol to oil molar ratio, x_1, catalyst concentration, x_2, and reaction time, x_3 are the three important variables that were studied using the response surface methodology. The real levels and coded of each parameter are given in Table 2. Using the central composite design method (CCD), Design of experiment (DOE) with 3 factors and each factor with 5 levels lead to a total of 20 runs of experiments as shown in Table 3. The fatty acid methyl ester (FAME) yields of biodiesel production were selected as the predicted response.

As shown in Table 3, the highest conversion of biodiesel obtained from the experiment was 88.06% for the parameter of 15.57 methanol to oil molar ratio, 9.05% of catalyst weight with 2.81 hours of reaction time. The lowest yield of 55.52% was obtained for methanol to oil molar ratio of 8.43:1, 20.95% of catalyst weight and 5.19 hours reaction time. It clearly shows that increase in methanol to molar ratio will results in higher yield and longer reaction time and causes reduction in the conversion yield.

Table 2 Codes, ranges and levels of independent variables (experimental)

Factor	Unit	Coded Level				
		-1.68 (-a)	-1	0	1	+1.68 (+a)
Methanol Molar ratio (x_1)	mol/mol	6.00	8.43	12.00	15.57	18.00
Weight catalyst (x_2)	wt%	5.00	9.05	15.00	20.95	25.00
Reaction time (x_3)	minute	2.00	2.81	4.00	5.19	6.00

Table 3 Central composite design of three independent variables (factors) with experimental response value

Run	Factors Level			Factors' Actual Value			FAME yield (%)	
	Molar ratio x_1	Weight catalyst x_2	Reaction time x_3	Molar ratio x_1	Weight catalyst, x_2	Reaction time (h), x_3	Experimental	Prediction
1	0	0	0	12.00	15.00	4.00	69.65	69.56
2	-1	-1	-1	8.43	9.05	2.81	77.54	75.36
3	0	0	0	12.00	15.00	4.00	69.70	69.56
4	-1	1	-1	8.43	20.95	2.81	65.94	67.20
5	1	1	-1	15.57	20.95	2.81	79.48	78.28
6	1	-1	1	15.57	9.05	5.19	78.92	77.50
7	1	1	1	15.57	20.95	5.19	69.67	71.69
8	1	-1	-1	15.57	9.05	2.81	88.06	85.98
9	-1.68	0	0	6.00	15.00	4.00	66.82	65.53
10	-1	1	1	8.43	20.95	5.19	55.52	57.44
11	0	-1.68	0	12.00	5.00	4.00	70.82	73.50
12	0	0	-1.68	12.00	15.00	2.00	77.60	80.03
13	0	0	0	12.00	15.00	4.00	69.70	69.56
14	0	0	0	12.00	15.00	4.00	68.73	69.56
15	0	1.68	0	12.00	25.00	4.00	64.22	61.76
16	-1	-1	1	8.43	9.05	5.19	62.66	63.70
17	1.68	0	0	18.00	15.00	4.00	84.92	86.44
18	0	0	0	12.00	15.00	4.00	69.04	69.56
19	0	0	0	12.00	15.00	4.00	70.59	69.56
20	0	0	1.68	12.00	15.00	6.00	66.90	64.70

Table 4 ANOVA for model terms

Source	df	Sum of squares	Mean squares	*F*-value	*p*-value
x_1- Methanol	1	56.063	56.0627	18.52	0.001
x_2- Weight catalyst	1	49.035	49.0350	16.20	0.001
x_3- Reaction time	1	79.968	79.9683	26.42	0.003
x_1x_2	1	24.957	24.9571	8.24	0.017
x_1x_3	1	0.932	0.9316	0.31	0.591
x_2x_3	1	11.592	11.5921	3.83	0.079
x_1^2	1	6.811	6.8105	2.25	0.165
x_2^2	1	0.774	0.774	0.26	0.624
x_3^2	1	0.453	0.4528	0.15	0.707
R^2 = 95.33%, R^2 adj.= 91.13, R^2 pred.= 65.21%					
Significant at 5% level					

Analysis of variance (ANOVA) of the experiment as shown in Table 4 indicated the values for R^2 and adjusted R^2 ; 0.9532 and 0.9111 respectively which shows that an acceptable level for the model accuracy which indicates the high degree of correlation between experimental and prediction data for FAME. The effect of process variables; x_1(molar ratio), x_2 (catalyst weight) and x_3 (reaction time) as well as the combined effect of parameters x_1x_2 were determines as significant model terms (*p*-values < 0.05), whereas x_1x_3, x_2x_3, x_1^2, x_2^2, and x_3^2 had insignificant effect on the ester yield (*p*-values > 0.1).The final equation in terms of coded factors is outlined in following equation:

$$Y = 119.3 - 3.37x_1 - 0.340x_2 - 12.68x_3 + 0.1784{x_1}^2 - 0.0193{x_2}^2 + 0.700{x_3}^2 + 0.0054x_1 * x_2 + 0.187x_1 * x_3 + 0.067x_2 * x_3 \qquad (2)$$

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Waste Calcined Shells

The elemental chemical composition analysis of the calcined sample was analyzed using XRF spectroscopy. It appears from Table 5 that the major mineralogical componenet is CaO having concentration of CaO 93.98 wt%. These results indicated that all $CaCO_3$ in the samples was completely transformed to CaO.

Table 5 Chemical composition of calcined cockle with XRF-XRD

Formula	Concentration
CaO	93.98
Na_2O	1.34
SrO	0.21
MgO	0.16
SO_3	0.12
SiO_2	0.04
TeO_2	0.03

Figure 1 shows the surface morphologies of the calcined heterogeneous catalyst which gave an irregular in shape and some of them bonded together as aggregate [8]. EDS analysis was conducted to determine the components of the surface. Typically, plenty of Calcium (Ca) and Oxygen (O_2) were observed. Moreover the calcium contents of the catalyst are much higher indicating that the catalysts are calcium compounds

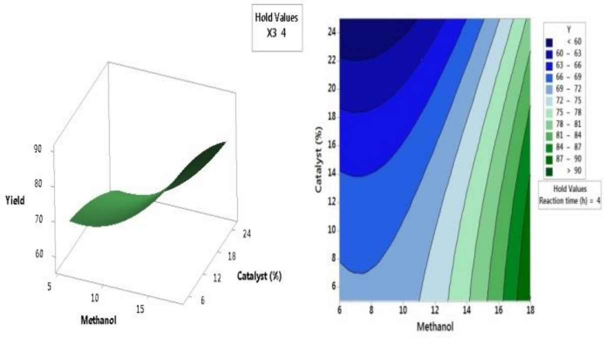
.

Figure 1 SEM images of the heterogeneous cockle calcined at 900◦C for 4 hours

3.2 Effect of Variables on Transesterification Process

There are three parameters that play important roles in transesterification process namely reaction time, methanol to oil molar ratio and catalyst loading. The methanol/oil ratio is one of the most important factors affecting the yield of biodiesel. Although stoichiometric ratio requires three moles of methanol for each mole of oil, the transesterification is commonly carried out with an extra amount of methanol in order to shift the equilibrium towards the direction of methyl ester formation.

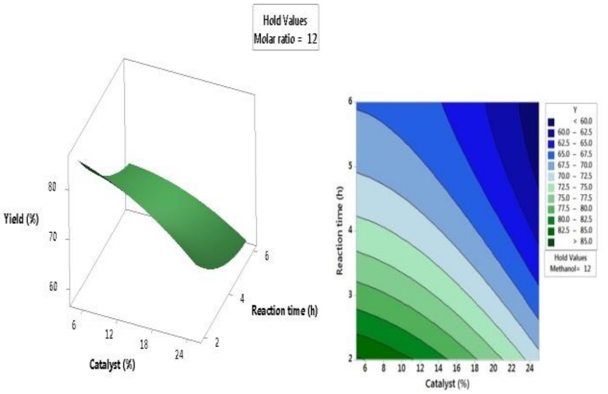
Figure 2 (a) and (b) reflects the effect of methanol to oil molar ratio on the yield conversion. As shown in this figure, the methanol to oil ratio has much greater effect on the increase of the yield percentage compared to catalyst loading. The yield increased from 55.52% to 88.06% with an increase in molar ratio of methanol to oil from ratio 8.43:1 to 15.57:1. Further increase in methanol to oil ratio up to18:1did not increase the yield. Higher ratio of methanol used could also minimize the contact of access triglyceride molecules on the catalyst's active sites which could decrease the catalyst activity [9]. Previous study from Gimbun [10] found that the optimum methanol to oil molar ratio was observed at 4:1 with more than 90% yield conversion using cement clinker as catalyst.



(a) (b)

Figure 2 Combined effects of alcohol molar ratio and catalyst (a) the three dimensional plot (b) contour plot

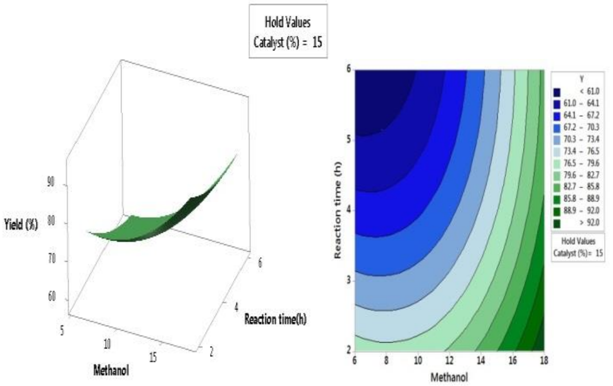
The effects of the amount of catalyst of calcined cockle on the conversion yield of biodiesel are illustrated both in Figure 3 (a) and (b). Applying the catalyst amount of 9.05%, the highest yield of 88.06% was obtained within 2.81 hours reaction time. Increasing the catalyst loading up to 25%, decreased the yield conversion to 64.22%. This is due to reversible nature of the transesterification process whereby the catalyst concentration levels greater than 9 wt% may have favored the backward reaction [10]. Due to the high surface area of calcined waste cockle catalyst, higher catalyst loading is not required [11]. A huge excess of catalyst contributed to the formation of soap that will lead to emulsion that increase the difficulty in separation process. Apart from that, the formation of soap will drive the losses of triglyceride molecules that can be used to produce biodiesel.



(a) (b)

Figure 3 Combined effects catalyst concentration reaction time (a) the three dimensional plot (b) contour plot

Similar trend can be observed in the performance of methanol to oil molar ratio and the reaction time as shown in Figure 3. There is a slight decreased in the FAME percentage when further increase in the reaction time. The individual effect of reaction time towards biodiesel yield has a negative correlation. The extending of the reaction time in the transesterification process may contribute to the decrease of biodiesel yield and causing more formation of free fatty acids.



(a) (b)

Figure 4 Combined effects of alcohol molar ratio and reaction time (a) the three dimensional plot (b) contour plot

3.3 Fuel Properties

The important fuel properties of the biodiesel produced from heterogeneous rubber seed oil methyl esters are compared with biodiesel and petro diesel standards and are presented in Table 6 [12]. Most of the physico-chemical properties of rubber seed oil methyl ester are comparable to those of biodiesel standard and petro-diesel. The heterogeneous transesterification process significantly reduced the viscosity and acid value of the oil.

Table 6 Comparison of Biodiesel Properties with ASTM Standard

Property	Unit	Biodiesel (RSO)	ASTM D-6751	EN 14212
Viscosity@ 40°C	mm^2/s	5.97	1.9 – 6.0	3.5-5
Acid Value	mgKOH/g	0.15	< 0.5	0.5 max
Flash Point	°C	157	> 93	120 min
Density	25°C kg/m^3	877	N/A	860-900

4.0 CONCLUSION

Using waste cockle shells as the primary heterogeneous catalyst in this study was found having a high potential to be commercialized as a cost effective catalyst in biodiesel production. From a very high FFA value as high as 78.9, it is treated via acid esterification method and proceed with transesterification process with final FFA value of 0.14. Overall biodiesel yield conversion is found to be as high as 88.06% via experimental and 86.44% yield conversion was achieved using RSM. Molar ratio of methanol to oil and catalyst loading played major roles in the production process. Using ratio of 15.57:1 methanol/oil, catalyst percentage of 9% and about 2.81 hours reaction time the optimum yield was achieved. Biodiesel properties are evaluated by standard methods. A significant reduction of viscosity and acid value is found.

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