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BIODIESEL PRODUCTION FROM WASTE COOKING OIL WITH CATALYSTS FROM CLAMSHELL

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ABSTRACT

This research was carried out to study the efectiveness of clamshell as catalyst in biodiesel process production, especially biodiesel from waste cooking oil. Waste cooking oil was pre-treated to remove water and others inert. The pre-treated process was used three methods namely purification with noni, purification with husk charcoal, and purification with wood charcoal. Clamshell was crhushed into powder, sieved to 200 mesh and calcined at three various temperature 700 ^oC, 750 ^oC and 800 ^oC. Purified waste cooking oil was used as raw material in transesterification reaction to obtain biodiesel and gliserol. The ratio of waste cooking oil to methanol and clamshell powder was 200 mL:600 mL:2 g. The results of the study show that pre-treatment processing of waste cooking oil using noni fruit, husk charcoal or wood charcoal can remove impurities in oil and reduce oil-free fatty acid content to meet the standards to be used as raw material for the biodiesel industry. CaO from clamshell is efective as a catalyst in the process of biodiesel production. The characteristics of biodiesel from waste cooking oil produced in this study are as follows; the acid number is in the range 0.51-0.56, mg KOH/g sample, saponification numbers in the range193-201 mg KOH/g sample, density 853-854 kg/m^3, and the viscosity in the range of 2.77 to 2.80 cSt. All these characteristics meet the provisions required by the Indonesian National Standard (SNI).

Keywords: biodiesel, waste cooking oil, clamshell catalyst.

INTRODUCTION

Biodiesel is an alternative energy that has been widely developed to reduce dependence on fossil fuels (Pasae et al, 2011). The use of biodiesel can reduce emissions from combustion products that cause air pollution, because biodiesel has a higher of cetane number than diesel fuel, thus providing better combustion performance (Pasae, 2017). Biodiesel is produced through the transesterification reaction of vegetable oil or animal fat in the presence of alcohol and catalyst (Pasae et al, 2016). The requirements for raw materials for the transesterification reaction must have free fatty acid content less than 1% (<1%).

To ensure the availability of sustainable biodiesel fuel, the main raw material for vegetable oil must also be guaranteed. The main raw materials in the biodiesel industry in Indonesia generally still rely on food oils such as palm oil and coconut oil. This raw material is feared to cause conflict with food needs, so that it can disrupt the sustainability of the biodiesel industry. In Indonesia, a variety of non-food oil-producing plants such as Jatropha Curcas, Kaliki and Kusambi are growing, but have not been specifically cultivated to support the availability of raw materials for the biodiesel industry. Therefore the use of waste cooking oil is one solution to ensure the availability of raw materials.

Waste cooking oil is used oil sourced from types of cooking oil such as palm oil, coconut oil, soybean oil and other food oils. Waste cooking oil is used oil for the culinary, hospitality, restaurant and household industries, often reused for culinary purposes but when viewed from its chemical composition, used cooking oil contains carcinogenic compounds, which are formed during the frying process. The use of used cooking oil repeatedly can damage human health, cause cancer, and consequently can reduce the intelligence of the next generation. For this reason, the use of used cooking oil as a raw material for the biodiesel industry can be more beneficial and does not cause harm from the aspects of human health and the environment. However, because used cooking oil contains various other compounds and generally has a high free fatty acid content, the use of waste cooking oli as raw material in biodiesel processing needs to be pre-treated. In this research, several pre-processing methods of waste cooking oil will be conducted to find out the best way that is more compatible with the stages of the biodiesel production process.

Other needs in the biodiesel industry that must be ensured are availability of catalysts. Commonly used catalysts are homogeneous and heterogeneous catalysts. Homogeneous catalysts have a deficiency in the production process because the catalyst is difficult to separate from the reaction product, and triggers the formation of byproducts in the form of soap so that the process is not economical (Pasae et al. 2018). Therefore, biodiesel production is better if using heterogeneous catalysts. One of the most widely used heterogeneous catalysts is CaO because of its strength and higher catalytic activity. However, CaO has a disadvantage because the price is relatively expensive, so it is necessary to find a cheaper source to obtain CaO (Kouzu, et al. 2008). Some natural materials that are waste can be used as a source of CaO including clamclamshell, snail clamshells, bones and other materials. The catalyst raw material used in this study was selected from clamshell because it was more easily obtained and abundant availability as a fishery industrial waste.

This study aims to obtain a comprehensive production process technology to produce biodiesel from waste cooking oil and CaO as catalyst from clamclamshell. The intended technology consists of pretreatment processing of waste cooking oil, preparation of catalysts from clamclamshell, biodiesel production technology and the characteristics of biodiesel produced.

METHODS

Materials

Both wasted cooking oil and clamshell used in this study are wastes obtained from several culinary industries such as restaurants and people's markets in the city of Makassar. Chemicals such as methanol, ethanol, sodium hydroxide are obtained from chemical stores in the city of Makassar.

Pretreatment of waste cooking oil

Three methods were carried out for the process of refining waste cooking oil in this study, namely purification using noni fruit, purification using husk charcoal, and purification using wood charcoal.

Purification using noni fruit: noni fruit that has been ripe crushed and then taken the juice. Noni juice as much as 5 gram mixed into cooking oil 500 mL and allowed to stand for 5-10 minutes. Then the mixture is heated to a temperature of 50 ^oC. Next the mixture is left until the oil is clear. The oil is then filtered to be separated from the sediment.

Purification using husk charcoal: 1 gram of husk charcoal is put into 100 grams of cooking oil. Then heated while stirring until the oil looks clear. The mixture is then precipitated, and filtered to separate the oil from the husk charcoal.

Purification using wood charcoal: wood charcoal is ground until smooth. wood charcoal powder as much as 5 gram mixed into waste cooking oil 500 mL and allowed to stand for about 5 minutes later. Then filtering is done to separate the sediment from oil.

Preparation of catalyst for clamshell

Clamshell are cleaned with water to remove the remaining dirt and sand. Clamshell are dried and roughly ground using a hammer. Then calcined at three difference temperature 700 ^oC, 750 ^oC dan 800 °C for 7 hours. After the calcination process is complete, the clamshells are crushed and sieved, which passes on the 200 mesh sieve stored in a desiccator to be used as a catalyst.

Biodiesel production process

Biodiesel production process using CaO catalyst was carried out as follows: 200 ml cooking oil, 600 ml methanol, and 2 g CaO catalyst were put into the reactor and reacted for 1, 2, andt 3 hours. After the reaction process is complete, the product is poured into a separating funnel, and let stand for 12 hours at room temperature. This deposition process will produce two layers in a separating funnel, the top layer of biodiesel, the bottom layer of glycerol with the catalyst. The bottom layer is separated then the catalyst is filtered using filter paper to recover the catalyst. The obtained biodiesel is heated to evaporate the water carried from the raw material. Dry biodiesel is stored in a storage bottle for further characteristic analysis.

Analysis of biodiesel characteristic

The characteristics of biodiesel analyzed in the study were acid number, saponification number, iodine number, viscosity and density. The analysis procedure uses standard procedures based on Indonesian National Standards.

RESULT AND DISCUSSIONS

Table-1 shows that the refined cooking oil from the three methods used in this study provides different yields and acid numbers. The highest yield 86.40% was obtained from the purification process using noni, then 80.00% obtained form purification process using husk charcoal and the last yiled 78.00%from the purification process using wood charcoal. These yields are also correlated with the acid number of refined waste cooking oil. The highest free fatty acid levels obtained in the process of purification using noni is 0.90 mg KOH / g sample, then purification products using husk charcoal 0.82 mg KOH /g sample and purification products using wood charcoal 0.73 mg KOH / g sample . These results indicate that the third methods of the purification process can be used for the refining process of waste cooking oil in the biodiesel industry because it provides a high yield with a much lower acid value than the standard acid number for raw material, which is 5 mg KOH / g sample.

Preparation of CaO as catalyst is done by calcining the clamshells that have been washed and dried. The purpose of calcination is to remove carbon dioxide compounds through the decomposition reaction of calcium carbonate contained in the clamshells so that calcium oxide compounds can be obtained. Table 2 shows that the highest CaO yield was obtained from the classification process at a temperature of 700 ^oC, but the texture of the CaO produced was still in the form of a white coarse powder. The best CaO as a catalyst is CaO in the form of fine powder in white color, obtained from the calcination process at a temperature of 800 ^oC. The finer powder-shaped CaO has a greater average amount of surface area than coarse-shaped CaO.

The ratio of methanol and oil used is 3: 1 by volume because transesterification process is a reversible reaction. The reaction was carried out at a temperature of 60 °C for 2 hours.Three phases of products are obtained, namely biodiesel at the top, glycerol and catalysts at the bottom. Separation of this layer occurs because of differences in polarity between biodiesel and glycerol. Biodiesel like oil is generally non-polar, whereas glycerol is a polar compound. In addition, the density of biodiesel is lower than glycerol, so biodiesel is located at the top of the layer.

Table-1. Yields and acid number of purified waste cooking oil.

Waste cooking oil (mL)	**Purified materials**	**Purified waste cooking oil** (mL)	**Yield** (%)	**Acid number mg KOH/g sampel**
500	Noni	432	86.40	0.90
500	Husk charcoal	400	80.00	0.82
500	Wood charcoal	390	78.00	0.73

Table-2. Yields and texture of Catalyst (CaO) results of calcined clamshells.

Clamclamshells (g)	**Time** (hr)	**Temperature** (^oC)	**CaO Product** (g)	**Yiled s** (%)	**texture**
400	7	700	330	82.50	Rough powder, white
400	7	750	325	81.25	Rough powder, white
400	7	800	305	76.25	Fine powder, white

Table-3. Yields of biodiesel and its characteristics are compared with SNI.

Time (hr)	**Waste cooking oil** (mL)	**Metha nol** (mL)	**Catalys t** (g)	**Biodies el** (mL)	**yield** (%)	**density kg/m^3**	**Viscosity mm^2/s** (cSt)	**Acid number mg KOH/g**	**Saponification number mg-KOH/g**
1	200	600	2	190	23.69	854	2.80	0.56	193
2	200	600	2	440	54.86	854	2.79	0.51	196
3	200	600	2	530	66.09	853	2.77	0.56	201
National Indonesian Standard of Biodiesel (SNI)						850-890	2.3-6.0	Max 0.8	Min 96.5

The reaction time is one of the important parameters that play a role in the transesterification reaction, the longer the reaction time; the more products are produced because the chance of reactants to collide with each other will occur longer. From Table-3 it can be seen that the maximum yield of 66.09 % is obtained in a reaction time of 3 hours.

Based on the results of the biodiesel characteristic test it is known that the density of biodiesel obtained is in the range 850-854 Kg / m3. This value meets the SNI-04-7182-2015 standard which specifies a range of density values of 850-890 Kg / m3. The viscosity of biodiesel in each time variation is in the range of 2.77-2.80 cSt. This viscosity value also meets the biodiesel specifications based on SNI-04-7182-2015, which sets the value range 2.3 - 6.0 cSt. The results of biodiesel saponification number analysis for 1 hour treatment were 193 mg KOH / g, 2 hours 196 mg KOH / g and 3 hours 201 mg KOH / g. The longer reaction time in the transesterification reaction will allow the saponification reaction to be made in the production of biodiesel so that the saponification number increases as the reaction time increases. The range of biodiesel saponification values in this study (193 - 201 mg KOH / g) meets the values specified in the SNI-04-7182-2015 Standard (min 96.5 mg KOH / g). The results of the analysis of the biodiesel acid number in this study were in the range of 0.51-0.56 mg KOH / g. This value also meet SNI-04-7182-2015, which applies the biodiesel acid number 0.8 mg KOH / g oil.

CONCLUSIONS

a) Pre-treatment processing of waste cooking oil using noni fruit, husk charcoal or wood charcoal can remove impurities in oil and reduce oil-free fatty acid content to meet the standards to be used as raw material for the biodiesel industry.
b) CaO from clamshells efective as a catalyst in the process of biodiesel production.
c) The characteristics of biodiesel from waste cooking oil produced in this study are as follows; the acid number is in the range 0.51-0.56, mg KOH/g sample, saponification numbers in the range193-201 mg KOH/g sample, density 853-854 kg/m^3, and the viscosity in the range of2.77 to 2.80 cSt. All these characteristics meet the provisions required by the Indonesian national standard.

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