BIODIESEL PRODUCTION FROM HIGH FFA RUBBER SEED OIL USING WASTE COCKLES

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ABSTRACT

A two-step heterogeneous catalyzed process of high free fatty acids (FFA) rubber seed oil was conducted to produce biodiesel in lab scale. Acid esterification process was first used to reduced the high FFA rubber seed oil from 78.9% to below 1%. The low cost cockle shell was utilized as a source of CaO heterogeneous catalyst by calcination process and its effect on transesterification process was studied. The optimum yield of 88.06% was obtained for the final product of biodiesel under optimal conditions of 16:1 molar ratio of methanol to oil, 9% catalyst weight percentage with 3 hours reaction time. All fuel properties were analysed according to the ASTM D 6751 standard and found within the requirements.

Keywords: rubber seed oil, biodiesel, waste cockle, transesterification.

INTRODUCTION

There are two main issues that must be considered when selecting biodiesel as a substitute fuel; (i) costs of feedstock and (ii) production process. These two issues have made many industries and researchers have shifted to the non-edible seeds for their potential biodiesel feedstock (Y.Yan *et al.*, 2014). The inexpensive of these 2nd generation feedstock has recently engrossed a great deal of attraction. In Malaysia for example, about 199,600 ton/year rubber seed oil was generated which made this plant as a promising source for producing highly efficient and yet quality biodiesel production.

It was reported by Department of Statistic Malaysia that around 1,244, 600 hectares of rubber plantation as of 2009 was developed in Malaysia producing more than 500 thousand tons of rubber seeds annually and this project aims to utilized these unused seeds to produce biodiesel. In paper of (Ramadhas *et al.*, 2005), reported that rubber seed oil consists 18.9% of saturated fatty acid (palmitic and stearic acids) and 80.5% unsaturated fatty acid (mainly of oleic, linoleic and linoleic acids). Saturation fatty acids will increase the cloud point, cetane number and improve oxidation stability. Moreover, (Ikwuagwu *et al.*, 2000) reported that rubber biodiesel has closer fuel properties with diesel fuel except slightly higher in viscosity.

Another major issue that need to be considered when dealing with this non- edible rubber seed oil is the high value of free fatty acids (FFA) and the increase in acid number. Some researchers (Marchetti and Errazu, 2008) reported that the large amount of FFA will contribute to the simultaneously soap production with the transesterification reaction. Via two steps process-acid esterification and base transesterification, the value of FFA should be less than 1% (M. Kouzu, J. Hidaka, 2012). in order to be utilized in a transesterification reaction.

Using heterogeneous catalysts transesterification from waste sources has become significant and popular as one of the alternatives to reduce the production cost. The major advantages of using heterogeneous catalysts is it's reusability that can reach more than 10 times, decrease the purification steps and reduce the amount of water used. 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 (F.N. Ani and A. Bakheit Elhameed, 2014). Apart from lower in cost, it also can withstand high temperatures and their performance are reported is comparable to homogeneous catalyst biodiesel production (M. Kouzu, 2008). Catalyst from mollusk shell such as mussel, cockle, scallop, oyster and crab can easily be found along coastal area and their waste shells production is quite large (A. Buasri, 2013). As the main source of CaO these highly potential catalyst has been of recent interest in the search for a sustainable process.

This aim of the present work is to investigate the performances of the heterogeneous catalyst derived from waste cockle on the production of biodiesel via two step process; acid esterification and base transesterification process. Furthermore, the effects of the selected process parameters such as reaction time, ratio of methanol to oil and catalyst concentration that influenced the yield production of the transesterification of high FFA rubber seed oils were also investigated.

METHODOLOGY

Materials and chemicals

The crude rubber seed oil with FFA value of 39.69% and acid value of 78.9 was purchased from Kinetics Chemical (M) Sdn Bhd, Malaysia. Chemicals that being 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 cockles purchased from local seafood restaurant in Melaka, Malaysia.

Catalyst preparation and characterization

The waste cockle shells were washed with raw water until all traces of dirt and dust were removed. The clean samples were sun dried for 2-3 days and then dried in the oven at 100 °C for 3 to 4 hours. The dried waste shells were then calcined in a furnace at 900 °C in air atm with a heating rate of 10 °C/min for 4 hours (A. Buasri *et al.,* 2013). The samples were crushed and grounded to different particles sizes (2 mm - 4 mm) using pestle and mortar. All calcined samples were kept in the close vessel to avoid the reaction with carbon dioxide (CO_2) and humidity in air before being used. All the produce catalyst samples were then stored in a highly sealed glass jars (desiccator) for later reactions.

Under catalyst characterization analysis, the chemical composition of cockle was observed using x-ray fluorescence in- build XRD (ARL 8660S) and SEM-EDS technique. The scanning electron microscopy with energy dispersive X-ray detector (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. The samples were coated with gold using a Sputter Coater The element composition was analyzed by using an energy dispersive X-ray detector (EDS) mounted on the microscope.

Properties of rubber seed oil

The pre- test of crude rubber seed oil (RSO) was conducted and the test result was tabulated as in Table-1. All tests were tested according to the Standard ASTM D675, EN 14214 and AOCS method. The crude RSO was sent for the gas chromatography analysis to determine the composition of the crude oil

Acid esterification

The esterification process is a pre-treatment process for the feedstock oil with the aim to reduce the FFA content. High FFA content may contributed to some negative effects on the production namely higher saponification level that lead to low yield production (M.M. Zamberi *et al*., 2011). 50 g of crude RSO was placed in a 250 ml three-necked round-bottomed flask and being heated to 60 °C while stirred with magnetic stirrer under atmospheric conditions to homogenize the oil. The concentrated sulphuric acid and methanol are measured according to selected ratio which is 10:1 methanol to oil ratio and 10% of the total weight of rubberseed oil for sulfuric acid and mixed together before heated to 60 °C. The reaction mixture was then added to the reaction flask containing preheated oil and again stirred for specific time. The temperature of the mixture was maintained at 45 °C and stirred for 90 minutes. The mixture was then poured into the separating funnel and left overnight so that separation can occur. After separation occurred, three different layers are present in the separation funnel, the bottom layer was glycerine, the middle layer was excess methanol and the top layer was the treated rubberseed oil. The bottom layer and middle layer are removed and the treated rubberseed oil was washed with distilled hot water. After washing, the sample was filtered in order to remove any contaminant in it. The amount of FFA content remaining was determined before conducting the transesterification process.

Table-1. Properties of methyl ester of crude rubber seeds oil.

Test	Unit	Method	Results
Acid Value	mg KOH/g	ASTM D664	78.9
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
Iodine Value	($g\ I_2/100\ g$)	AOCS Id 3-92	129.8

Heterogeneous catalyst transesterification

Transesterification process is done by heating 50g of rubber seed oil to a selected temperature which ranges from 60 to 64 °C on a constant temperature electric heater with magnetic stirrer. Methanol and the catalyst is measured according to pre-determined ratio and mixed beforehand. The mixed methanol and cockle are heated up to 60 °C and at the same time rubber seed oil was also heated before it being mixed together. The mixture was stirred at all-time throughout the transesterification process. The measurement of temperature was observed by using a digital thermocouple at certain interval. After the reaction time was over, 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 ester was the end product obtained which is the biodiesel. The yield obtained was calculated using the formula shown in equation (1):

$$\text{Yield (\%)} = \frac{\text{Raw RSO weight,g}}{\text{Biodiesel (Ester) weight,g}} \quad (1)$$

RESULT AND DISSCUSSIONS

Characterization of waste calcined shells

The elemental composition analysis of the calcined sample with XRF spectroscopy was tabulated as shown in Table-2. This results indicated that it was composed mainly of calcium oxide with 93.98, wt.%. These results indicated that all $CaCO_3$ in the samples was completely transformed to CaO. The X-ray diffraction pattern (XRD) for calcined catalyst at 900 °C for 4 hours is shown is Figure-1. The presence of CaO and $CaCO_3$ was clearly show in the analysis. Most of the diffractogram of CaO gave intensified and narrowed peaks at 2θ angles of 32.2°, 37.3° and 53.8°. It is clearly observed indicated by the highest peak that the major component of the calcined cockle at 900oC for 4h was CaO species.

Table-2. Chemical composition of calcined cockle with XRF-XRD.

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

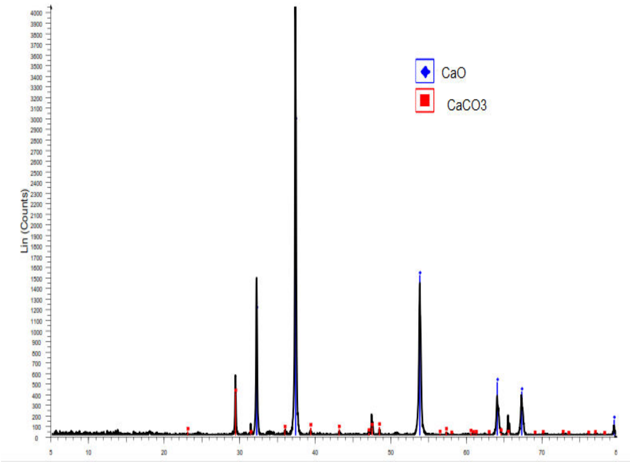

Figure-1. X-ray structure of the calcined cockle catalyst at 900 °C for 4 hours.

Figure-2. SEM images of the heterogeneous cockle calcined at 900 °C for 4 hours.

Figure-2 shows the surface morphologies of the calcined heterogeneous catalyst which gave an irregular in shape and some of them bonded together as aggregate (A. Buasri *et al.,* 2013). 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.

Effect of variables on transesterification process

In this study, there are three parameters that play important roles in transesterification process namely reaction time, methanol to oil molar ratio and catalyst loading. The performances of the transesterification process were also associated with the type of catalysts used. 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.

Effect of methanol to oil molar ratio

Figure-3 presented the effect of methanol to oil molar ratio on the yield conversion over the calcined waste cockle catalyst. As shown in this figure, the yield conversion was increased from 66.82% at 6:1 molar ratio to 88.06% at 16:1 molar ratio. This results is consistent with findings by (C. Ngamcharussrivichai *et al.,* 2007) which found that the amount of molar ratio of methanol to oil at the ratio of 10 or lower than that is not sufficient enough to dissolve the oil and catalyst phase.

It was also reported that by increasing the ratio of methanoil to oil up to 15, will led the mixture become more miscible and enhance the transesterification process. However, further increased in methanol to oil molar ratio up to 18:1 result in decreased of biodiesel yield conversion which is due to the reversible transesterification process. The present findings also found that the formation of soap was not developed in all experiments (X.Deng *et al.*, 2011).

Effect of catalyst amount

The effect of catalyst concentration on the biodiesel conversion yield are illustrated in Figure-4. Applying the catalyst amount of 9 wt. %, the highest yield of 88.06% was obtained within 3 hours reaction time. As shown in the Figure-4, the yield conversion was decreased to 64.22% after amount of the catalyst loading up to 25 wt.%. The result is in the line with findings by Gimbun and Ilgen (J. Gimbun *et al.*, 2013), (O.ilgen, 2011) which reported that the catalyst concentration levels which is greater than 9 wt% may have not able to promote the reaction to form more prodcuts because it is already achieved the equilibrium state. Another finding by (W.Roschat *et al.*, 2012) also highlight the effect of high surface area of calcined waste cockle catalyst which ot required higher catalyst loading. 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.

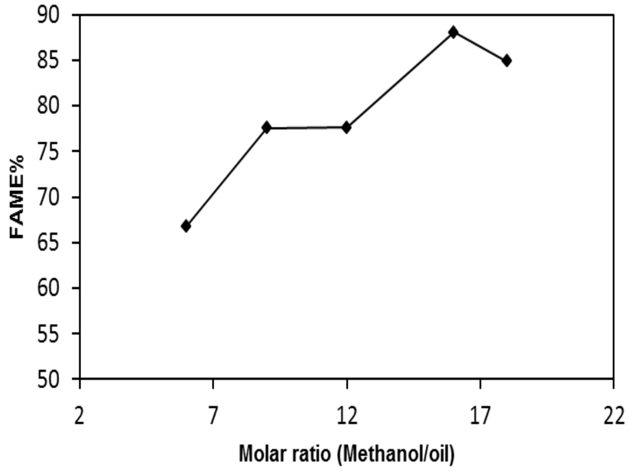

Figure-3. Effect of methanol to oil molar ratio on the biodiesel yield. Reaction conditions: catalyst loading, 9 wt%, reaction time, 3h and reaction temperature ±65 ^{0}C.

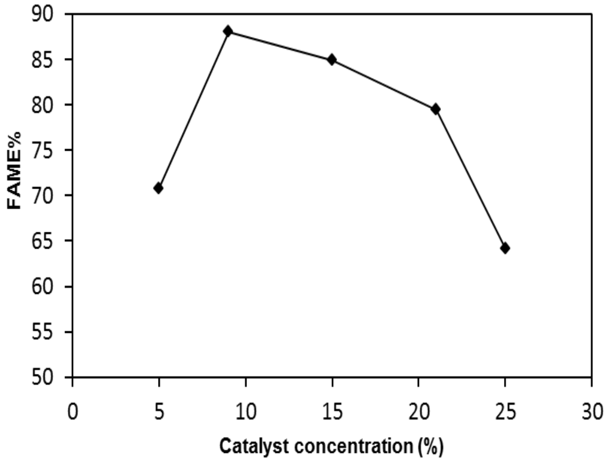

Figure-4. Effect of catalyst concentration on the biodiesel yield. Reaction conditions: methanol to oil molar ratio, 16:1, reaction time, 3h and reaction temperature ±65 ^{0}C.

Effect of reaction temperature

Similar trend can be observed in the effect of reaction time as shown in Figure-5. There is a slight decreased in the FAME percentage when further increased in the reaction time. The maximum yield of 88.06% was obtained in 3h reaction time and continues to diminish in about 6h of reaction. 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 decreased of biodiesel yield and accelerate the ester formation (K. Srilatha *et al.*, 2012). The reversible process between oil and alcohol during the long period of transesterification process may also contributed to this phenomena (C. Samart *et al.*, 2009).

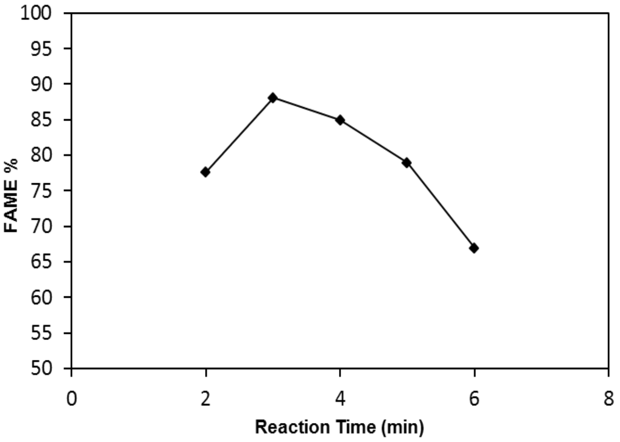

Figure-5. Effect of reaction time on the biodiesel yield. Reaction conditions: methanol to oil molar ratio, 16:1, catalyst loading, 9 wt% and reaction temperature ±65 ^{0}C.

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 (M. Morshed, 2011) and are presented in Table-3. 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-3. Comparison of biodiesel properties with ASTM standard.

Property	**Unit**	**Biodiesel** (RSO)	**ASTM 6751-02**	**Diesel**
Viscosity @40°C	mm^2/s	5.94	1.9 – 6.0	1.4-4.1
Acid Value	mgKOH/g	0.14	< 0.5	-
Flash Point	°C	149	> 93	60-80

CONCLUSIONS

Biodiesel production from transesterification process of high fatty acids (FFA) rubber seeds oil using cost effective waste calcined cockle shells is investigated in the present study. The waste cockle contains $CaCO_3$ and then was calcined at 900 °C for 4 hours to transform it into CaO species. From very high FFA with acid value as high as 78.9, it is treated via acid esterification method to reduces the FFA content and proceed with transesterification process with final acid value of 0.14. Overall biodiesel yield conversion was found as high as 88.06%. Molar ratio of methanol to oil and catalyst loading played major role in the production process. Using ratio of 16:1 methanol/oil, catalyst percentage about 9 wt. % and about 3 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. The waste cockle was found had high potential to be commercialized as a green low cost heterogeneous catalyst. The produce biodiesel also indicated that rubber seed oil is a promising non edible feedstock for green fuel.

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