Utilization of cacao peel waste to K_2O heterogeneous catalyst in biodiesel synthesis by waste cooking oil: effect of catalyst calcination temperature

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Abstract. Calcination is one way to take advantage of K_2O content of cocoa pods husks potential as a catalyst in the production of biodiesel. The purpose of this research is the utilization of waste pod husks as heterogeneous catalysts in the manufacture of biodiesel from waste cooking oil. The catalyst preparation procedure of the cocoa shell ash is waste cocoa husk first cleaned by washing, so free from impurities such as mud and other substances. The peel then cut into small pieces and dried in the sun for two weeks to reduce the water content of the cocoa peel and smoothed by using ballmill. In this study, an analysis that is proximate analysis such as the water content of the sample and the catalyst, volatile matter, ash content, yield of ash, fixed carbon, pH and also do analysis of the pore structure of the catalyst by using analysis of SEM-EDS analysis and potassium (K_2O) with AAS analysis. The best conditions are obtained the purity of 99.58% with a methyl ester methyl ester yield of 92.68% with a mole ratio of alcohol and the use of used cooking oil 12: 1, a reaction temperature of 65°C, the amount of catalyst is 6% (w / w) which are calcined at a temperature of 650 °C and reaction time of 180 minutes. The results of the present study indicate that the use of cocoa peel and used cooking oil is a catalyst and cheap raw materials suitable in the manufacture of biodiesel.

Keywords: biodiesel, potassium oxide, calcining, waste cooking oil, transesterification

1. Introduction

The catalyst is one of the materials used in the manufacture of biodiesel. Generally, basic heterogen catalysts are used in the manufacture of commercial biodiesel through the trans esterification process. The alkaline catalyst has been acknowledged to give a greater conversion than the acid catalyst. Commonly used alkali catalysts are CaO and K_2O. As done by Sinaga *et all*, 2016. Methyl esters are produced from Crude Palm Oil with CaO catalysts derived from chicken bones. In this study, cocoa skin heterogeneous catalysts were used [1-4].

Cacao (*Theobrema cacao* L.) is one of the leading commodities of plantation sub-sector. Cocoa occupies the fourth largest area after palm oil, coconut and rubber. Cocoa shells (CPH/Cocoa Pod Husk) are one of the heterogeneous base catalyst types. Cocoa leather is the main agricultural waste of the cocoa industry and has been found to be a rich source of potassium carbonate (K_2CO_3). One way to utilize K_2CO_3 content from cocoa skin is by calcination process [5-7].

Calcination is the process of heat dissipation under the melting point of a solid material under vacuum for the occurrence of thermal decomposition, phase transition or the removal of the volatile fractions, the formation of oxides such as potassium oxide (K_2O) and oxide reactions with buffers [8]. As for the reaction that occurs at the time of calcination is:

$$K_2CO_3 \rightarrow K_2O + CO_2$$

Cocoa peel (CPH) after the calcination process will turn K_2CO_3 into K_2O which can be used as a catalyst for biodiesel production. Biodiesel is a mono alkyl ester of fatty acids such as from vegetable oils and animal fats used as a substitute for fossil fuels (diesel) and is tangled, as a clean and sustainable alternative fuel. Cooking oil is a promising raw material as a substitute for vegetable oil for biodiesel production [9,10].

2. Method

The raw materials used in this research are waste cooking oil obtained from fried sellers around campus of University of Sumatera Utara (USU), methanol obtained from Rudang Jaya chemical store and cocoa leather as catalyst obtained from cocoa plantation. The equipment used is hot plate, furnace, digital scales, Ostwald viscometer, ball mill, and oven. The research was carried out with variations of catalyst temperature of 650, 700 and 750ºC, time variation of 2,3,4 hours with comparison of methanol molar ratio: oil 9:1, 12:1 and 15:1 at catalytic percentage 6% and reaction temperature 65 ºC with 500 rpm rotation.

2.1 Preparation stage of cocoa fruit peel ash.

Cacao peel is calcined in a furnace with variations in combustion temperatures of 650, 700, and 750 ºC for 4 hours to ash. Determination of potassium content in cacao peel ash was analyzed by atomic absorption spectrophotometer (AAS).

2.2 Pretreatment process of raw material waste cooking oil.

The first steps are filtering WCO with Whatman filter paper number 41, cooking oil is accommodated and silenced for a few days then raw material is weighed. Two oil-water emulsion layers are formed. The oil-water emulsion is heated for approximately 30 minutes at a temperature of 110ºC to remove the water content by hot plate.

2.3 Analysis of FFA (Free Fatty Acid) content by AOCS ca5a-40 method.

A total of 20 g of WCO sample were fed into the erlenmeyer flask and then 150 m of 95% ethanol (v/v) was added. The mixture is shaken strongly until the sample is dissolved and taken as much as 10 ml. Added 3 drops of phenolphthalein indicator and then titrated with 0.1 N NaOH until it turns from clear to red rose. Note the volume of 0.1 N NaOH used.

2.4 Process of Decreasing FFA Levels of Waste Cooking Oil

This FFA decrease procedure is performed by adopting a procedure performed by Putra et al [9] with some modifications: WVO (WCO) filtered with filter paper to remove impurities, then weighed 50 grams and heated to 110°C, 0.5 g of activated carbon (1% w/w) and then stirred for 80 min. The mixture is filtered and FFA concentration analysis procedure is performed, if FFA level is <1%, then proceed to trans esterification process.

The results obtained are then analyzed quantitatively and qualitatively ie yield, purity, density and viscosity analysis in accordance with Indonesian National Standard (SNI 04-7182-2012) shown in Table 1 [10] below:

Table 1. Biodiesel quality requirements

Parameters and Units	Value Limit
Purity (%)	>96
Biodiesel density at 40ºC (kg/m^3)	850-890
Kinematic viscosity at 40ºC mm^2/s (cSt)	2,3-6

3. Result

This WCO raw material was analyzed by using GC (Gas Chromatography) to find out the composition of the fatty acids contained therein and to calculate the molecular weight of WCO (in the form of triglycerides).

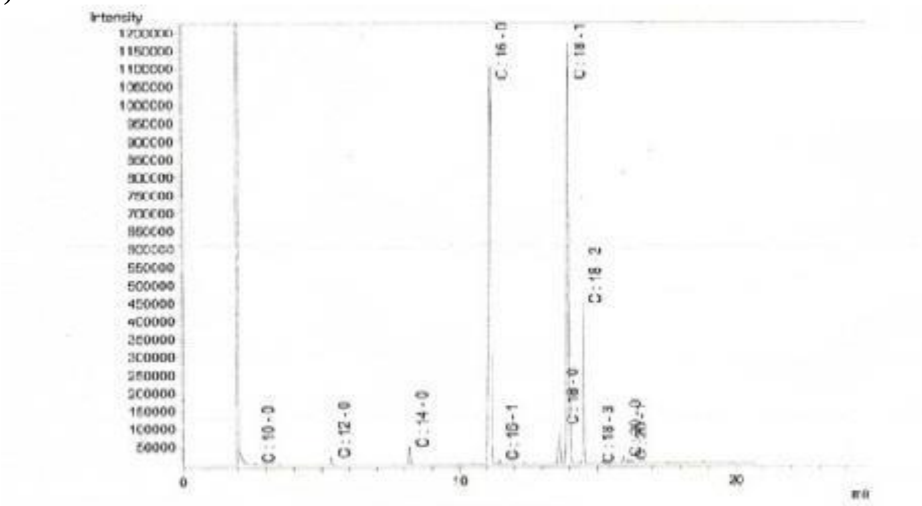

Figure 1. Result of GC analysis of fatty acid composition from WCO

Figure 1 is the composition of WCO fatty acids of GC analysis analyzed at the Laboratory of Research Center for Oil Palm (PPKS) Jl. Brigjen Katamso 51, Medan by using the GC type Shimadzu QP 2010 Brands. The following is the composition of WCO fatty acids GC results can be seen in Table 2.

Table 2. Fatty acid composition of WWC results

No	Physic properties and components	Value
1.	Saturaty Fatty Acids	
	- Decanoic acid ($C_{10:0}$)	0.07777
	- Lauric acid ($C_{12:0}$)	0.3935
	- Mirroric acid ($C_{14:0}$)	0.9550
	- Palmitic acid ($C_{16:0}$)	41.0134
	- Stearic acid ($C_{18:0}$)	3.9562
	- Arachid acid ($C_{20:0}$)	0.3465
	Total	46.725
2.	Unsaturated Fatty Acid	
	- Palmitoleic acid ($C_{16:1}$)	0.2126
	- Oleic acid ($C_{18:1}$)	44.1591
	- Linoleic acid ($C_{18:2}$)	8.7113
	- Linolenic acid ($C_{18:3}$)	0.0819
	- Eicobioc acid ($C_{20:1}$)	0.1559
	Total	53.257

Based on GC analysis, fatty acid composition of WCO can be seen in the above table. From the calculation, the average molecular weight of FFA Waste Cooking Oil is 270.005 g/mol and the average molecular weight of Waste Cooking Oil (in the form of triglyceride) is 848.1908 g/mol. The content of saturated fatty acids in the sample of cooking oil is 46.725% and unsaturated fatty acids of 53.257%. WCO Free Fatty Acids can be seen in Table 3.

Table 3. WCO free fatty acids

FFA Content (%)		
Before Pretreatment	After Pretreatment	% Decreasing
3.13	0.82	73.80

From the above Table 3 it can be seen that with WCO pretreatment with free fatty acid free car is 0.82% (has <1%).

3.1 Morphological Characteristic Analysis and Potassium and K2O Levels of Cocoa Peel Absorption

The correlation of cocoa skin calcination temperature to potassium and K_2O levels can be seen in Figure 2.

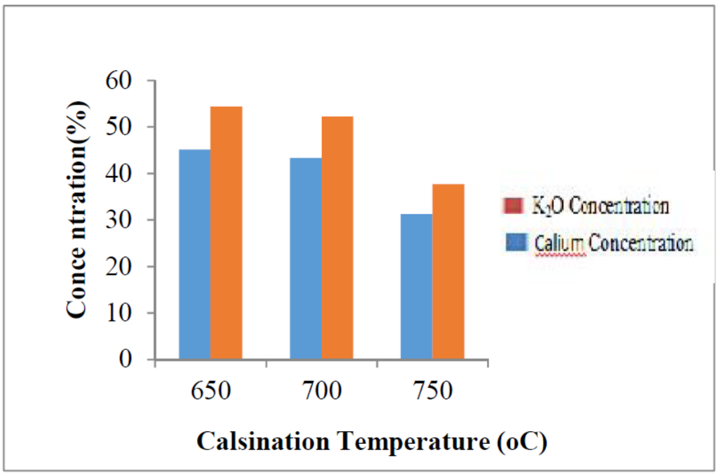

Figure 2. Effect of calcination temperature of cacao husk ash on potassium and K_2O

From Figure 2 it can be seen that the content of K_2O produced from cocoa husk ash at the calcination temperature of 650, 700 and 750°C for 4 hours respectively is 54.38%, 52.18%, and 37.70%. From Figure 2 it can be seen that the higher the calcination temperature, causing the component of potassium content of cocoa ash to decrease. This suggests that high combustion temperatures lead to the decline of alkali ions, especially potassium ions, thus decreasing carbonate ion ($CO3^{2-}$) composition and catalyst activity [8]. Here is the result of SEM test on catalyst with calcination of 650°C can be seen in the following Figure 3.

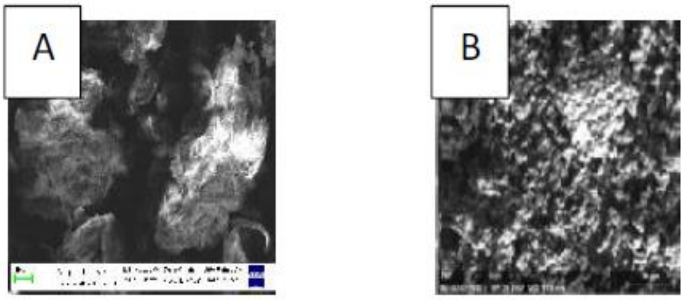

Figure 3. Results of SEM analysis of cocoa peel catalyst at 1000 x magnification: (a) before calcination and (b) after calcination at 650°C for 4 hours

3.2 Effect of reaction time and temperature of calcination of catalyst on biodiesel yield

The relation of reaction time and temperature of catalyst calcination to yield of biodiesel can be seen in Figure 4.

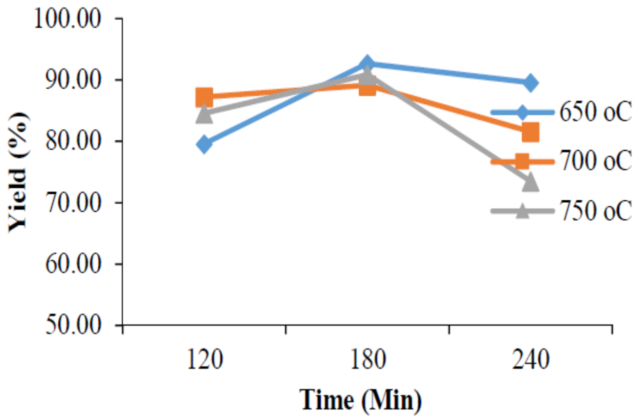

Figure 4. Relation of reaction time and temperature of catalyst calcination to yield of biodiesel at reaction temperature condition 65°C and ratio ratio of methanol: oil 12: 1.

The increasing reaction time results in increased biodiesel yields [11]. In addition to the reaction time, the yield of biodiesel is also influenced by the temperature of calcination. The temperature of calcination is too high then it causes the component of the potassium content to decrease [12]. From Figure 4 it can be seen that the best conditions obtained were at the reaction time of 180 minutes, the ratio of mole ratio of alcohol and 1 oil, the reaction temperature of 65°C, and the number of 6% calculated K_2O 6% catalysts at 650°C, gave a biodiesel yield of 92.68%.

3.3 Effect of reaction time and temperature of calcination of catalyst on purity of biodiesel

The relation of reaction time and temperature of catalyst calcination to purity of biodiesel can be seen in Figure 5.

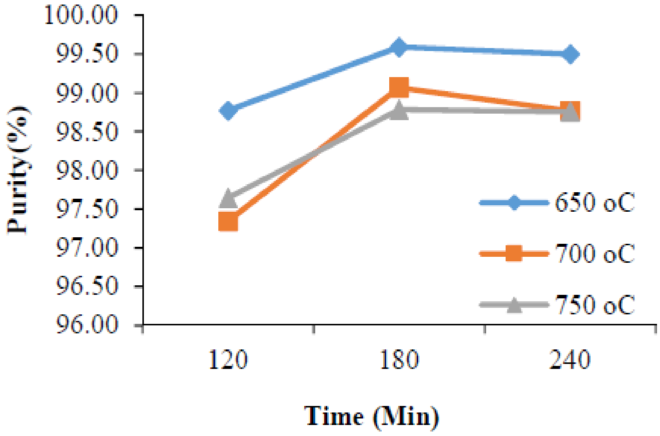

Figure 5. Relation between reaction time and temperature of calcined catalyst on biodiesel purity at condition of reaction temperature 65 °C and methanol molar ratio: oil 12: 1

Biodiesel purity increases with increasing reaction time but when the reaction equilibrium is reached the purity decreases [13]. In addition to reaction time, the purity of biodiesel is also influenced by the temperature of the calcination of the catalyst. The higher the calcination temperature then causes the component of potassium content of the cocoa ash to be reduced [12].

From Figure 5 it can be seen that the best conditions obtained are in the ratio of mole ratio of alcohol and 12: 1 oil, reaction time 180 min, reaction temperature 6 °C, and the amount of 6% calcined K2O 6% catalyst gives a biodiesel purity of 99. 5874%.

3.4 Density Analysis

The relation between reaction time and catalyst calcination temperature to biodiesel density at reaction temperature condition 65 ºC and ratio molar ratio of methanol: oil 12: 1 can be seen in Figure 6.

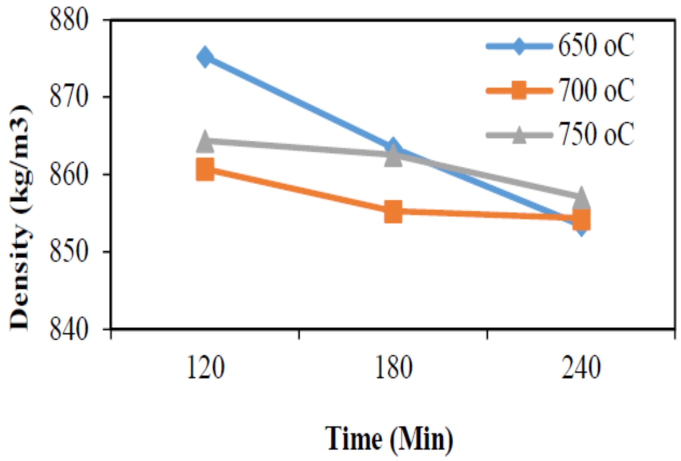

Figure 6. Relationship between reaction time and catalyst calcination temperature to biodiesel density at condition of reaction temperature 65 ºC and methanol molar ratio: oil 12:1

From Figure 6 it can be seen that the longer the reaction time the density of biodiesel produced will be smaller. This is because there has been a breakdown of glycerol from triglycerides to form compounds with smaller molecular sizes [14]. The results of this study have been in accordance with the existing theory that the longer reaction time takes place the resulting density will be smallen [15]. According to Indonesian National Standard (SNI 04-7182-2012), the biodiesel density at 40°C is 850-890 kg/m^3 [10]. From the research results for various variations, the density ranged from 850-875 kg/m^3. Thus, the biodiesel obtained has met the biodiesel density standard.

4. Conclusion

The pretreatment process of purifying the cooking oil by using activated carbon can lower the free fatty acid (ALB) from 3.13% to 0.82%. The content of potassium ash of cocoa husk at the calcination temperature of 650, 700, and 750ºC was 45.13%, 43.30% and 31.28%, respectively, while the K2O content at the calcining temperature was 650, 700, and 750ºC respectively 54.38%, 52.18%, and 37.70% respectively. The highest yield and methyl ester yield was 99.5874%, and 92.68% obtained at 65ºC operating temperature with 6% catalyst percent, methanol molar ratio: WCO of 12:1 for 3 hours. The density of methyl ester produced between 850-875 kg/m^3 and the kinematic viscosity of methyl ester produced between 5.0-6.0 mm^2/s (cSt). This research has met the requirements of biodiesel standards because the highest purity has reached 99.5874%, while the purity standard of biodiesel must reach> 96.5%.

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