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Biodiesel Production of Waste Cooking Oil Catalyzed by CaO Derived from Snail (*Achatina Fulica*) Shell Waste

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Abstract

Biodiesel can be production from waste cooking oil and catalyzed by base heterogeneous catalysts. One type of heterogeneous base catalyst is CaO. CaO can be produced from mollusc animal waste, one of which is snail shell waste (*Achatina fulica*). The main constituent of snail shell waste (*Achatina fulica*) is a calcium oxide compound (CaCO3) which can be decomposed into CaO at high temperatures. In this study, a temperature of 900 ^oC for 10 hours was used to convert $CaCO_3$ compounds into CaO compounds. Biodiesel production using CaO catalyst occurs at the mole ratio of oil: methanol 1: 6, 3 g weight of catalyst, the reaction temperature at 60 °C, the reaction time of 3.5 hours, and stirring speed of 250 rpm with biodiesel results obtained at 84,28%.

Keywords: Biodiesel, Heterogeneous base catalyst, Waste cooking oil, Snail (*Achatina fulica*) Shells

INTRODUCTION

The processing of waste into renewable energy is a hot topic of conversation for researchers, especially in the fields of physical chemistry and inorganic chemistry. One of the wastes that we often encounter is Waste cooking oil. Waste cooking oil is one of the potential raw material sources to be developed in making biodiesel. Waste cooking oil is an alternative raw material for making biodiesel which is cheap, environmentally friendly, and reduces household or food industry waste and does not compete with food needs.

Biodiesel is an alternative fuel for diesel engines in the form of methyl esters or ethyl esters which are produced by transesterification and esterification reactions of plant oils or animal fats with short-chain alcohols such as methanol with the help of an acidic or alkaline catalyst. The catalysts commonly used for biodiesel production are homogeneous and heterogeneous catalysts. Homogeneous catalysts have shortcomings, including the catalyst mixed with biodiesel so that it requires further processing to obtain biodiesel, a lot of byproducts are formed in the form of soap if the raw material has a high ALB content, and is less economical (Anshary et al, 2012).

Therefore, the researchers used heterogeneous catalysts for biodiesel production. Heterogeneous catalysts are more environmentally friendly, easier to separate from the residual biodiesel processing, and can be reused so that they can reduce the cost of biodiesel production (Mittelbach and Remschmidt, 2004). Many basic heterogeneous catalysts have been used for biodiesel production, such as modification of potassium fluoride with hydrotalcite (Fatimah et al, 2018), modification of CaO using metal group IA (Li, Na, and K). The heterogeneous base catalyst that is often used for the transesterification reaction is calcium oxide (CaO).

CaO is a strong alkaline oxide which has high catalytic activity, low reaction conditions and a long catalyst service life (Kumar and Ali, 2012). However, the use of commercial CaO has disadvantages such as it is difficult to degrade so that its use is not economical. Natural Calcium Oxide (CaO) can be obtained by calcining the snail shell waste (*Achatina fulica*) at high temperature and certain time (Nurhayati et al, 2016). Snail (*Achatina fulica*) shell waste is used because it has low costs, thus reducing the cost of biodiesel production (Fatimah et al, 2017). Snail (*Achatina fulica*) shell waste also has high catalytic activity (Fatimah et al, 2018).

Materials and Methods

Materials

The tools used in this research are Mortar, Furnace, 200 Mesh sieve, Hotplate Magnetic Stirrer, Magnetic Stirrer, Analytical Balance, Three neck flask complete with condenser, water pump, mercury thermometer, desiccator, flash point determination device (Clevand BBS product type BAP-243), and other research glassware according with work procedures.

The materials used in this research are snail shells (*Achatina fulica*), waste cooking oil, CaO pa, methanol pa, isopropyl propanol, phenolphthalein indicators, NaOH, KOH, Concentrated H_2SO_4, potassium hydrogen pthalat (PHP), starch solution, CH_3COOH, aquabides and distilled water, Acetone, HCl 0.5 N, CCl_4, Wijs reagent, KI, $Na_2S_2O_3$ (1 and 0.1 N), and materials- other chemicals in accordance with work procedures.

Preparation and Synthesis of CaO Catalysts of Waste Snail Shells (*Achatina fulica*)

Shell of the snail (*Achatina fulica*) is cleaned of its flesh by boiling it for 1 hour. After that, the shells were dried using an oven at 100 ^oC for 2 hours. Furthermore, the shell of the snail (*Achatina fulica*) is coarsely ground using a mortar and calcined using a furnace for 10 hours at a temperature of 900 ^oC.

Results and Discussions

Initial Treatment of Waste Cooking Oil

Before being used as a raw material for making biodiesel, the waste cooking oil waste is washed first using warm water at 50 ^oC with a ratio of 1: 1. After that we tested the water content and the free fatty acid content

EXPERIMENTAL SECTION

Provide sufficient detail to allow the work to be reproduced, which may include Materials, Instrumentation, and Procedure.

Materials

Please provide details of the manufacture and purity of the materials used, e.g., CH_3COOH (99% purity Merck, Germany).

Instrumentation

Please provide details of the instrumentation used.

Procedure

Methods already published should be indicated by a reference: only relevant modifications should be described. For theoretical or computational work, this experimental section may be modified into Computational Details, which may include the Software, Algorithms, Equations, etc. It is not necessary to include the Materials or Instrumentations for a sole theoretical/computational work.

Table 1. Water content and free fatty acids of waste cooking oil waste

Parameter	Results (%)
Water content	0.04
The content of free fatty acids	0.55

In **Table 2**, we can conclude that the synthesized CaO from the Snail (*Achatina fulica*) shell waste has the potential to be used as a catalyst in the biodiesel production process.

Biodiesel Quality Characteristics according to SNI

The characteristics of biodiesel produced in Indonesia must comply with the established standards, namely according to SNI-7182-2015. The quality of biodiesel produced in this study was analyzed through general parameters such as in this study, the quality of biodiesel obtained was characterized by several parameters, namely water content, density, viscosity, flash point, carbon residue, acid number, saponation number, iodine number and cetane number. . The results of the characterization of biodiesel quality can be seen in **Table 3**.

Table 3. Results of comparison of biodiesel characters with biodiesel quality requirements SNI-7182-2015.

Number	Parameters	Unites	This Riset	SNI
1	Water content	% v	0,025	Maks. 0,05
2	Density at 40ºC	kg/m^3	870	850-890
3	Viscosity at 40ºC	mm^2/s	3,8	2,3-6,0
4	Flash point	ºC	150	Min. 100
5	Carbon residue	%	0,045	Maks. 0,05
6	Acid number	mg KOH/g	0,45	Maks. 0,5
7	Saponation number	mg KOH/g	198,05	-
8	Iodine number	$g\text{-}I_2/100g$	55,02	Maks. 115
9	Cetane number	-	67,50	Min. 51

The results of testing the biodiesel water content in this study of 0.025% were obtained from neutralized waste cooking oil raw materials. This result does not exceed the standard limit of SNI-04-7186-2006 which has been set, namely 0.05%. The water content whose value is above the stipulated value will cause the reaction that occurs in the conversion of vegetable oils to be imperfect (there is a lathering reaction). There can also be a hydrolysis process in biodiesel so that it will increase the acid number, lower the pH, and increase its corrosive properties.

Density shows the ratio of mass to volume. This specific gravity test is carried out by comparing the biodiesel density with the specific gravity of water at a temperature of 40 ^oC. Density has a direct relationship with viscosity, if the density value is large, the viscosity value is also large. The results of the measurement of biodiesel density are 870 kg/m^3. These results are in the standard range of SNI-7182-2015. Biodiesel which has a specific gravity that exceeds the provisions will result in incomplete combustion (Kurniawan and Nurhayati, 2020). So that it will increase wear, emissions and damage to the engine used.

Viscosity is the main parameter in determining biodiesel, because it has a big influence on the effectiveness of biodiesel as a fuel. The result of biodiesel viscosity determination was 3.8 mm^2/s. This value is in accordance with the SNI-7182-2015 biodiesel quality standard. If the viscosity is too low it will cause a leak in the fuel injection pump, while the high biodiesel viscosity will cause the formation of fog grains when atomizing the fuel into the engine, causing incomplete combustion in the engine (Prihandana et el, 2006).

Flash point or flash point is the temperature of a fuel burning by itself by the surrounding air accompanied by a flash of light. The lower the flash point of a fuel, the more flammable it is. In this study, the biodiesel flash point determination was obtained at 150 ºC, this value meets the SNI-7182-2015 biodiesel quality standard, which is a minimum of 100 ºC. This shows that this fuel is safe to use, making it easy to store and handle. If the flash point is too high it will cause a delay in ignition of the engine, while the biodiesel flash point is too low it causes detonation, namely small explosions that occur before the fuel enters the combustion chamber (Madja, 2007).

Carbon residue is the carbon content that remains after experiencing combustion for a certain time which is usually determined by weight percent. The impurities in the combustion chamber from a diesel engine are caused by carbon deposits which can occur if the fuel contains components that cannot burn completely. The residual carbon content indicates a tendency for soot formation in diesel engines. The carbon residue value obtained in this study was 0.045% and met the SNI biodiesel standards that had been determined, namely a maximum of 0.05%. A large carbon residual value will cause a buildup of carbon in the engine combustion chamber which results in decreased or damaged engine performance. So, the value of the carbon residue must be small to reduce carbon build-up in the engine combustion chamber.

The value of the acid number is an indicator of the quality of biodiesel which still contains free fatty acids, by dissolving a number of oils or fats. The high value of biodiesel acid number indicates damage or degradation of biodiesel quality due to oxidation. In this study, the acid number was obtained at 0.7 mg KOH/g. The acid number in the resulting biodiesel product does not exceed the provisions of the SNI-04-7182-2006 biodiesel quality standard, namely 0.8 mg KOH/g. Biodiesel which has a high acid number will cause the biodiesel to be corrosive and can cause rust on the engine injector (Kurniawan and Nurhayati, 2020).

The soaping number is the number of milligrams of KOH needed to lather one gram of biodiesel. The saponification number obtained in this study was 198.05 mg KOH/g. This means that 198.05 mg of KOH is needed to lather 1 gram of biodiesel. The saponation number indicates the value of the content of intermediate compounds (mono and diglycerides) and unreacted triglycerides (Prihandana et al, 2006). The presence of intermediates and triglycerides in biodiesel can cause blockage in the injection engine. In the SNI-04-7182-2006 biodiesel quality standard, there is no provision for what is the threshold of the saponification number in biodiesel.

The iodine number is used as an indicator of biodiesel saturation or to show the number of double bonds in the fatty acids that make up biodiesel. The iodine number obtained is 55.02 g I_2/100 g, this result meets the SNI-04-7182-2006 biodiesel quality standard, which is a maximum of 115 g iod/100 g. Fuels with too high iodine value will show a tendency to polymerize and form deposits in the injector bore, piston ring and piston ring groove when heated (Madja, 2007).

The characterization of the cetane number is to show how fast the diesel engine fuel that is injected into the combustion chamber can burn spontaneously. Cetane number is the percentage by volume of cetane in the mixture with alphamethyl napthalen ($C_{10}H_7CH_3$), an aromatic hydrocarbon compound which has a large ignition delay, has the same quality as combustion (Hardjono, 2000). The cetane number shows how fast the diesel engine fuel injected into the combustion chamber can burn spontaneously. The value of cetane numbers in this study was obtained 67.50, the value obtained was higher and met the quality standards of SNI-7182-2015, meanwhile, for biodiesel at least 51. The higher the value, the better the quality of the fuel. A high cetane number indicates that the biodiesel can ignite at a relatively low temperature so that it will burn easily in the cylinder so as not to cause knocking and not accumulate (Satriana et al, 2012).

Conclusion

Snail shell waste has the potential to be used as a source of natural CaO catalyst which can be used as a catalyst for biodiesel production. Waste cooking oil waste can also be used as raw material for biodiesel production with a water content of 0.04% and a free fatty acid content of 0.55%. The biodiesel produced was 84.28%. The resulting biodiesel meets the standards set according to SNI-7182-2015, namely water content of 0.025%, specific gravity 870 kg/m^3, viscosity 3.8 mm^2/s, flash point 150 ^oC, carbon residue 0.045%, acid number 0,7 mg KOH/g, saponation number 198.05 mg KOH/g, Iodine number 55.02 g-I_2/ 100g, and Cetane number 67.50.

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