EKSAKTA
Journal of Sciences and Data Analysis

E-ISSN: 2720-9326
P-ISSN: 2716-0459
DOI: 10.20885/EKSAKTA.vol1.iss1.art1

Research Article

Transesterfication Process of Waste Cooking Oil Catalyzed by Na/CaO Derived from Blood Clam (*Anadara Granosa*) Shells

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Received: 29 September 2019; Accepted: 2 December 2019; Published: 15 January 2020

Abstract: Blood clam (*Anadara granosa*) shells has the potential to be developed as a base heterogeneous catalysts for biodiesel production. Blood clam (*Anadara granosa*) shells has a high mineral content of calcium carbonate ($CaCO_3$). $CaCO_3$ can be decomposed into CaO at high temperature heating. In this study, CaO catalyst synthesized from the blood clam (*Anadara granosa*) shells calcined of 900 °C for 10 hours and then impregnated using NaOH (1, 3, and 5% w/w) the activation temperature of 600 °C for 5 hours. 3% Na/CaO catalyst was the most better catalyst with maximum biodiesel results obtained at 83,57% using the 3% Na/CaO catalyst. The maximum conditions obtained from biodiesel production using the 3% Na/CaO catalyst on the reaction temperature at 60 °C, the reaction time of 3.5 hours, stirring speed of 250 rpm, 3 g weight of catalyst, and the mole ratio of oil: methanol 1: 6.

Keywords: Biodiesel, Transesterification, Blood clam shells, Heterogeneous base catalyst

Introduction

Biodiesel has become a popular alternative of mineral diesel fuel in recent past as it has several advantages over latter, viz., environment friendly, biodegradable, non-toxic, has low emission profile of particulate matter, aromatic hydrocarbon, SOx, NOx, CO, green house gases, and renewable. In the last studied, blood shells (Anadara granosa) can be used as a catalyst in biodiesel production [1, 2]. Blood clam shells (Anadara granosa) have high calcium carbonate ($CaCO_3$) mineral content. $CaCO_3$ minerals can be decomposed into CaO at high temperature heating (> 800 °C) [3]. Blood clam (*Anadara granosa*) shells have the potential as a source of heterogeneous catalysts for biodiesel production because they contain CaO of 99.09% by weight [2]. Heterogeneous catalysts are catalysts that have different phases than reactants. The working principle of heterogeneous catalysts is based on adsorption (chemisopsy) of one or more reactants on the surface of the catalyst, bonding occurs, and finally a separate product.

Recently, in order to increase biodiesel production, some researchers have modified CaO catalysts by adding alkali metals with the aim of increasing basicity, expanding the surface of the catalyst and increasing the number of active sites. Thus it is expected that contact between the reactants and the catalyst will increase so that the reaction will be easier and faster.

In 2013, Tarmidzi, et al. [4] conducted a study of the effect of doped lithium concentration in the CaO catalyst on the palm oil transesterification reaction although characterization of the catalyst produced was not carried out, but it produced a 90.88% methyl ester. In 2010, Kaur and Ali [5] impregnated lithium ions into calcium oxide as nanocatalysts for biodiesel production from jatropha curcas oil and karanja oil obtained in the form of Calcite and Porlandite catalysts, with a base strength of 15.0 <H_<18.4, TEM particle size 50-70 nm and SEM 2 μm, surface area 1.7 m^2/g, and produce methyl esters with levels >99%. Kumar and Ali (2012) [6] examined the K-CaO nanocrystalline for transesterification of grain varieties

obtained catalysts in the form of Calcite and Porlandite, with base strength of 11.1 <H_<15.0, particle size of TEM 39 nm and SEM 2-5 μm, catalyst surface area of 5.84 ± 0.02 m^2/g, and produces methyl esters with 98% content. Afandi (2015) impregnated KOH on calcined shells (Andara granosa) calcined at 900 °C as a heterogeneous catalyst in the production of biodiesel from used cooking oil to obtain catalysts in the form of Calcite, and Porlandite, with the strength of 1.865 mmol of benzoic acid/g, surface area of 5.7 m^2/g, and produces optimum biodiesel 76.33% with a methyl ester content of 98.36%.

Nowadays, Na/CaO allows it to be developed into a heterogeneous catalyst for the production of biodiesel from used cooking oil. Sodium (Na) was chosen because it is an alkali metal with a strong base and is expected to increase alkalinity, increase surface area, and increase the number of active sites of CaO. In this study, sodium ions were impregnated into CaO obtained through calcination of Blood clam (*Anadara granosa*) shells and it was hoped that Na/CaO nanocatalysts and biodiesel produced would be higher than those previously achieved.

Materials and Methods

Materials

X-Ray Diffraction (XRD) data for powder samples were collected on Philip Analytical X-Ray B.V., Mortar, Oven (*GallenKemp*), *Furnace* (*Vulcan^{TM} seri A-300*), ayakan 200 Mesh, *Hotplate Magnetic Stirrer* (Rexim RSH-IDR As One), *Magnetic Stirrer* (Spinbar), *Sibata Waterbath Shaker* (WS-120), analytical balance (*Mettler AE 200*), three neck flask with condenser, water pump, mercury thermometer, desiccator, flash point determination device (Clevand BBS product type BAP-243), and other research glassware according to work procedures.

The ingredients used in this research are Blood clam (*Anadara granosa*) shells, used cooking oil, methanol p.a., Iso Propyl Propanol (IPA), indicators of phenolphthalein, NaOH, KOH (0.1 N and 0.5 N), H_2SO_4 concentrated, potassium hydrogen pthalat (PHP), Acetone, 0.5 N HCl, CCl_4, Wijs reagent, 10% KI, $Na_2S_2O_3$ (1 N and 0.1 N), starch solution, CH_3COOH, aquabides and aquades, and chemicals others that are in accordance with work procedures.

Preparation of the CaO Catalyst from Blood Calm (*Anadara granosa*) Shells

The Blood clam (*Anadara granosa*) shells were cleaned from the remaining meat attached and then boiled for 0.5 hours. After that, the shells are dried and cleaned again using aquades. The Blood clam (*Anadara granosa*) shells are then heated using an oven at 105 °C for 2 hours. After that the blood shells are crushed using a mortar and filtered using a 200 mesh sieve, then calcined at 900 °C for 10 hours. Calcined shells are crushed using a mortar and reheated using an oven at 120 °C for 3 hours, then stored in a desiccator [1].

Synthesis of Na/CaO Catalyst from Blood Calm (*Anadara granosa*) Shells

Synthesis of Na/CaO catalyst using wet impregnation method, where 50 grams of CaO from a sample of a Blood clam (*Anadara granosa*) shells mixed 25 ml NaOH solution dropwise while stirring using a magnetic stirrer with a variation of weight percent Na in CaO 1%, 3%, and 5% 200 ml of distilled water is added and the mixture is stirred for 3 hours. Stirring is continued by heating to dry the water in a mixture at a temperature of 120 °C for 3 hours and continued with calcination of 600 °C for 5 hours.

Purification of Waste Cooking Oil

In this study, crude of waste cooking oil is first filtered to separate the dirt using ordinary filter paper. The sample of used cooking oil is washed using distilled water at a temperature of 50 oC in a ratio of 1: 1, ie weighed 200 g and distilled water weighed 200 g. The distilled water is heated at 50 °C in a beaker glass. The sample is put into a separating funnel and added with distilled water (temperature 50 °C) and homogenized. The sample is allowed to stand for more or less a day to form two layers. The lower layer is in the form of water and the upper layer is used cooking oil that has been washed. Used cooking oil that has been washed, is prepared for the determination of water content.

E-ISSN: 2720-9326
P-ISSN: 2716-0459

Determination of Water Content in Waste Cooking Oil

Waste cooking oil samples was determined of the water content, namely by entering the evaporating cup into the oven with a temperature of 105 °C for 1 hour, weighing the evaporating cup to a constant weight. After that, weigh 5 g of used cooking oil and put it in the vaporizer cup. Put it in the oven at 105 °C for 2 hours. After that, reconsider the used cooking oil sample and calculate the water content using the equation (1) :

$$Water\ content\ (\%) = \frac{a-b}{Weight\ of\ Sample\ (gr)} x100\% \text{.....(1)}$$

Determination of Free Fatty Acid Content of Waste Cooking Oil

The next analysis is to determine the free fatty acid content, namely by weighing 20 g of used cooking oil and heating it at 60 °C in 250 mL Erlenmeyer. The sample of used cooking oil that has been heated is then added 50 mL of hot isopropyl propanol (temperature 50-60 °C) to the Erlenmeyer. The mixture is shaken and added 2-3 drops of the indicator phenolphthalein and homogenized. After that, titrate with 0.1N KOH solution (which has been standardized) until it turns pink. The volume of titrant used is recorded (V mL).

The amount of free fatty acids is calculated using the equation (2) :

$$\%\ FFA = \frac{(mlxN)\ KOH\ x\ 256}{gr\ sample\ x\ 1000} x\ 100 \text{.....(2)}$$

Synthesis of Biodiesel from Waste Cooking Oil using Na/CaO Catalyst from Blood Calm (*Anadara granosa*) Shells

100 g of used cooking oil is put into a beaker and heated to a temperature of 50-60 °C and at the same time we reflux 21.719 grams of methanol and 3 g of catalyst Na/CaO in three neck flasks each for 1 hour (methanol ratio: waste cooking oil = 6:1 (mol/mol) and catalyst 3% (w/w) waste cooking oil). After 1 hour, waste cooking oil is put into the reactor and the mixture is reacted for 3 hours at 60 °C. The stirring speed is set at 250 rpm. After the reaction is complete, the reaction mixture is put into a 250 ml beaker and allowed to stand for 24 hours to separate the Na/CaO catalyst from the reaction mixture. To separate the top phase reaction product which is rich in biodiesel from the lower phase product which is rich in glycerol, decantation is carried out using a separating funnel. This step is repeated for other Na/CaO catalyst variations.

Results and Discussions

Catalyst Characterization

The types of minerals from the Na/CaO catalyst with variations of % Na (1,3, and 5%) are shown in Figure 1. The highest peak intensity is shown at 2θ = 37.32°; 53.81°; and 32.14° which shows the peak of CaO (JCPDS 881811), peak of $Ca(OH)_2$ at 2θ = 34.0861°; and 18.0170° (JCPDS 841266), and the peak $CaCO_3$ at 2θ = 29.3406°; and 62,4591° (JCPDS 050586). The catalyst with the highest CaO content was shown by a 3% Na/CaO catalyst. While in the catalyst 5% Na/CaO there are still many $Ca(OH)_2$ compounds. This is probably due to the 5% Na/CaO catalyst contact with outside air. NaOH impregnation has no effect on the XRD peak. The absence of other types of minerals such as Na_2O in the diffractogram due to the activation temperature of the catalyst used is not enough to make Na_2O into crystals so that the Na_2O formed is amorphous.

Initial Treatment of Waste Cooking Oil Ingredients

Before being used for the transesterification reaction the waste cooking oil sample is first filtered to separate the impurities using ordinary filter paper then the waste cooking oil sample is washed using distilled water at a temperature of 50 °C in a ratio of 1: 1. After that, used cooking oil samples were measured for

E-ISSN: 2720-9326
P-ISSN: 2716-0459

water content and free fatty acid content, and the results are shown in Table 1. In Table 1 it can be seen that waste cooking oil contains free fatty acids of 0.495% and water content of 0.2%. A good oil has a free fatty acid content of less than 1%. The higher the content of free fatty acids, the oil is not good to be used as a raw material in making biodiesel. Oil that has a free fatty acid value of less than 1% can be directly transesterified without going through the esterification reaction first [7]. Water content is one of the more dominant factors when compared to oil-free fatty acid content, because the amount of water in oil must be less than 0.06%, while the free fatty acid content must be less than (0.5-1%) [8]. If the water content and free fatty acids are too high in the reaction, soap will form which is forming an emulsion, so that the methanolysis reaction cannot occur.

Tabel 1. Water and free fatty acid contents of waste cooking oils

Parameter	Results (%)
Water content	0.2
The content of free fatty acids	0.495

The Results of Biodiesel Synthesis

In this study, biodiesel synthesis was carried out under 3% catalyst weight reaction conditions, 3 hour reaction time, reaction temperature 60 °C, mole ratio of oil-methanol 1:6 [1] using CaO and Na/CaO catalysts with percent variation Na 1%, 3%, and 5% weight 3 g and the results can be seen in Figure 2.

Effect of Na concentration on catalyst 3% Na/CaO

The amount of Na concentration impregnated into CaO affects biodiesel production. If the Na metal is spread evenly on the surface of CaO, it will increase the surface area and also will add basicity to the catalyst. The greater the surface area and the basicity of the catalyst, the greater biodiesel production will be produced.

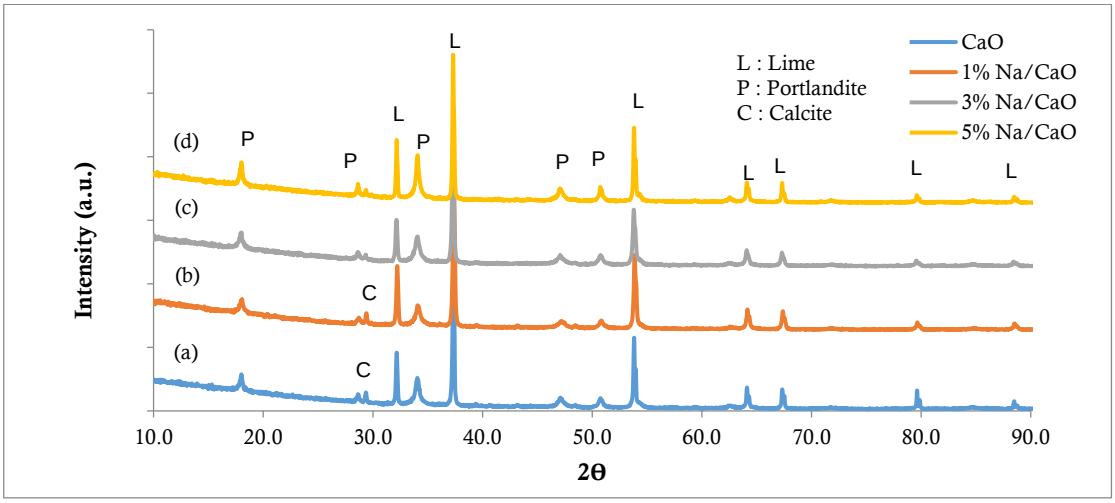

Figure 1. Catalyst diffractogram: (a) CaO from the shell of a blood clam, (b) Catalyst 1% Na/CaO, (c) Catalyst 3% Na/CaO, and (d) 5% Na/CaO catalyst.

E-ISSN: 2720-9326
P-ISSN: 2716-0459

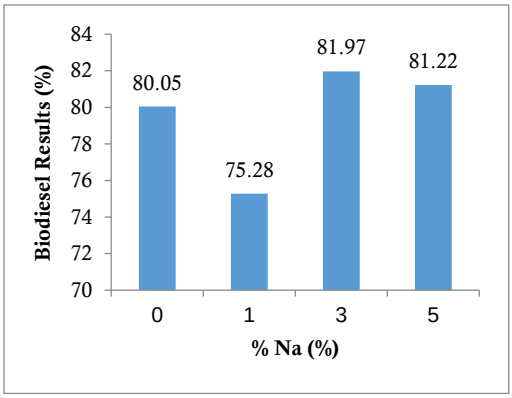

Figure 2. The results of the acquisition of biodiesel using a Na/CaO catalyst of 900 °C calcined blood shells for 10 hours.

Biodiesel production is higher along with the increasing concentration of Na in CaO from CKD. The yield of biodiesel on the CaO catalyst from CKD is 80.05%. And when the amount of Na concentration is added as much as 1%, biodiesel production has decreased. This is caused by the unequal distribution of Na metal on the CaO surface causing the surface area of the catalyst to decrease. In the catalyst 3% Na/CaO biodiesel production experienced a significant increase. This is caused by the even distribution of Na metal on the catalyst surface so that the catalyst surface area is getting bigger. While the catalyst of 5% Na/CaO biodiesel production has decreased again. This is probably due to the catalyst being filled with Na Metal due to too much Na metal being distributed on the CaO surface so that it clogs the active side of the catalyst and causes the catalyst surface area to decrease.

From the XRD pattern it can be seen that the most CaO peaks appear on the catalyst 3% Na/CaO, this is also marked on the maximum yield of biodiesel production which is 81.97%. On 5% Na/CaO catalyst, biodiesel production has decreased, this is caused by the number of $Ca(OH)_2$ peaks formed while the CaO peaks that appear to have decreased. The active site sequence of catalyst activity in biodiesel production is CaO> $Ca(OH)_2$>$CaCO_3$ [9]. The more CaO content in a catalyst, the better catalyst activity in biodiesel production.

Effect of Reaction Time

Biodiesel production is affected by the reaction time during the transesterification process. The duration of the reaction time depends on the quality of the oil and the type of catalyst, oil with large free fatty acids, the reaction time is longer than oil with small free fatty acids [7]. The working principle of heterogeneous catalyst is adsorption, so that with the longer reaction time the conversion of biodiesel produced will increase, but if it has reached the optimum conditions then the conversion of biodiesel produced will decrease because it will produce a lot of glycerol and emulsion products.

In this study, data were obtained that during the reaction time of 2 hours to 3.5 hours biodiesel production was increasing. In Figure 3 it can be seen that the optimum reaction time is obtained in the transesterification reaction for 3.5 hours, which is 83.57% with a catalyst of 3% Na/CaO activation temperature of 600 °C for 5 hours, reaction temperature of 60 °C, catalyst weight of 3 grams, ratio oil: methanol 1:6, and stirring speed of 250 rpm.

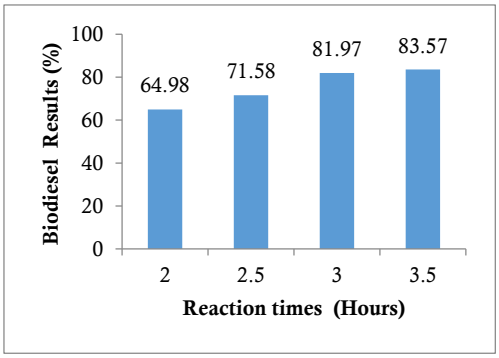

Figure 3. Effect of reaction time on biodiesel production

Conclusion

The 3% Na/CaO catalyst is the best catalyst with optimum biodiesel production containing Calcite, Portlandite and Lime minerals. The optimum biodiesel yield obtained was 83.57%. The optimum conditions obtained from biodiesel production using a 3% Na/CaO catalyst are reaction temperature 60 °C, reaction time of 3.5 hours, stirring speed of 250 rpm, catalyst weight of 3 grams, and oil: methanol 1: 6 mole ratio.

Acknowledgement

The author thanks Mrs. Dr. Nurhayati, M.Sc and Prof. Dr. Amir Awaluddin, M.Sc and all parties who have helped so that this research can be completed.

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