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Cockles Shell as Heterogeneous Catalyst for Biodiesel production from Jatropha seed oil

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Abstract

Cockles shell currently found to be a potential alternative and biomass-driven source for calcium oxide (CaO). It fits to be the best candidate as the alternative material as they are made up of at least 95% of calcium carbonate ($CaCO_3$). In this research, biodiesel production by transesterification of crude *Jatropha curcas* oil (CJCO) has been studied using a cockle shell as a heterogenous catalyst. The calcium oxides; heterogeneous catalyst were produced from the calcination process of cockles shell at various temperature range from 600 to 800°C. Different catalyst dosage have been used during the transesterification process. The amounts of catalyst added were varied from 0.5 wt% until 2.0 wt%. It was found that 94% of conversion was achieved when 1.5 wt % of 700 °C calcination temperature catalyst was added into the transesterification process. The component of fatty acids profiles contain within the biodiesel from CJCO were obtained using gas chromatography (GC) and found to be significant with the standard fatty acid methyl ester (FAME). The physical properties analysis results indicated that the value of flash point, relative density and kinematic viscosity were within the range of American Society for Testing and Materials (ASTM) standard for biodiesel.

Keywords: Cockles shell, Heterogeneous catalyst, Biodiesel, Jatropha seed oil, Transesterification

Introduction

The depletion of petroleum-derived fuels, the threat of climate changes and increasing prices for petroleum products have influenced researchers to seek alternative energy sources. Therefore, for several decades, many researchers have been developing new alternative energy sources that are readily available, technically feasible, economically viable and environmentally acceptable Biodiesel has been accepted worldwide as the immediate solution to the heavily reliance on petroleum- derived diesel oil. Adding with the global warming issues that the earth are suffering, thus it is essential to find new alternative transportation fuel that emitting less dangerous gaseous in to the environment (Aleklett *et al.*, 2010).

However, current commercial production technologies of biodiesel through chemicals transesterification have a lot of limitations and contribute to the high cost of production with a less yield of biodiesel. Therefore, a research of new unusual among tree crops has been done. *Jatropha Curcas* seed oil has the ability to be processed into biodiesel, which having the similar properties to the diesel fuel. The reason why this seed is not being preferable among the But due the additional process that needed to be done during the transesterification process it become unfavorable to industries (Rahman *et al.*, 2014).

Conventionally, homogeneous catalysts are commonly applied in the transesterification of vegetable oils. However, they are difficult to recover, lead to downstream waste treatment and increasing the cost of biodiesel production (Kumar *et al.*, 2010). The application of heterogeneous catalysts appears promising because they can simplify the production and purification processes, decrease the amount of basic waste water, downsize the process equipment, and reduce the environmental impact and process cost. Unlike homogeneous, heterogeneous catalysts can be recycled and used several times with better separation of the final product and can be used in a continuous process without the need for further purification steps (Nakatani *et al*., 2009).

Calcium oxide has attracted much attention for transesterification reaction since it has high basic strength and less environmental impact due to its low solubility in methanol and can be synthesized from cheap sources (Zhang *et al*., 2010).

The aim for this study is to identify the capability of cockle shell as heterogeneous catalyst for biodiesel production from *Jatropha Curcas* seed and to determine the optimum conditions for the process. The composition of fatty acid methyl ester and the physical properties of the biodiesel produced were measured and compared with the ASTM standard value.

Materials and Methods

Preparation of Feedstock

CJCO was purchased from Energy Farm Sdn. Bhd. at Pantai Klebang, Melaka. It was extracted from the *Jatropha curcas* seed by using oil pressed method.

Preparation of Catalyst

The cockle shells were obtained from the market. It was thoroughly washed with tap water for several times to remove dirt and subsequently sun–dried for 1 day. The shells were crushed into fine pieces using kitchen mortar and sieved using 500 µm sieve tray. Then the powdered shells were heated in the furnace for two hours three different temperature of 600, 700 and 800 °C. The sample was cooled down to room temperature to ensure the completion of the process.

Esterification process

The main purpose of the esterification process is to reduce the free fatty acid (FFA) content in crude oil below 2%. This is done by pouring 100g of raw oil into a beaker and heated to 65 °C. Then the mixture of methanol and 1 wt% of sulphuric acid were added into the beaker. The reaction was run for 45 minutes. After acid-catalyzed transesterification step, the mixture was cooled and allowed to settle overnight. The top layer of methanol–water fraction was then removed.

Transesterification Process

100 grams of treated Jatropha oil was poured into 250 mL conical flask and heated to a temperature of 65°C. Then, the mixture of CaO and methanol solution (ratio methanol to oil of 3.5:1) was slowly added to the heated oil. The mixture was heated and stirred at reaction temperature of 60°C and reaction time of 30 minutes. The catalyst dosages used were varied from 0.5 wt% to 2.0 wt%. The mixture was then allowed to settle for 24 hours in a separating funnel. The biodiesel was then poured into a separate beaker, while the lower layer (which comprises of glycerol and soap) was collected from the bottom of the separating funnel. Warm water was then used to wash the biodiesel to remove any excess glycerol and soap that remain in the funnel. The reaction was repeated by varying the catalyst dosage and calcination temperature as shown in Table 1.

Table 1. Run of experiment.

Calcination Temperature (°C)	**600**	**700**	**800**
Amount of Catalyst (gram)	0.5	0.5	0.5
	1.0	1.0	1.0
	1.5	1.5	1.5
	2.0	2.0	2.0

Determination of FFA

The FFA in the oil was determined by titrating it against Sodium hydroxide (NaOH) using phenolphthalein as indicator. 5 g of oil was dissolved in 50 mL of isopropanol in 250 mL conical flask, 3 to 4 drops of phenolphthalein indicator was then added and titrated against 0.1 M NaOH. The content was constantly stirred until a pink colour which persisted for fifteen seconds was obtained. The volume of titration solution was recorded and the percentage of FFA was calculated by using the following equation.

$$\%FFA = \frac{V \times M \times 28.2}{W} \qquad \text{Eq. 1}$$

Where:
V = Volume of titration solution in mL
M = Molarity of NaOH solution
W = Weight of the sample in g

Characterization of the biodiesel produced

A. Determination of FAME composition

The composition of biodiesel products were analyzed using a GC equipped with flame ionization detector and capillary column fused silica (30m x 0.25mm x 0.25mm). Hydrogen and inert air was used as carrier gas and hexane was used as injection flusher. The injector temperature was programmed about 200°C and the detector at a temperature higher than the column with flow rate of 20 psi. 0.1µL of methyl ester solution was injected to the equipment for analyzing. The formed methyl ester was identified by comparing the retention time of FAME standards.

B. Determination of Kinematic Viscosity

The viscosity of biodiesel produced was tested using Polyviscometer. The oil was filled in a measuring cylinder. The spindle which is the number three, will be submerge in this sample. This spindle was stirred at 30 rpm. The viscosity of the oil was obtained when the reading is stable. The viscosity reading was appeared at the front panel.

C. Determination of Density

Digital densitometer was used to determine the density of the biodiesel. 2 – 5 ml of oil was introduced into the instrument by pushing and releasing the pump button. The result was appeared on the display.

D. Determination of Flash Point

The Pensky-Martens Flash Point Close Cup Tester (FP93 5G2) was used to determine the flash point of biodiesel produced. The method implied in the equipment was ASTM D93-13.

Results and Discussions

Effect of Calcination Temperature

Figure 1 shows that the yield of biodiesel was increased from 90.4% to 94% as the calcinations temperature increase from 600 to 700 °C. As the temperature keeps increasing to 800 °C, the yield is slowly reduced to 92.3%. The same finding was found by Granados *et al.* (2007).

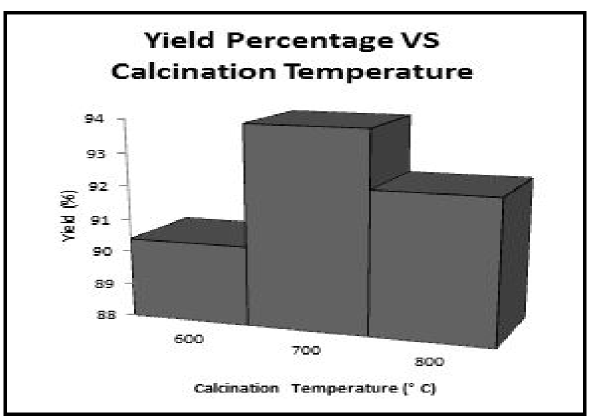

Figure 1. Effect of calcination temperature on biodiesel yield; 600 – 800 °C.

Rashidi *et al.* (2011) stated that the catalytic activities depended significantly on the calcination temperature, and for all cases, the optimum calcination temperature was found to be 800 °C. The existence of the same optimum calcination temperature for all reactions indicates the relationship between catalyst physico-chemical properties, such as, crystalline structure and molecular structure of the metal oxide overlayer and acid site density and strength.

Effect of Catalyst Dosage on Transesterification Process

Figure 2 shows the effect of catalyst dosage and calcination temperature on the transesterification process. The catalyst dosage of 1.5 wt% at calcination temperature of 700 °C showed a tremendous yield percentage of biodiesel (94%). It was proved by previous research done by Mehta (2001). About 95% of yield was obtained by using 1.5 wt% of catalyst dosage.

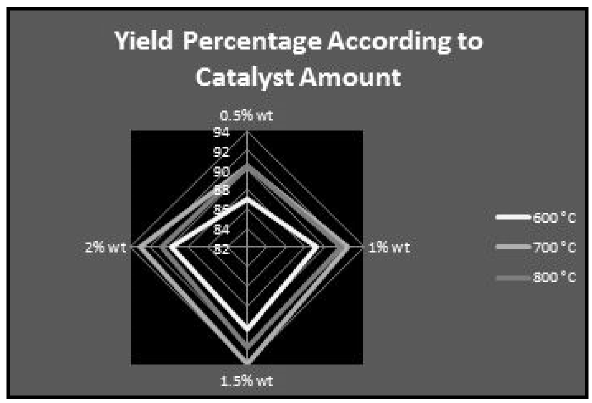

Figure 2. Effect of Catalyst Dosage for different Calcination Temperature; 0.5 – 2.0 wt%.

However, the yield of biodiesel was decreased as the catalyst dosage increase to 2.0 wt%. According to Hawash *et al.* (2011), more products will be adsorbed into the catalyst as the catalyst dosage increase. Pinzzi *et al.* (2011) stated that catalyst act as a enhancer to the reaction where it helps in breaking the bond of the free fatty acid chain with the glycerol in order to enable the methanol molecule to combine with the glycerol producing FAME. Thus, if the amount of catalyst dosage used in the process is insufficient, the breaking process will also being affected, hence resulting in incomplete transesterification where only small portion of biodiesel could be produced. While the excess catalyst causes more triglycerides participation in the saponification reaction leading to a marked reduction in the ester yield.

Characterization of biodiesel produced

A. FAME composition

According to Emil Akbar (2009), the major fatty acids contain in *Jatropha* seed oil were oleic acid, linoleic acid, palmitic acid and the stearic acid. Based on Figure 3, Oleic acid showed the highest percentage of composition of 39.54% followed by linoleic acid with 36.3%. From a previous study, Jatropha oil were known as oleic-linoleic oil since this two fatty acid will presented the most in the oil (Gerpen *et al.*, 2007). It was found that the percentage composition of fatty acid methyl ester occurred are nearest to standard as compared to Berchmans and Hirata (2008) finding .

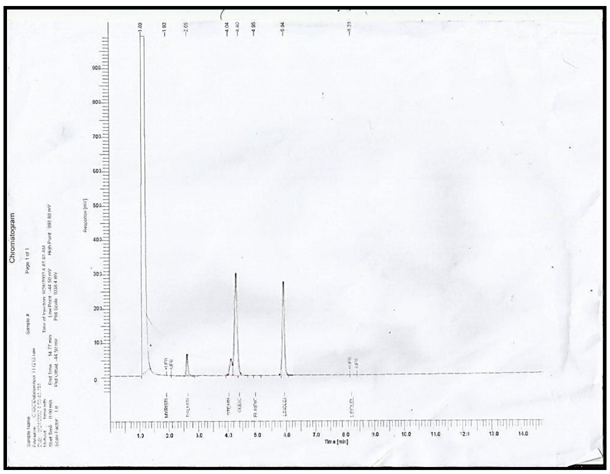

Figure 3. Chromatograms of FAME.

B. Physical properties

The physical properties of the biodiesel produced were evaluated based on certain parameters. The physical characteristics that have been obtained were showed in Table 2. It was found that the value of flash point, relative density and kinematic viscosity obtained are well within the range of ASTM standard (Luque de Castro and Dorado, 2011).

Table 2. Physical Properties of biodiesel produced.

Physical Properties	Result
Flash Point	>130 °C
Kinematic Viscosity	3 mm^2/sec
Relative Density	909.4 kg/m^3
Total Acid Number	0.164 mgKOH/gram

Conclusions

Calcium oxide produced from cockles shell was found to be a potential alternative of heterogeneous catalyst for biodesel production. The highest yield of biodiesel were achieved by using 1.5 wt % of 700 °C calcination temperature catalyst. The component of fatty acids profiles contain within the biodiesel from CJCO found to be significant with the standard FAME.

The physical properties values were found to be within the range of ASTM standard for biodiesel.

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