Walisongo Journal of Chemistry Vol. 6 Issue 1 (2023), 54-60
ISSN: 2621-5985 (online); 2549-385X (print)
DOI: https://doi.org/10.21580/wjc.v6i1.15334

Synthesis of Biodiesel from Avocado Seed Oil Transesterification Method Using Beef Bone Catalyst

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Received: 3 April 2023; Accepted: 18 July 2023; Published: 25 July 2023

Abstract

Avocado seeds have a relatively high content of Fatty Acid Methyl Ester, so they have the potential to be used as raw material for biodiesel. The process of processing biodiesel from avocado seeds is through a transesterification reaction, using a heterogeneous catalyst in the form of a stable bovine bone and green technology. This study uses a cow bone catalyst to produce biodiesel from avocado seed oil through a transesterification process. Biodiesel has characteristics; density of 0.75 g/cm^3, FFA 0.468%, and acid number 0.732 mg-KOH/g. The transesterification process at 60° for 1 hour obtained an FFA of 1.50% to 0.468% and yield biodiesel 28.8%. The research showed that all biodiesel quality tests at SNI 04-7182-2015 except for the quality density test. The FTIR results of biodiesel are: wave number 2585-2956 cm^{-1} C-C (alkane) asymmetrical stretching shows free fatty acid chain bonds, 1749.88 cm^{-1} Carbonyl ester group C=O, peak-C-H group wavelength at 1459 cm^{-1}, The position of the carbonyl ester is strengthened by the presence of the C-O ester position at a wavelength at 1378 cm^{-1}, the C-H group (alkane) with a length at 1060 cm^{-1}.

Keywords: *avocado seed; biodiesel; beef bone catalyst; transesterification*

Introduction

One of the energy sources that is a primary need in human activity is fuel oil (BBM). The use of BBM among the people is quite high; according to Downstream Oil and Gas Statistics, BBM sales in semester 1 of 2021 were recorded at 598.975 Kiloliters (Ministry of Energy and Mineral Resources, 2021). On the other hand, petroleum supplies are dwindling and unrenewable. This has the potential to trigger an energy crisis in the future. To overcome this problem, it is necessary to have a variety of energy in the form of utilizing alternative renewable energy, which is sourced from vegetable or animal oils (Lestari, 2018). Indonesia has abundant in natural vegetable resources, one of which is avocado. Based on data from the Central Statistics Agency (BPS), avocado production is relatively high. In 2021 it was recorded that 669.260 tons of avocados were produced. Avocado production every year shows an increase which will indirectly impact the high waste of avocado seeds (BPS.

2021). So far, the processing of avocado seeds has only been used as a stress reliever, while avocado seeds have the potential as an ingredient for making biodiesel because they contain Fatty Acid Methyl Ester (Rachmanita & Safitri, 2020). In addition, avocado seeds contain quite high oil, which is 32.8% (Marlina & Pratama, 2018). Biodiesel can be made using a one-step method (transesterification) and a two-step process (esterification-transesterification). Oils containing *Free Fatty Acid* (FFA) values above 1% are advised to use the esterification-transesterification stage (Hadrah et al., 2018), such as avocado seed oil with an FFA value of 64% (Ginting et al., 2020). In avocado seed oil there is Fatty Acid Methyl Ester (FAME) which can be converted into biodiesel through a transesterification or esterification reaction (Erghuis et al., 2019). This two-stage process applies because oil containing more than 1% Free Fatty Acids will form a soap emulsion, making biodiesel difficult to separate (Hadrah et al., 2018).

The transesterification reaction in biodiesel production cannot take place without a catalyst, whereas, in general, the synthesis of biodiesel from triglycerides with alcohol uses a homogeneous base catalyst in the form of KOH and NaOH. Homogeneous base catalysts have the high catalytic activity to produce biodiesel in a soft state and short reaction time (Zaki et al., 2019). However, these catalysts have drawbacks, including the separation of the catalyst from the product, which is quite complicated, the formation of soap, the production of wastewater on a large scale, and the quality of glycerol as a by-product (Zaki et al., 2019). Another basic catalyst that can be used is a heterogeneous base catalyst. This catalyst has a positive value because it can support green technology at a low cost and is more stable and environmentally friendly (Husin et al., 2018). The reaction mechanism can be seen in Figure 1.

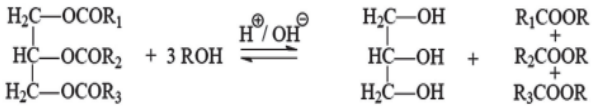

Figure 1. Transesterification Reaction Mechanism (Thanh et Al, 2012)

Heterogeneous catalysts commonly used in converting vegetable oil into biodiesel include SrO, CaO, and TiO_2-based. (Zaki et al., 2019). These catalysts are relatively expensive and are made from unrenewable materials. In addition, there are several sources of environmentally friendly calcium oxide: egg shells, eggs, and crab shells. (Simpen *et al.*, 2021). Bones are one of the culinary solid wastes that are quite large in number but have not been utilized optimally.

This study used a cow bone catalyst to process avocado seeds oil into an environmentally friendly as alternative fuel.

Methods

Tools and materials

The materials used in this study included: Fresh beef bone from Ngaliyan district market of Semarang, avocado seeds taken from fruit workers, 99% technical methanol (CH_3OH), n-hexane (C_6H_{14}), aquadest, 1% phenolphthalein (PP) indicator, aquadest, and anhydrous Na_2SO_4 obtained from PT. Alkemi Semarang.

The instrument used for measuring and characterizing biodiesel samples is the *Fourier Transform Infrared* (FT-IR) Termo Nicolet Avatar 360 at the UIN Walisongo Semarang Chemistry Laboratory.

Work procedures

The use of avocado seed oil (Persea americana) as a raw material for making biodiesel fuel is procedurally through several stages, namely the extraction of seed oil using the Soxhlet method, identification of fatty acid levels, density test, acid number, free fatty acids of avocado seed oil, transesterification process and biodiesel characterization using FTIR.

Avocado Seed Oil Extraction

The avocado seed powder produced through refining and drying will be re-extracted to obtain oil. The extraction was done through the soxhlation stage using two variations of methanol and n-hexane solvents. The extracted avocado seed oil is then separated from the solvent using a vacuum rotary evaporator to obtain pure and concentrated oil.

Beef Bone CaO Catalyst Preparation

The beef bones are cleaned and broken into small pieces, then dried using an oven for 2 hours at a temperature of 200°C. Dried beef bones will be heated for 2 hours at 900°C until they turn into a fine white powder with a size of 80 mesh.

Free Fatty Acid Analysis

After obtaining avocado seed oil, free fatty acid analysis was performed using 0.1 M KOH solvent. At first, 100 mL of 0.1 M KOH solution was added, then 2 g of sample, 20 mL of methanol, and 2-3 drops of 1% PP indicator were added into Erlenmeyer flask and titrated until it turned pink. The titration was done three times. The titration results are calculated using the formula below:

$$FFA = \frac{V\ KOH \times M\ KOH \times 256}{sample\ (g) \times 1000} \times 100\% \quad (1)$$

Transesterification Process

30 mL of avocado seed oil samples was made in a 1:5 ratio with methanol solvent. 30 mL of avocado seed oil samples were used in a 1:5 ratio with methanol solvent. Methanol solvent mixed with beef bone catalyst as much as 0.5% of the sample weight. The mixture will be formed into two layers: methyl ester (biodiesel) and glycerol (remaining catalyst and solvent). Ater that, This process is done by heating the mixed solution at 60°C for 1 hour using a reflux tool. Then the results are left in a separatory funnel.

The methyl ester layer (biodiesel) was separated and washed with distilled water at 60°C until the colour became clear yellow. High-temperature water here evaporates the methanol from the methyl ester content. Then the results of the biodiesel obtained will be bound by the remaining water in its content by adding anhydrous Na_2SO_4 crystals.

Characterization of Biodiesel Avocado Oil
Density (40°C)

30 mL of biodiesel was put into a 50 mL beaker glass at 40°C using a hotplate, then put into a 25 mL pycnometer until all were filled. The formula used to determine density is as follows.

$$\rho = \frac{(pycnometer + aquadest) - (empty\ pycnometer)}{pycnometer\ volume\ (mL)} \quad (2)$$

Viscosity (40°C)

20 mL of biodiesel is heated to a 40°C stop. After that, it was pipetted into a vertical upright Ostwald viscometer, sucked past the mark, and released. Use the Stopwatch to measure the time pycnometer volume.

Acid number

2 grams of biodiesel added 40 mL of methanol and 2-3 drops of PP indicator. Then titrated using 0.1 M KOH solution.

$$BA = \frac{V\ KOH \times M\ KOH \times Mr\ KOH}{sample\ (g)} \quad (3)$$

Results and Discussion

Avocado Seed Preparation

Avocado seeds into small pieces. To reduce the water content in the seeds, they were dried at 120°C for 5 hours using an oven, then the avocado seeds were mashed with a mortar pestle. then sieved with a size of 80 mesh until the texture becomes powder, as can be seen in Figure 2.

Figure 2. Avocado seed chunk and smoth powder using 80 mesh sieves

132g of avocado seed powder was put into soxhletation with 400 mL of methanol solvent. The results of the extract obtained were 250-300 mL with full orange color. 232 g sample using 800 mL n-hexane solvent, a clear yellow extract was obtained with total volume of around 725mL.

The next step is the evaporation process for 1 hour at a stable temperature of 60°C to separate the sample extract from the polar alcohol solvent until the sample solution becomes more concentrated. The evaporation results of sample 1 obtained as much as 27.5 mL of brownish yellow with a yield of 20.8%. In sample 2, the evaporation results had a clear yellow color of around 66 mL, yield 28.4%.

The identified colors have different clarity levels between the two samples, as seen in Figures 3a and 3b.

Figure 3a. Methanol Dissolving Avocado Seed Oil

Figure 3b. Avocado Seed Oil n-hexane solvent

Then the samples were tested for density (40°C), FFA, Acid Number, and color, presented in Table 1 and 2.

Table 1. Characteristics of methanol solvent avocado seed oil

No.	characteristics	value
1	density (40°C)	0.9556 g/cm^3
2	FFA	11.86%
3	Acid number	1.186 mg/KOH-g
4	colour	Slight yellow brown

Table 2. Characteristics of n-hexane solvent avocado seed oil

No.	characteristics	value
1	density (40°C)	0.918 g/cm^3
2	FFA	1.491%
3	Acid number	3.21 mg/KOH-g
4	colour	yellow

These results indicate that avocado seed oil can directly enter the transesterification process because the FFA value is <2% and the solvent does not entirely dissolve the methyl ester component contained in the avocado seed. So selecting the n-hexane solvent is the right choice to dissolve the oil component in the avocado seed.

Beef Bone Preparation

200 g of beef bones were cut into 2-3 cm pieces, cleaned of remaining meat, then dried at 130°C for 3 hours. After that, Calcination was carried out using a furnace with a temperature of 900°C for 2 hours until the white color can be seen in Figure 4.

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Figure 4. chunk beef bone and powder calcination of beef bones at 900°C.

Analysis FFA and acid number

Based on the test results, using 0.5% CaO catalyst from beef bone reduced the free fatty acid content from 1.50% to 0.468% and the acid number level to 0.732 (Table 3)

Table 3. FFA and the acid number of biodiesel of avocado oil.

V KOH (mL)	*Free Faty Acid*	Acid Number	Colour
0.4	0.468%	0.732	Violet
0,4	0.468%	0.732	Violet
0.4	0.468%	0.732	Violet

Using 0.5% CaO catalyst in this study based on the using temperature variables of 60 minutes resulted in a decrease in FFA, and the density and viscosity obtained were lower (Suzuki & Itoh, 2020). Parameter test results are presented in Table 4.

Table 4. biodiesel test results from avocado seed oil

No.	Parameter	SNI-04-7182:2015	value	units
1	density (40°C)	0.85-0.890	0.75	g/cm3
2	Viscosity (40°C)	2.3-6,0	-	cSt
3	acid number	0,5	0.732	mg-KOH/g. max
4	pH	7	6.5	-
5	yield biodiesel	96.5	28.8	%
6	flash point	100	130	°C
7	colour	clear yellow	clear yellow	-
8	FFA	2.5	0.468	%, max

Based on the results of Table 4, the results of this study density at 40°C methyl ester is 0.75 g/cm^3. Low density can result in poor biodiesel purity and lower triglyceride conversion into methyl ester (Novalina et al., 2020). Yield results obtained a biodiesel yield of 28.8% so it is not so good for use in diesel engines can increase damage to diesel engines and increase carbon dioxide (CO_2) gas emissions (Miskah, et al., 2008). Free

Fatty Acid (FFA) levels decreased from 1,491% to 0.468%. Free Fatty Acid levels decreased from 1.491% to 0.468%. The temperature of 60°C during the transesterification process, there is a change of methanol from the liquid phase to vapor so that the FFA level can be reduced measurement of the pH value obtained of pH 6.5 and flash point have met the standard, while the acid number of 0.732 mg-KOH/g does not meet the standard. Based on previous research conducted by Berghuis et al. (2019) using the mole ratio between oil and methanol, namely 1:6 with a 2.5% base catalyst, the transesterification process lasted 1 hour at 50-60°C succeeded in reducing FFA levels from 15.16% to 0.54% after the esterification process was carried out and transesterification.

Analysis FTIR Biodiesel and Glycerol

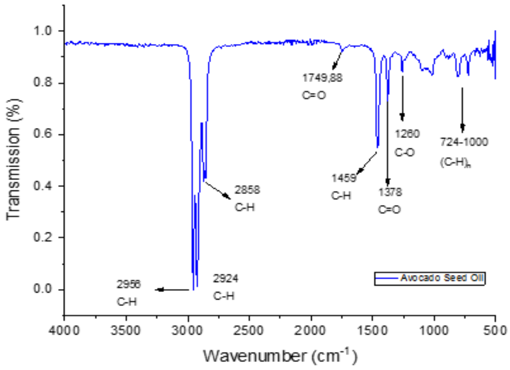

Figure 5. FTIR spektrum of Biodiesel

The results of the *Fourier Transform Infrared* (FT-IR) test show peak wave number at 2585-2956 cm^{-1} C-C (alkane) unsymmetrical stretching showing free fatty acid chain bonds, wavelength at 1749.88 cm^{-1} shows the carbonyl ester group C=O, the peak of the C-H group with a wavelength at 1459 cm^{-1}. The position of this carbonyl ester is strengthened by the presence of the C-O ester position at a wavelength at 1378 cm^{-1}, the C-H group (alkene) with a length at 1060 cm^{-1}.

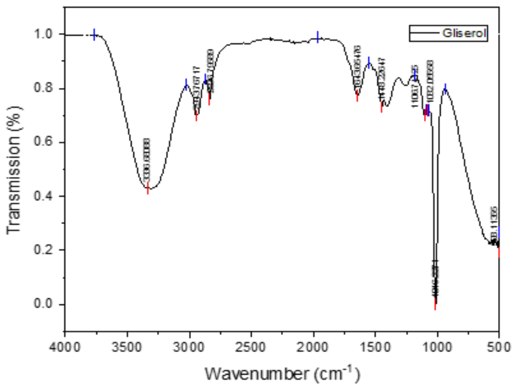

Figure 6. FTIR Glycerol

There is a wide absorption area from the alcohol group (OH) at 3336.68 cm^{-1}.The alkane group (C-H) at 2836.79-2943.76 cm^{-1} binds to methylene (CH_2), showing an absorption area of 1448.22 cm^{-1}. Compared with commercial glycerol, there is a sharp absorption of the alcohol group (OH) of around 3.300 cm^{-1}, the alkane group (C-H) bonds at 2900 cm^{-1} and carbon bond alcohol (C-OH) bending with an absorption at 1.370-1.430 cm^{-1} (Saifuddin et al., 2014).

Conclusion

Avocado oil biodiesel characteristics Test obtained some suitable data, not by SNI 04-7182.2015 regarding biodiesel. The percentage of data values that are by biodiesel standards include a Free Fatty Acid (FFA) yield rate of 0.468%, an acid number of 0.732 mg KOH/g, a pH value of 6.5, flash point level at a temperature of more than 130°C and yield biodiesel 28.8%. Conformity of the data values with the standard is affected by the comparative condition of using CaO catalyst which is too low. The Fourier Transform Infrared (FT-IR) test results show a peak wave number of 2585-2956 cm^{-1} C-H (alkane). The peak of the -C-H group with a wavelength of 1459 cm^{-1}, the results of the glycerol spectrum have an absorption area from the alcohol group (OH) 3336.68 cm^{-1}. The alkane group (C-H) 2836.79-2943.76 cm^{-1} binds to methylene (CH_2), indicating an absorption area of 1448.22 cm^{-1}.

Suggestion

Seeing the results of research that has been done, it is suggested to use a variety of CaO catalysts with various comparisons to determine the optimization of biodiesel yields by SNI 04-7182.2015 standards.

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