**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 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 CaCO3 compounds into CaO compounds. Biodiesel production using CaO catalyst on 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 used cooking oil. Used cooking oil waste is one of the potential raw material sources to be developed in making biodiesel. Used 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*), used cooking oil, CaO pa, methanol pa, isopropyl propanol, phenolphthalein indicators, NaOH, KOH, Concentrated H2SO4, potassium hydrogen pthalat (PHP), starch solution, CH3COOH, aquabides and distilled water, Acetone, HCl 0.5 N, CCl4, Wijs reagent, KI, Na2S2O3 (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 used 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.

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

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

In **Table 1**, it can be seen that used cooking oil contains free fatty acids of 0.55% and a water content of 0.04%. From the data obtained, the oil samples used have good purity to be used as raw material for biodiesel production. Good oils have a free fatty acid content of less than 1%. The higher the free fatty acid content, the oil is not good for use as a raw material for making biodiesel. The water contained in the oil greatly disrupts the biodiesel production process. The amount of water in the oil must be less than 0.06%, while the free fatty acid content should be less than (0.5-1%) (Ma and Hanna, 1999). The content of water and free fatty acids is too high in the reaction, it will form a lathering reaction, so that the methanolysis reaction cannot occur (Haryanto, 2002).

**Results of Biodiesel Production**

In this study, biodiesel production was carried out using an oil-methanol mole ratio of 1: 6, 3% CaO catalyst, 250 rpm rotation speed, 60 oC reaction temperature, and 3.5 hours reaction time (Kurniawan and Nurhayati, 2020). Where the biodiesel synthesis results can be seen in Table 2. This result following formula :

**Table 2**. biodiesel produced

|  |  |
| --- | --- |
| Catalyst samples | Biodiesel (%) |
| Synthesized CaO | 84.28 |

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/m3 | 870 | 850-890 |
| **3** | Viscosity at 40ºC | mm2/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-I2/100g | 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 used 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/m3. 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 mm2/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 I2/100 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 (C10H7CH3), 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. Used 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/m3, viscosity 3.8 mm2/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-I2/ 100g, and Cetane number 67.50.

**Acknowledgement**

The author would like to thank DRPM, Directorate General of Research and Development Strengthening who has funded this research.

**References**

Alonso, D. M., Granados, M. L., Mariscal R., and Douhail, A., (2009), Surface Chemical Promotion of Ca Oxide Catalyst in Biodiesel Production Reaction by the Addition of Monoglycerides, Diglycerides, and Glycerol, *Journal Catalyst*, 276 229-236.

Anshary, M. I., Damayanti, O., dan Roedyadi, A., (2012), Pembuatan Biodiesel dari Minyak Kelapa Sawit dengan Katalis Padat Berpromotor Ganda Dalam Reaktor *Fixed Bed. Jurnal Teknik Pomits*. 1: 1-8.

Fatimah I., Kurniastuti EA., Basthiani IA., Fakhri A., (2017), Low cost heterogenous catalyst from (Achatina Fulica) snail shell and its application for biodiesel conversion via microwave irradiation, J Phys Conf Ser 909:012082,  <https://doi.org/10.1088/1742-6596/909/1/012082>

Fatimah I., Rubiyanto D., and Nugraha J., (2018), Preparation, characterization, and modelling activity of potassium flouride modified hydrotalcite for microwave assisted biodiesel conversion,” Sustain. Chem. Pharm., vol. 8, pp. 63–70, Jun. <https://doi.org/10.1016/j.scp.2018.02.004>

Fatimah I., Nurillahi R., Fahrani D., Harmawantika T., Aulia GR., and Puspitasari W., (2018), Hydroxyapatite prepared from snail (*Pilla ampulacea*) and scallop (*Anadara granosa*) shells as low cost-renewable catalyst in biodiesel conversion, J Phys Conf Ser 2026, 020072; <https://doi.org/10.1063/1.5065032>

Hardjono, A., (2000), Teknologi Minyak Bumi, Gajah Mada University Press, Yogyakarta.

Haryanto, B., (2002), Bahan Bakar Alternatif Biodiesel, *Jurnal Teknik Kimia* 1, 5-12.

Kumar, D. and Ali, A., (2012), Nanocrystalline K-CaO for the Transesterification of a Variety of Feedstocks: Structure, Kinetics, and Catalytic Properties, *Renewable Energy* 46, 459-468.

Kurniawan, E., and Nurhayati, (2020), Transesterification process of waste cooking oil Catalized by Na/CaO derived from Blood clam (Anadara granosa) shell, EKSAKTA : Journal of Science and Data Analysis 1(1) 1-6.

Ma, F., and Hanna, M. A., (1999), Biodiesel production: a review 1, *Bioresource Technology* 70, 1–15.

Madja, (2020), *Minyak Sawit, Dari Biodiesel Hingga Karoten.* [http://madja.wordpress.com/2007/12/20/minyak-sawit-dari-biodiesel-ingga -karoten/.Tanggal](http://madja.wordpress.com/2007/12/20/minyak-sawit-dari-biodiesel-ingga%20-karoten/.Tanggal) akses 20 November 2020.

Mittelbach M., and C. Remschmidt, (2004), Biodiesel The Comprehensive Handbook. Martin Mittelbach Publisher, Austria, 56-89

Nurhayati, Muhdarina, Linggawati A., Anita S., and Amri A. T., (2016), Preparation and Characterization of Calcium Oxide Heterogeneous Catalyst Derived from Anadara Granosa Shell for Biodiesel Synthesis, *J.* *KnE Engineering* 1, 1-8.

Prihandana, R., Hendroko, R. dan Nurmin, M,(2006), *Menghasilkan Biodiesel Murah Mengatasi Polusi dan Kelangkaan BBM*, Agromedis Pustaka, Surabaya.

Satriana., Husna, N. E., Desrina., dan Supardan., M. D., (2012), Karakteristik Biodiesel Hasil Transesterifikasi Minyak Jelantah Menggunakan Teknik Kavitasi Hidrodinamik, *Jurnal Teknologi dan Industri Pertanian Indonesia* 4 (2).